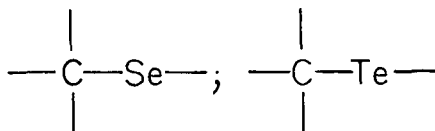The chemistry of
organic selenium and tellurium compounds
compounds
Volume 2

THE CHEMISTRY OF FUNCTIONAL GROUPS

A series of advanced treatises under the general editorship of
Professor Saul Patai

The chemistry of alkenes (2 volumes)
The chemistry of the carbonyl group (2 volumes)
The chemistry of the ether linkage
The chemistry of the amino group
The chemistry of the nitro and nitroso groups (2 parts)
The chemistry of carboxylic acids and esters
The chemistry of the carbon–nitrogen double bond
The chemistry of amides
The chemistry of the cyano group
The chemistry of the hydroxyl group (2 parts)
The chemistry of the azido group
The chemistry of acyl halides
The chemistry of the carbon–halogen bond (2 parts)
The chemistry of the quinonoid compounds (2 parts)
The chemistry of the thiol group (2 parts)
The chemistry of the hydrazo, azo and azoxy groups (2 parts)
The chemistry of amidines and imidates
The chemistry of cyanates and their thio derivatives (2 parts)
The chemistry of diazonium and diazo groups (2 parts)
The chemistry of the carbon–carbon triple bond (2 parts)
The chemistry of ketenes, allenes and related compounds (2 parts)
The chemistry of the sulphonium group (2 parts)
Supplement A: The chemistry of double-bonded functional groups (2 parts)
Supplement B: The chemistry of acid derivatives (2 parts)
Supplement C: The chemistry of triple-bonded functional groups (2 parts)
Supplement D: The chemistry of halides, pseudo-halides and azides (2 parts)
Supplement E: The chemistry of ethers, crown ethers, hydroxyl groups and
their sulphur analogues (2 parts)
Supplement F: The chemistry of amino, nitroso and nitro compounds
and their derivatives (2 parts)
The chemistry of the metal–carbon bond (4 volumes)
The chemistry of peroxides
The chemistry of organic Se and Te compounds Volume 1
The chemistry of the cyclopropyl group (2 parts)

$$\overset{|}{\underset{|}{-C}}-Se-; \quad \overset{|}{\underset{|}{-C}}-Te-$$

The chemistry of

organic selenium and tellurium

compounds

Volume 2

Edited by

SAUL PATAI

The Hebrew University, Jerusalem

1987

JOHN WILEY & SONS

CHICHESTER – NEW YORK – BRISBANE – TORONTO – SINGAPORE

An Interscience ® Publication

Contributing Authors

F. J. Berry	Department of Chemistry, University of Birmingham, P.O. Box 363, Birmingham B1S 2TT, UK
T. G. Back	Faculty of Science, Department of Chemistry, University of Calgary, 2500 University Drive N.W., Calgary, Alberta, Canada T2N 1N4
C. Carletti	Universita' degli Studi di Roma, 'La Sapienza', Dipartimento di Chimica, Piazzale Aldo Moro 5, 00185 Roma, Italy
L. Castle	Department of Chemistry, Royal Holloway and Bedford New College, University of London, Egham TW20 OEX, UK
L. Christiaens	Laboratoire de Chimie Organique, University of Metz, Faculte des Sciences, Ile du Saulcy 57045 – Metz Cedex, France
L. Christiaens	Department of Organic Chemistry, State University of Liège, Place du 20-Aôut 7, 4000-Liège, Belgium
D. O. Cowan	Department of Chemistry, The Johns Hopkins University, Remsen Hall – Dunning Hall, Baltimore, Maryland 21218, USA
G. Distefano	C.N.R. Laboratorio dei composti del Carbonio contenenti Eteroatomi, Via Tolara di Sotto 89, 400064 Ozzano Emilia (BO), Italy
N. Esaki	Institute for Chemical Research, Kyoto University, Uji, Kyoto-Fu 611, Japan
Z. Goldschmidt	Department of Chemistry, Bar Ilan University, Ramat Gan 52100, Israel
F. Guziec	Department of Chemistry, New Mexico State University, Box 3C/Las Cruces, New Mexico 88003, USA
L. Henriksen	Department of General and Organic Chemistry, The H. C. Ørsted Institute, DK-2100 Copenhagen, Denmark
R. Hensel	Fachbereich Chemie, Universität Oldenburg, Carl-von-Ossietzky Str. 9–11, D-2900 Oldenburg, FRG
A. Kini	Department of Chemistry, The Johns Hopkins University, Remsen Hall – Dunning Hall, Baltimore, Maryland 21218, USA
G. Kirsch	Laboratoire de Carbochimie et de Synthèse Organique, Faculté des Sciences, Université de Metz, Ile du Saulcy, 57045-Metz, France
A. Krief	Department of Chemistry, University of Namur, Rue de Bruxelles 61, B-5000 Namur, Belgium

S. Kubiniok   Fachbereich Chemie, Universität Oldenburg, Carl-von-Ossietzky Str. 9–11, D-2900 Oldenburg, FRG

L. Lange   Fachbereich Chemie, Universität Oldenburg, Carl-von-Ossietzky Str. 9–11, D-2900 Oldenburg, FRG

T. Masukawa   Department of Pharmacology, Faculty of Pharmacy, Setsunan University, Nagaotoge-cho, Hirakata, Osaka-Fu 573-01, Japan

W. R. McWhinnie   Department of Chemistry, University of Aston in Birmingham, Gosta Green, Birmingham B4 7ET, UK

W.-W. du Mont   Fachbereich Chemie, Anorganische Chemie, Universität Oldenburg, Ammerlander Heerstrasse 67–99, D-2900 Oldenburg, Federal Republic of Germany

M. J. Perkins   Royal Holloway and Bedford Colleges, University of London, Egham Hill, Egham TW20 0EX, UK

T. B. Rauchfuss   Department of Chemistry, University of Illinois at Urbana-Champaign, 505 South Mathews Avenue, Urbana, Illinois 61801, USA

T. Sadeh   Department of Radiopharmacology, Israel Atomic Energy Commission, Soreq Nuclear Research Centre, Yavne, Israel

K. Soda   Institute for Chemical Research, Kyoto University, Uji, Kyoto-Fu 611, Japan

H. Tanaka   Institute for Chemical Research, Kyoto University, Uji, Kyoto-Fu 611, Japan

A. Toshimitsu   Institute for Chemical Research, Kyoto University, Uji, Kyoto-Fu 611, Japan

S. Uemura   Institute for Chemical Research, Kyoto University, Uji, Kyoto-Fu 611, Japan

Z. Witczak   Whistler Centre for Carbohydrate Research, Purdue University, West Lafayette, Indiana 47907, USA

Foreword

The first volume of '*The Chemistry of Organic Selenium and Tellurium Compounds*' was published in 1986. For various reasons, several chapters which were planned for that volume, had to be omitted. All these chapters are included in the present volume, with the exception of a chapter on UV, visible, IR and Raman spectroscopy, which did not materialize.

Thus I believe the coverage of the organic chemistry of the derivatives of selenium and tellurium is reasonably complete in these two volumes. The coverage of the literature in the present second volume is, in most chapters, up to the end of 1985 or even to the middle of 1986.

I would be very grateful to readers who would let me know about omissions or mistakes in this volume as well as in other volumes of the Functional Groups series.

Jerusalem   SAUL PATAI
July 1987

The Chemistry of Functional Groups

Preface to the Series

The series 'The Chemistry of Functional Groups' is planned to cover in each volume all aspects of the chemistry of one of the important functional groups in organic chemistry. The emphasis is laid on the functional group treated and on the effects which it exerts on the chemical and physical properties, primarily in the immediate vicinity of the group in question, and secondarily on the behaviour of the whole molecule. For instance, the volume *The Chemistry of the Ether Linkage* deals with reactions in which the C—O—C group is involved, as well as with the effects of the C—O—C group on the reactions of alkyl or aryl groups connected to the ether oxygen. It is the purpose of the volume to give a complete coverage of all properties and reactions of ethers in as far as these depend on the presence of the ether group but the primary subject matter is not the whole molecule, but the C—O—C functional group.

A further restriction in the treatment of the various functional groups in these volumes is that material included in easily and generally available secondary or tertiary sources, such as Chemical Reviews, Quarterly Reviews, Organic Reactions, various 'Advances' and 'Progress' series as well as textbooks (i.e. in books which are usually found in the chemical libraries of universities and research institutes) should not, as a rule, be repeated in detail, unless it is necessary for the balanced treatment of the subject. Therefore each of the authors is asked *not* to give an encyclopaedic coverage of his subject, but to concentrate on the most important recent developments and mainly on material that has not been adequately covered by reviews or other secondary sources by the time of writing of the chapter, and to address himself to a reader who is assumed to be at a fairly advanced post-graduate level.

With these restrictions, it is realized that no plan can be devised for a volume that would give a *complete* coverage of the subject with *no* overlap between chapters, while at the same time preserving the readability of the text. The Editor set himself the goal of attaining *reasonable* coverage with *moderate* overlap, with a minimum of cross-references between the chapters of each volume. In this manner, sufficient freedom is given to each author to produce readable quasi-monographic chapters.

The general plan of each volume includes the following main sections:

(a) An introductory chapter dealing with the general and theoretical aspects of the group.

(b) One or more chapters dealing with the formation of the functional group in question, either from groups present in the molecule, or by introducing the new group directly or indirectly.

(c) Chapters describing the characterization and characteristics of the functional groups, i.e. a chapter dealing with qualitative and quantitative methods of determination including chemical and physical methods, ultraviolet, infrared, nuclear magnetic resonance and mass spectra: a chapter dealing with activating and directive effects exerted by the group and/or a chapter on the basicity, acidity or complex-forming ability of the group (if applicable).

(d) Chapters on the reactions, transformations and rearrangements which the functional group can undergo, either alone or in conjunction with other reagents.

(e) Special topics which do not fit any of the above sections, such as photochemistry, radiation chemistry, biochemical formations and reactions. Depending on the nature of each functional group treated, these special topics may include short monographs on related functional groups on which no separate volume is planned (e.g. a chapter on 'Thioketones' is included in the volume *The Chemistry of the Carbonyl Group*, and a chapter on 'Ketenes' is included in the volume *The Chemistry of Alkenes*). In other cases certain compounds, though containing only the functional group of the title, may have special features so as to be best treated in a separate chapter, as e.g. 'Polyethers' in *The Chemistry of the Ether Linkage*, or 'Tetraaminoethylenes' in *The Chemistry of the Amino Group*.

This plan entails that the breadth, depth and thought-provoking nature of each chapter will differ with the views and inclinations of the author and the presentation will necessarily be somewhat uneven, Moreover, a serious problem is caused by authors who deliver their manuscript late or not at all. In order to overcome this problem at least to some extent, it was decided to publish certain volumes in several parts, without giving consideration to the originally planned logical order of the chapters. If after the appearance of the originally planned parts of a volume it is found that either owing to non-delivery of chapters, or to new developments in the subject, sufficient material has accumulated for publication of a supplementary volume, containing material on related functional groups, this will be done as soon as possible.

The overall plan of the volumes in the series 'The Chemistry of Functional Groups' includes the titles listed below:

The Chemistry of Alkenes (two volumes)
The Chemistry of the Carbonyl Group (two volumes)
The Chemistry of the Ether Linkage
The Chemistry of the Amino Group
The Chemistry of the Nitro and Nitroso Groups (two parts)
The Chemistry of Carboxylic Acids and Esters
The Chemistry of the Carbon–Nitrogen Double Bond
The Chemistry of the Cyano Group
The Chemistry of Amides
The Chemistry of the Hydroxyl Group (two parts)
The Chemistry of the Azido Group
The Chemistry of Acyl Halides
The Chemistry of the Carbon–Halogen Bond (two parts)
The Chemistry of the Quinonoid Compounds (two parts)
The Chemistry of the Thiol Group (two parts)
The Chemistry of Amidines and Imidates
The Chemistry of the Hydrazo, Azo and Azoxy Groups (two parts)
The Chemistry of Cyanates and their Thio Derivatives (two parts)
The Chemistry of Diazonium and Diazo Groups (two parts)
The Chemistry of the Carbon–Carbon Triple Bond (two parts)

Supplement A: The Chemistry of Double-bonded Functional Groups (two parts)
The Chemistry of Ketenes, Allenes and Related Compounds (two parts)
Supplement B: The Chemistry of Acid Derivatives (two parts)
Supplement C: The Chemistry of Triple-Bonded Functional Groups (two parts)
Supplement D: The Chemistry of Halides, Pseudo-halides and Azides (two parts)
*Supplement E: The Chemistry of Ethers, Crown Ethers, Hydroxyl Groups and their Sulphur
    Analogues (two parts)*
The Chemistry of the Sulphonium Group (two parts)
*Supplement F: The Chemistry of Amino, Nitroso and Nitro Groups and their Derivatives
    (two parts)*
The Chemistry of the Metal–Carbon Bond (four volumes)
The Chemistry of Peroxides
The Chemistry of Organic Se and Te Compounds Vol. 1
The Chemistry of the Cyclopropyl Group (two parts)
The Chemistry of Se and Te Compounds Vol. 2

Titles in press:

The Chemistry of the Quinonoid Compounds Vol. 2
The Chemistry of Sulphones and Sulphonides Vol. 2
The Chemistry of Organo-silicon Compounds

Advice of criticism regarding the plan and execution of this series will be welcomed by
the Editor.
The publication of this series would never have started, let alone continued, without the
support of many persons. First and foremost among these is Dr Arnold Weissberger,
whose reassurance and trust encouraged me to tackle this task. The efficient and patient
cooperation of several staff-members of the Publisher also rendered me invaluable aid (but
unfortunately their code of ethics does not allow me to thank them by name). Many of my
friends and colleagues in Israel and overseas helped me in the solution of various major
and minor matters, and my thanks are due to all of them, especially to Professor Z.
Rappoport. Carrying out such a long-range project would be quite impossible without the
non-professional but none the less essential participation and partnership of my wife.

The Hebrew University
Jerusalem, ISRAEL   SAUL PATAI

Contents

Contents

CHAPTER **1**

Photoelectron spectroscopy of organic derivatives containing selenium and tellurium

CARLA CAULETTI

Dipartimento di Chimica, Università La Sapienzà di Roma, Piazzale Aldo Moro 5, 00185 Rome, Italy

GIUSEPPE DISTEFANO

Istituto dei Composti del Carbonio Contenenti Eteroatomi e loro Applicazioni, Ozzano Emilia, Via Tolara di Sotto 89, 40064 Ozzano Emilia, Italy

I. INTRODUCTION

A. Preliminaries and Scope

Photoelectron spectroscopy is now a well established technique which permits the direct measurement of the energies required to remove electrons from atoms and molecules. When a photon of sufficient energy impinges on a neutral molecule, M, it is possible to eject an electron, leaving behind a radical cation, M^+, in one of several possible electronic states. If hv is the energy of the incident photons, IE the ionization energy involved in a given ionization event and KE the excess kinetic energy of the emitted photoelectron, the equation:

$$hv = IE + KE \qquad (1)$$

provides a means of finding IE by measuring KE. When the ionizing source is of medium or high energy, such as those produced in a inert gas discharge (for instance 21.22 eV in He I 2p → 1s or 40.81 eV in He II 2p → 1s) and the target is in the gas phase, the information obtained concerns the ionization energies of valence shells of free molecules and the technique is named UV photoelectron spectroscopy (UPS). When hv is in the fields of the soft X-rays (up to a few thousand electronvolts) the primary information concerns core electrons and the technique is named X-ray photoelectron spectroscopy (XPS).

A deeper discussion of the general aspects and the chemical applications of UPS may be found in some reviews and books [1-11].

This present chapter reports UPS studies on selenium- and tellurium-containing organic molecules. The number of investigations on such compounds by this technique is limited, probably owing to the instability of most of them. Nevertheless, recent developments in the analysis and interpretation of the experimental data allowed valuable information to be obtained on the electronic structure, i.e. the energy and composition of molecular orbitals (MOs), even of transient molecules.

In the presentation and discussion of the results, we shall often refer to the oxygen and sulphur analogues of the examined compounds for the sake of completeness and comparison.

B. Ionization Energies, Ionic States and Molecular Orbitals

A photoelectron spectrum consists of a plot of the number of electrons with a given kinetic energy, KE (which may be converted into ionization energy, IE, through equation 1), versus that energy. Hence the primary information obtained by UPS is the energy of the molecular ion states relative to the ground-state molecule and the IEs are strictly energy differences between states of M^+ and the ground state of M. There is therefore a correlation between the energy sequence of ionic levels, which is directly drawn out by a UP spectrum, and the sequence of the MOs of the corresponding molecular ground state, but they are not necessarily coincident. However, the approximation of Koopmans' theorem[12] states that the ionization energies of a molecule are equal to the negative of the self-consistent field (SCF) orbital energies, ε_i:

$$IE_i = -\varepsilon_i \qquad (2)$$

Equation 2 obviously does not apply to open-shell molecules.

Following this theorem, a photoelectron spectrum should be a reflection of the molecular orbital diagram, the sequence of UPS bands matching the sequence of the negative of the energies of the occupied molecular orbitals. Koopmans' theorem would be fully valid if the electronic configuration of the remainder of the molecule remained unchanged or 'frozen' during the ionization process, neglecting relaxation phenomena, which may be important, e.g. when ionization of metal-centred orbitals is involved. However, in most organic molecules, relaxation effects are nearly constant in the ionization of all valence orbitals, so that Koopmans' approximation allows correct qualitative correlations, in addition to semiquantitative comparisons.

The following may give more bands in a UP spectrum than there are valence orbitals in a molecule:

 (i) ionization of one electron with simultaneous excitation of a second electron to an unoccupied excited orbital, i.e. a two-electron process, referred to as shake-up or configuration interaction (CI) processes;
 (ii) removal of degeneracy in the molecular ion by mechanisms such as spin–orbit coupling and the Jahn–Teller effect;
 (iii) the presence of one or more open shells, the ionization of which may give rise to a multiplicity of ionic states.

C. Analysis of a UP Spectrum

The analysis of a UP spectrum consists in assigning each spectral band to an electronic state of the molecular ion and identifying the orbital from which electrons are ejected. In this interpretative work some approaches may be of help, as follows.

a. *Spectral fine structure.* The observation of fine structure in spectral bands, such as that arising from spin–orbit coupling and the Jahn–Teller effect, or vibrational pro- gressions can lead to positive identification of the nature of the ionized MO. In particular, analysis of the vibrational structure, whenever present, of a photoelectron band may give precise information on the non-bonding, bonding or antibonding character of the orbital. In fact, removal of a non-bonding electron does not cause changes in the geometry of the molecular ion with respect to the neutral molecule, so

that the corresponding UPS band is sharp and without any vibrational progression. In contrast ionization of a bonding or antibonding orbital decreases or increases the bond-lengths, this being reflected in a change in the vibrational spacing (in this case a vibrational structure does exist) on passing from the molecule to the ion. For instance, the first band of the UP spectrum of the hydrides H_2X[13,14] (X = O, S, Se and Te) (See Figure 1) is very sharp, indicating its origin from the ionization of the lone pair orbital of X. The second $(2a_1^{-1})$ and third $(1b_2^{-1})$ bands show progression in the symmetrical bending (v_2) and stretching (v_1) vibrations, respectively. Their frequencies are reduced from the corresponding values in the neutral state indicating a strong H—X bonding character for these orbitals.

b. *Intensity arguments.* The areas of photoelectron bands in a photoelectron spectrum are approximately proportional to the relative probabilities of ionization to the different ionic states. These probabilities are called relative partial photoionization cross-sections (for details, see, e.g., Refs. 7 and 10). The most important factors that determine the cross-sections and consequently the UPS band intensities are the following.

   (i) The partial cross-section for ionization from a given orbital is proportional to the number of equivalent electrons that are available to be ionized (in the case of closed-shell molecules) or to the statistical weight of the ionic state produced (in the case of atoms or open-shell molecules).

   (ii) The photoionization cross-section (σ) depends on the character of the ionized orbital, i.e. its size, number of nodes, location in the molecule, etc. Further, it varies with the wavelength of the ionizing radiation, the variation following different trends for the various orbitals. This point is most meaningful when intensity
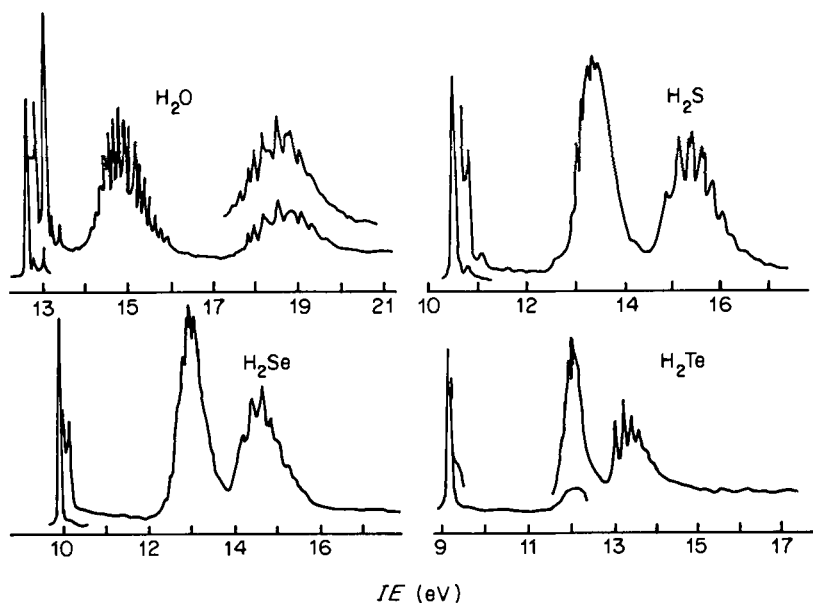

FIGURE 1. He I photoelectron spectra of the H_2X molecules (X = O, S, Se and Te). *Reproduced by permission of the Royal Society from Reference 14*

arguments are used as interpretative tools. The large number of UPS experiments performed with two or more ionizing sources (mainly He I and He II) allow some empirical rules to be drawn. Firstly, in photoionization by He I, the cross-section of the valence atomic orbital increases on going down a Group of the Periodic Table. This trend is a least partially reversed when light of shorter wavelength, particularly the He II line, is used for ionization. Thus, the cross-sections of p orbitals of chlorine, bromine and sulphur decrease significantly on passing from He I to He II, whereas that of carbon 2p orbitals remains roughly unchanged and those of nitrogen 2p and oxygen 2p orbitals show an increase. Not many data are available on the behaviour of Se 4p and Te 5p orbitals, whose photoionization cross-sections are, however, expected to decrease relative, for instance, to that of C 2p on passing from 21.22 to 40.81 eV ionizing radiation. Theoretical calculations suggest a $\sigma_{HeI}/\sigma_{HeII}$ ratio of ca. 17 for Se 4p orbitals[15] and ca. 14 for Te 4p orbitals[16], whereas there is experimental evidence that this ratio is roughly 1 for C 2p orbitals. As for molecular orbitals, the Gelius model[16a] allows σ to be evaluated starting from that of the contributing atomic orbitals (AOs):

$$\sigma_j = \sum_{A,i} P_{j,i_A} \sigma_i^A \qquad (3)$$

where σ_j is the one-electron photoionization cross-section for the jth MO and the summation extends over atomic orbitals, ϕ_i^A, on the different atomic centres A. The σ_i^A are one-electron atomic cross-sections and P_{ji_A} are factors describing the effective occupancy of the MO.

The main application of equation 3 in UPS has been in identifying the predominant AO character in the MO giving rise to a particular band. Hence bands corresponding to halogen lone pairs are easily recognizable by their strong decrease in intensity in He II relative to bands corresponding to C 2p-based orbitals. The same occurs for sulphur-, selenium- and tellurium-centred orbitals.

As an example of use of intensity considerations in the analysis of the nature of valence orbitals in molecules, we can quote UPS studies on the isomeric compounds MeNCS[17] and MeSCN[18]. Of the first two bands of the spectrum of the former compound, assigned to π non-bonding and π bonding orbitals, respectively, that at lower IE does not change in intensity on switching from He I to He II, whereas the other shows an interesting increase. Since for nitrogen and sulphur p orbitals the expected intensity changes are in opposite directions, the experimental findings suggest that the π non-bonding orbital has contributions from both atoms, whereas the π bonding MO has a large charge density on the nitrogen atom. This behaviour contrasts with that for methyl thiocyanate, where the first band shows a marked intensity decrease in the He II spectrum (see Figure 10), which implies that the corresponding orbital is largely localized on the sulphur atom. The behaviour is the same in the spectrum of MeSeCN, indicating that the highest occupied MO (HOMO) is essentially a lone-pair orbital of selenium.

c. *UP spectroscopic comparison of chemically related compounds.* This is often the most valuable tool in the assigment. The observation of trends, variations, etc., depending on various factors such as electronegativities, size and steric hindrance of substituents or the presence or absence of conjugative interactions, is usually of great help in the understanding of the valence-shell structure even of large molecules. Many examples of such an analysis can be found in the following sections of this review.

d. *Theoretical calculations.* Sometimes molecular orbital calculations are the only means of achieving at least a tentative assignment of the UP spectra. Calculation of the molecular ground-state energies and derivation of ionization energies through the

Koopmans theorem is by far the most commonly used approach. It is usual to distinguish four types of molecular orbital calculations:

(i) Exact Hartree–Fock (HF) calculations. In these, made by the self-consistent-field (SCF) method, no terms are neglected and no further improvement in the total energy can be gained either by increasing the number of iterations or by expanding the basis set. These calculations are unfortunately limited to relatively small molecules because of their cost in terms of computer time.

(ii) *Ab initio* SCF calculations. These are made possible by mathematical simplification through contraction of the basis set, but do not involve any arbitrary parameters. The general theory of *ab initio* calculations for closed-shell molecules was derived by Roothaan[19] and by Hall[20] in 1951 and are becoming increasingly common for polyatomic molecules[21,22].

(iii) Semi-empirical calculations. These calculations are simplified further by the neglect of certain integrals and the empirical rather than the theoretical evaluation of others. The different methods that have been extensively used are generally known by their acronyms, CNDO[23–26], INDO[27], MINDO[28–32] and SPINDO[33], where NDO = neglect of differential overlap, C = complete, I = intermediate, M = modified and SP = spectroscopic potentials adjusted. Because of the simplifications achieved, these calculations can be applied to large and complex molecules.

(iv) Empirical calculations. In empirical calculations no attempt is made to mimic the HF method, the aim being rather to evolve the simplest possible theory, using only a small number of arbitrary parameters. The Hückel molecular orbital (HMO) method[34] concerns only π electron systems of conjugated and aromatic molecules. The extended HMO (EHMO) method as developed by Hoffmann[35] includes all valence electrons and is of considerable use in assigning spectra.

The simplest Hückel-type method is the linear combination of bond orbitals (LCBO)[36], which starts not from atomic orbitals but from the occupied group orbitals of the building blocks of a molecule, thus reducing the number of terms of the secular determinant. The matrix elements are not mathematically evaluated but are empirical parameters which can compensate for the neglected integrals and the lack of empty orbitals. In particular, the numerical values of the self energies (α) and of the interaction parameters (β) can be derived from the IEs of reference systems.

II. SMALL MOLECULES

In this section we shall describe some examples of UPS studies of small molecules, often discussing non-organic molecules which will be useful as comparisons in the following sections of this chapter.

A. Diatomic Species

1. Homonuclear molecules

The photoelectron spectra of the open-shell system X_2 (X = O, S, Se and Te) are characterized by a large number of bands because each ionization process gives rise to a multiplicity of ionic states. Further, spin–orbit coupling is expected to produce significant splittings.

The electronic configuration of $O_2{}^+$ has been extensively investigated both theoretically and experimentally by UPS[37,38].

In the heavier Group VI homonuclear diatomics, spin–orbit splitting is expected to play

TABLE 1. Vertical ionization energies (eV) for S_2, Se_2 and Te_2[a]

State	S_2[b]	Se_2[c]	Te_2[c]
$^2\Pi_{g,1/2}$		8.93	8.23
$^2\Pi_{g,3/2}$	9.41	9.10	8.73
$^4\Pi_u$	11.82	10.65	9.38
$^2\Pi_u(1)$	12.33	11.19	10.07
$^4\Sigma_g$	13.20	12.25	11.01
$^2\Pi_u(2)$	d	(13)	11.53
$^2\Sigma_g$	14.62	13.33	11.84
$^2\Pi_u(3)$	15.58	14.00	12.34
CI	—	—	13.43[c]
$^4\Sigma_u$	17.70	(17.2)[e]	16.36[e]
$^2\Sigma_u$	18.10[f]	18.44[e]	18.16[e]
	18.66	(23.68)[e]	(20.56)[e]
	23.33		(23.63)[e]
	25.99		

[a]Parentheses indicate uncertainty in measurement.
[b]From Reference 40.
[c]From Reference 42.
[d]Predicted to be very weak in S_2.
[e]Feature observed in He II spectrum only.
[f]Assignment of this band is uncertain.

an increasingly important role as the atomic weight of the chalcogen increases. Despite the severe difficulties in avoiding contamination of the diatomic species in the vapour phase, UP spectra were obtained for S_2[39-42], Se_2 and Te_2[39,41,42]. Table 1 reports the observed ionization energies.

The valence molecular orbital configuration of X_2 can be represented, in the ground state, by $\ldots(\sigma_g ns)^2(\sigma_u ns)^2(\sigma_g np)^2(\pi_u np)^4(\pi_g np)^2$.

Ionization of the π_g orbital leads to a $^2\Pi_g$ state, which can be split into the two spin-orbit components $^2\Pi_{g,1/2}$ and $^2\Pi_{g,3/2}$. This splitting is actually not appreciable in $S_2{}^+$, whilst being evident in $Se_2{}^+$ (0.17 eV[42]) and $Te_2{}^+$ (0.50 eV[42]). Of the five possible $X_2{}^+$ states following ionization of the π_u orbital ($^4\Pi_u$,$^2\Phi_2$ and three $^2\Pi_u$ states), four may be reached by a direct one-electron transition. The corresponding UPS bands are observed in all the members of the series. The multiplet splittings in the Π_u ion states of these species are reported in Table 2. It can be seen that the $^4\Pi_u - {}^2\Pi_u(1)$ gap initially decreases with

TABLE 2. Multiplet splitting data (eV) for $^{4,2}\Pi_u$ $(\pi_u np)^{-1}$ states of O_2, S_2, Se_2 and Te_2

	O_2[a]	S_2[b]	Se_2[c]	Te_2[c]
$^4\Pi_u - {}^2\Pi_u(1)$	1.03	0.51	0.54	0.69
$^4\Pi_u - {}^2\Pi_u(2)$	2.6	—	2.35	2.15
$^4\Pi_u - {}^2\Pi_u(3)$	7.3	3.76	3.35	2.96

[a] From Reference 38.
[b] From Reference 40.
[c] From Reference 41.

TABLE 3. He II/He I photoionization cross-section ratios for
Se_2 and Te_2

Molecule	Orbital	$\sigma_{HeII}/\sigma_{HeI}$	Theoretical ratio for the valence p shells of atomic Se and Te[b]
Se_2[a]	π_g	0.046	0.06
	π_u	0.066	
	σ_g	0.105	
Te_2[a]	π_g	0.074	0.07
	π_u	0.103	
	σ_g	0.21	

[a] From Reference 42
[b] From References 15 and 16

increasing atomic weight until the effects of large spin–orbit coupling cause the gap to increase. The same decrease is observed for the $^4\Pi_u - {}^2\Pi_u(3)$ separation.

The analysis of the ionization phenomena accompanying the expulsion of an electron from the $\sigma_u ns$ and $\sigma_g ns$ orbitals is definitely more complex and the occurrence of two-electron processes, suggested by Streets and Berkowitz[41], should be further confirmed by more refined experiments, for instance by using synchrotron radiation as the ionizing source.

The He II spectra of Se_2 and Te_2, studied by Potts and Novak[42], gave interesting information on the relative photoionization cross-sections of the various orbitals. Table 3 reports the measured He II/He I cross-section ratios compared with theoretical values for atomic Se[15] and Te[16]. It is of interest that the He II Se 4p photoionization cross-section is markedly lower than the He I cross-section, whereas the He II Se 4s cross-section is predicted to be markedly higher than the He I cross-section.

2. Heteronuclear molecules

The electronic configuration of TeO, which is the predominant species in the vapour produced by heating solid TeO_2 at 773 K, is analogous to that of the above molecules and

TABLE 4. Ionization energies for
TeO[a]

State	IE(eV)
$^2\Pi_{1/2}$	8.72
$^2\Pi_{3/2}$	9.32
$^4\Pi$	10.80
$^2\Pi(1) + {}^4\Sigma$	11.17
$^2\Sigma$	12.00
$^2\Pi(2)$	12.7
$^2\Pi(3)$	13.49

[a] From Reference 43.

the assignment of its photoelectron spectrum[43] follows the same lines (see Table 4). In this case the highest π orbital is largely localized on tellurium and is antibonding in character.

The Group IV–VI diatomics GeX (X = O[44], S[44,45], Se[44,45], Te[44]), SnX (X = S[44,45], Se[44], Te[44,45]) and PbTe[45] have been extensively studied by UPS. One $^2\Pi_{1/2,3/2}$ and three $^2\Sigma^+_{1/2}$ ionic states correspond to the electronic configuration.

$$(1\sigma)^2(2\sigma)^2(3\sigma)^2(1\pi)^4$$

of these molecules. Tables 5 and 6 report the experimental ionization energies for these molecules together with the results of CNDO calculations. An interesting aspect is the appearance in the spectra of features arising from many-electrons effects (CI) involving the $(2\sigma)^{-1}$ primary hole state. For both GeX and SnX series, an energy stabilization of the 3σ orbital relative to the 1π orbital develops with increasing molecular weight. Wu and Fehlner[45] suggested that this is due to a sharp decrease in the π-type interaction between the atoms whereas White and coworkers[44] support this hypothesis on the basis of the CNDO overlap population and charge distribution. The 1π orbital is localized principally

TABLE 5. Experimental and theoretical (CNDO) ionization energies for GeX (X = O, S, Se, Te) molecules[a]

Molecule	MO	Ionic state	Experimental IE (eV)[b]	Theoretical IE (eV)[c]
GeO	3σ	$^2\Sigma^+_{1/2}$	11.25(1)	11.61
	1π	$^2\Pi_{1/2,3/2}$	11.40(5)	12.16
	2σ	$^2\Sigma^+_{1/2}$	15.16(2)	15.21
	1σ	$^2\Sigma^+_{1/2}$	—	30.97
GeS	1π	$^2\Pi_{1/2,3/2}$	10.36(5)	10.17
	3σ	$^2\Sigma^+_{1/2}$	10.43(2)	10.24
	2σ	$^2\Sigma^+_{1/2}$	14.00(4)	14.40
	2σ	CI	14.6(1)	—
	2σ	CI	15.28(5)	—
	2σ	CI	18.86(6)	—
	1σ	$^2\Sigma^+_{1/2}$	—	22.22
GeSe	1π	$^2\Pi_{3/2}$	9.8(1)	10.14
	1π	$^2\Pi_{1/2}$	9.95(5)	
	3σ	$^2\Sigma^+_{1/2}$	10.16(1)	10.37
	2σ	$^2\Sigma^+_{1/2}$	13.56(5)	13.92
	2σ	CI	14.0(1)	—
	2σ	CI	14.88(5)	—
	2σ	CI	16.31(5)	—
	1σ	$^2\Sigma^+_{1/2}$	—	22.50
GeTe	1π	$^2\Pi_{3/2}$	9.1(1)	8.67
	1π	$^2\Pi_{1/2}$	9.32(2)	
	3σ	$^2\Sigma^+_{1/2}$	9.76(1)	9.55
	2σ	$^2\Sigma^+_{1/2}$(?)	13.31(1)	13.56
	2σ	CI	13.88(6)	—
	2σ	CI	15.20(5)	—
	1σ	$^2\Sigma^+_{1/2}$	—	20.63

[a] From Reference 44.
[b] Vertical IEs. Uncertainties in parentheses.
[c] Values empirically reduced by 0.8 to reflect final ionic state relaxation.

Carla Cauletti and Giuseppe Distefano

TABLE 6. Experimental and theoretical ionization energies for SnX
(X = S, Se, Te) and PbTe molecules

Molecule	MO	Ionic state	Experimental IE (eV)[a]	Theoretical IE (eV)[b]
SnS[c]	1π	$^2\Pi_{1/2,3/2}$	9.42(5)	9.33
	3σ	$^2\Sigma_{1/2}^+$	9.73(3)	9.53
	2σ	CI	11.93(5)	—
	2σ	$^2\Sigma_{1/2}^+$	13.09(5)	13.08
	2σ	CI	14.03(5)	—
	2σ	CI	15.46(6)	—
	2σ	CI	18.12(6)	—
	1σ	$^2\Sigma_{1/2}^+$	—	20.80
SnSe[c]	1π	$^2\Pi_{3/2}$	9.0(1)	9.30
	1π	$^2\Pi_{1/2}$	9.26(3)	
	3σ	$^2\Sigma_{1/2}^+$	9.56(1)	9.77
	2σ	$^2\Sigma_{1/2}^+$	12.7(1)	12.89
	2σ	CI	13.65(5)	—
	2σ	CI	14.99(5)	—
	1σ	$^2\Sigma_{1/2}^+$	—	20.85
SnTe[c]	1π	$^2\Pi_{3/2}$	8.61(4)	8.58
	1π	$^2\Pi_{1/2}$	8.91(2)	
	3σ	$^2\Sigma_{1/2}^+$	9.30(1)	9.57
	2σ	CI	10.55(5)	—
	2σ	CI	11.02(5)	—
	2σ	$^2\Sigma_{1/2}^+$ (?)	11.91(1)	12.48
	2σ	CI	12.8(1)	—
	2σ	CI	14.33(5)	—
	1σ	$^2\Sigma_{1/2}^+$	—	18.89
PbTe[d]	1π	$^2\Pi_{3/2}$	8.04	—
	1π	$^2\Pi_{1/2}$	8.34	—
	3σ	$^2\Sigma_{1/2}^+$	9.01	—

[a] Vertical IEs. Uncertainties in parenthese.
[b] Value empirically reduced by 0.85 to reflect final ionic state relaxation.
[c] From Reference 44.
[d] From Reference 45.

on the chalogenide whereas the 3σ orbital is more equally distributed between both atoms. Hence, as one proceeds down the GeX or SnX series, the IEs of the $(3\sigma)^{-1}$ and $(1\pi)^{-1}$ states decrease, following the decrease in IE of the chalogenide ns and np atomic orbitals, the $(1\pi)^{-1}$ IE decreasing faster owing to its higher atomic character.

B. Triatomic Species

1. Linear molecules

The photoelectron spectra of the linear molecules X=C=Y (X = O, Y = Se[46,47]; X = S, Y = Se[46,47]; X = Y = Se[46,48]) have been investigated and compared with those of the analogous well known species CO_2, COS and CS_2, already studied by UPS[49,50]. Figure 2 shows the He I UP spectra of these molecules.
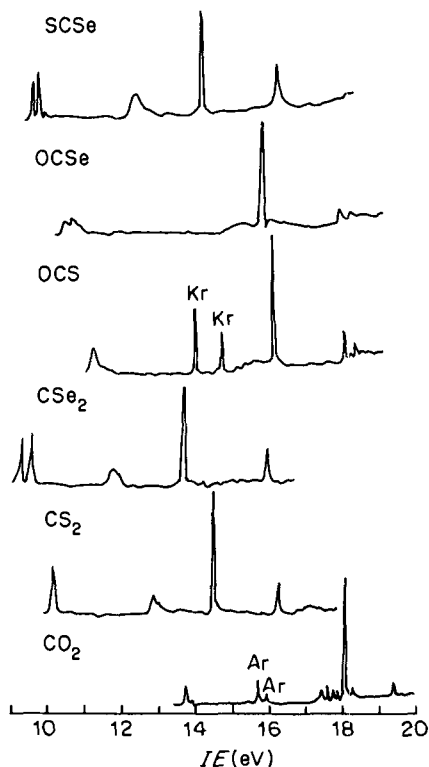
FIGURE 2. He I photoelectron spectra of some X=C=Y molecules. *Reproduced by permission of the American Institute of Physics from Reference 46*

The assignment of the spectra is the same for all members of the series, as expected in view of their chemical similarity. The first band corresponds to the $^1\pi_g$ level, essentially non-bonding, consistent with its sharpness and poor vibrational structure. It shows a spin–orbit splitting increasing in the order $CO_2 < OCS < CS_2 < SCSe < OCSe < CSe_2$. The second band is broad with a vibrational progression indicating a strongly bonding character of the ionised level, $^1\pi_u$. The third and fourth bands correspond again to essentially non-bonding orbitals, $^2\sigma_u$ and $^2\sigma_g$ respectively.

Frost and coworkers[46] measured the vibrational Franck–Condon factors for each ionic state, of which they estimated the geometry, using the method of Coon and collaborators[51]. A selection of the results obtained are reported in Table 7.

Figure 3 is a correlation diagram of the ionic states which shows several interesting trends. The energy of each ionic state is lowered if one end atom is replaced by a heavier atom. The effect of replacement of S by Se is much smaller than that of O by S or Se. The latter replacements result in a decrease in energy of more than 1 eV, whereas the former produces a change of far less than 1 eV. This reflects the well established fact that the resemblance between two successive elements in a Periodic Group becomes closer as one proceeds down the Group.

TABLE 7. Bond lengths of the ionic states of some X=C=Y estimated from Franck–Condon factors[a]

Molecule XCY	Electronic state	r(C—X) (Å)	r(C—Y) (Å)
SeCSe	$X^1\Sigma_g^+$	1.711[b]	1.711[b]
SeCSe[+]	$X^2\Pi_g$	1.711	1.711
	$A^2\Pi_u$	1.799	1.799
	$B^2\Sigma_u^+$	1.731	1.731
	$C^2\Sigma_g^+$	1.711	1.711
OCSe	$X^1\Sigma^+$	1.159[a]	1.1709[a]
OCSe[+]	$X^2\Pi$		
	$A^2\Pi$	1.90	1.890
	$B^2\Sigma^+$	1.145	1.718
	$C^2\Sigma^+$	1.111	1.776
SCSe	$X^1\Sigma^+$	1.557[a]	1.709
SCSe[+]	$X^2\Pi$	1.537	1.750
	$A^2\Pi$	1.620	1.813
	$B^2\Sigma^+$	1.550	1.738
	$C^2\Sigma^+$	1.540	1.759

[a] From Reference 46.
[b] From Reference 52.
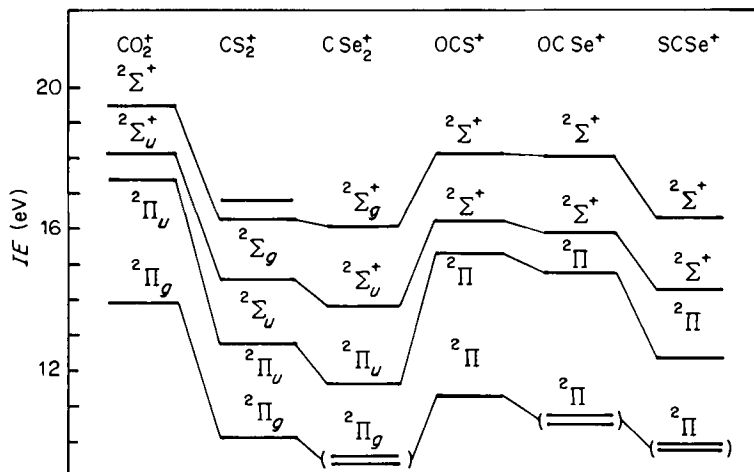
FIGURE 3. Correlation diagram for the electronic states of some (XCY)[+] molecular ions. *Reproduced by permission of the American Institute of Physics from Reference 46*

Cradock and Duncan found in the UP spectra of OCSe[47], SCSe[47] and CSe$_2$[48] some weak extra bands, not observed by Frost et al.[46]. They attributed these features to shake-up processes, leading to $^2\Pi_u$ states derived from the $(1\pi_g)^2 (2\pi_u)^1$ configuration of the ion.

2. *Bent XA_2 molecules*

The valence shell configuration of the XO_2 dioxides (X = S, Se, Te) is

$$(1a_1)^2(1b_2)^2(2a_1)^2(1b_1)^2(3a_1)^2(2b_2)^2(3b_2)^2(1a_2)^2(4a_1)^2$$

The photoelectron spectrum of SeO_2[53] strongly resembles that of SO_2, which has been widely discussed[50,54-56].

Figure 4 shows the He I and He II spectra of both molecules and Table 8 reports the observed *IEs* for SEO_2 with the proposed assignment. The first band in SeO_2, at 11.76 eV, strongly decreases in intensity compared with the second band on passing from He I to
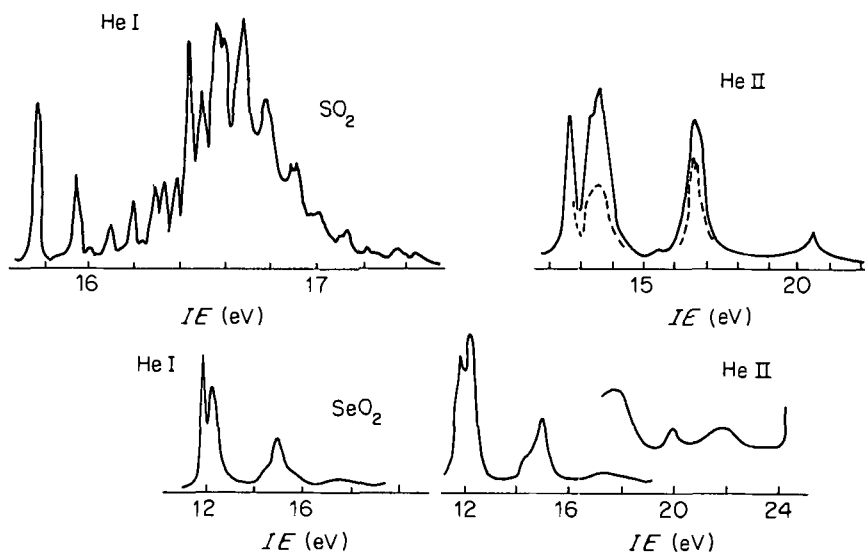
FIGURE 4. Photoelectron spectra of SO_2 (*reproduced by permission of Taylor and Francis from Reference 55*) and SeO_2 (*reproduced by permission of Elsevier Science Publishers from Reference 53*)

TABLE 8. Ionization energies for SeO_2[a]

IE^b (eV)	Assignment
11.76	$4a_1(n_{Se})$
12.18	$1a_2(\pi_{Se-O}) + 3b_2(\pi_{O-O})$
14.56	$2b_2(\sigma_{O-Se-O})$
14.95	$3a_1(\pi_{O-Se-O}) + 1b_1(\pi_{O-Se-O})$
17.61	CI
19.90	$2a_1(4s_{Se})$
21.80	CI

[a] From Reference 53.
[b] Values refer to band maxima.

He II ionizing radiation. This supports the assignment to the ionization of a substantially non-bonding orbital $(4a_1)$ with the main contribution from the Se 4p atomic orbital. The second band, at 12.18 eV, accounts for two ionizations, $(1a_2)^{-1}$ and $(3b_2)^{-1}$, of a π Se—O bonding orbital and an antibonding O—O orbital. The third, broad band, with a peak at
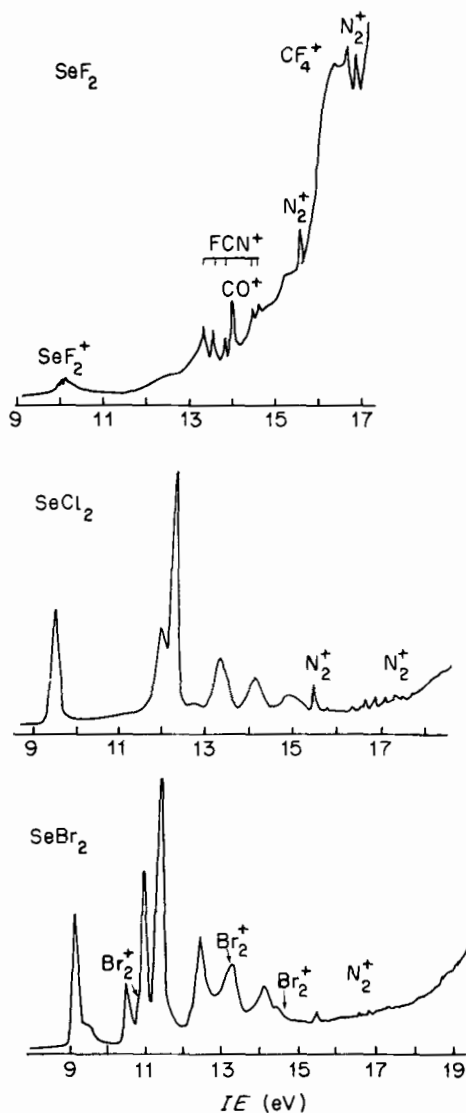
FIGURE 5. He I photoelectron spectra of SeA$_2$ molecules (A = F, Cl and Br). *Reproduced by permission of North-Holland Physics Publishing from Reference 61*

14.95 eV and a shoulder at 14.56 eV, arises from ionization of the $2b_2$, of σ nature, $3a_1$ and $1b_1$, both bonding between oxygen and selenium.

The weak band at 19.9 eV observed in the He II spectrum corresponds to the non-bonding $2a_1$ orbital. The features at 17.61 and 21.80 eV derive from configuration interaction (CI) processes.

In the spectrum of TeO_2[53], the vapour in equilibrium with this substance was shown to consist largely of TeO (see Section II.A.2). However, analysis showed that bands at 11.15 eV, presumably due to $(3b_2)^{-1} + (1a_2)^{-1} + (4a_1)^{-1}$ ionization, and 12.7 eV, due to $(2b_2)^{-1} + (3a_1)^{-1} + (1b_1)^{-1}$ ionization, could probably be attributed to the TeO_2 molecule.

In recent years significant progress has been made in the study of transient species in the gas phase by means of UPS[57]. Because of the importance of short-lived species in various branches of gas-phase chemistry, and since physical information is often scarce, the study of transients by means of spectroscopic techniques does not lack incentive.

Related small molecules studied extensively by UPS are the XA_2 (X = O, S, Se, Te; A = F, Cl, Br) compounds. Only the three stable members of this series were studied with conventional experimental methods, viz. OF_2[58], OCl_2[58] and SCl_2[59,60]. Application of UPS to the remaining members of the series has been met with varying degrees of experimental difficulty. He I photoelectron spetra of SeF_2[61], $SeCl_2$[61,62] and $SeBr_2$[61,63] were described and interpreted on the basis of comparison with the spectra of the related sulphur and oxygen dihalogenides and with the results of theoretical calculations. In the UP spectrum of these molecules seven bands are expected from 14 p electrons. In fact, each halogen atom contributes two lone pairs and one unpaired electron, while the selenium atom contributes one lone pair and two unpaired electrons. The combined lone-pair orbitals on both halogen atoms transform as a_1, a_2, b_1, b_2 in C_{2v} symmetry, while the selenium lone-pair orbital transforms as b_2. The out-of-plane b_2 orbitals interact strongly to form the widely separated antibonding $2b_2$ and bonding $1b_2$ combinations. The remaining a_1, a_2 and b_1 halogen orbitals are relatively unshifted with respect to their positions in the atomic halogens and lie between the two b_2 MOs. The remaining two unpaired selenium electrons combine with those of the halogen atoms to form the strongly bonding $3a_1$ and $2b_1$ MOs, which will lie below $1b_2$. The UP spectra, shown in Figure 5, are consistent with this description. Unfortunately, only the first ionization of $SeFe_2$ could be observed. In the spectrum of this molecule bands due to CF_4, N_2, CO and FCN were also detected.

The LCBO model, applied to the series $SeCl_2$, SCl_2 and OCl_2, gives good results[61] but fails for $SeBr_2$ because insufficient UPS data are available for OBr_2 and SBr_2.
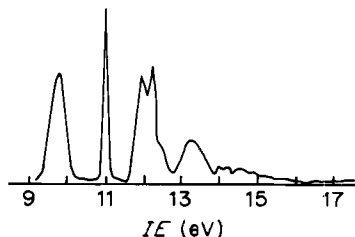
FIGURE 6. He I photoelectron spectrum of Se_2Cl_2 stripped by the spectrum of the mixture $SeCl_2/Se_2Cl_2$, product of the reaction Se + Cl_2. *Reproduced by permission of the Royal Society of Chemistry from Reference 62*

TABLE 9. Ionization energies (eV) for S_2Cl_2[a] and Se_2Cl_2[b]

	S_2Cl_2			Se_2Cl_2	
Assignment[c]	Experimental	Calculated (CNDO)	Assignment[c]	Experimental	Calculated (VEOMP)
$n_S^-(17a)$	$(10.1)^d$	11.02	$n_{Se}^-(26a)$	9.81	10.00
$n_S^+(16b)$	(10.3)	11.30	$n_{Se}^+(25b)$	9.81	10.30
$n_{Cl} \begin{bmatrix} (16a) \\ (15b) \\ (15a) \\ (14b) \end{bmatrix}$	11.43	12.32	$n_{Cl} \begin{bmatrix} (25a) \\ (24b) \\ (23b) \\ (24a) \end{bmatrix}$	11.05	11.01
	12.20	13.59		12.03	12.52
	12.52	14.05		12.28	12.98
	(12.6)	14.13		12.50	13.00
$\sigma_{SS}(14a)$	14.07	15.88	$\sigma_{Se-Se}(23a)$	13.41	13.61
$\sigma_{SCl}^-(13b)$	15.65	16.05	$\sigma_{SeCl}^-(22b)$	13.65	13.66
$\sigma_{SCl}^+(13a)$	(17.02)	16.72	$\sigma_{SeCl}^+(22a)$	14.66	14.34
$3s_S(12b)$	(19.3)	23.29			

[a] From Reference 64.
[b] From Reference 62.
[c] The figures and letters in parentheses refer to the numbering and symmetry of MOs.
[d] Values in parentheses are ill-defined maxima.

Nagy-Felsobuki and Peel[62] detected, in the He I spectrum of the gaseous products of the reaction of chlorine with powdered selenium at room temperature, bands arising from Se_2Cl_2 species. Figure 6 shows the stripped spectrum of Se_2Cl_2. It is very similar to that of S_2Cl_2, reported by Solouki and Bock[64], and the assignment follows the same lines [see Table 9, where the results of valence-electron-only-model-potential (VEOMP) calcu-
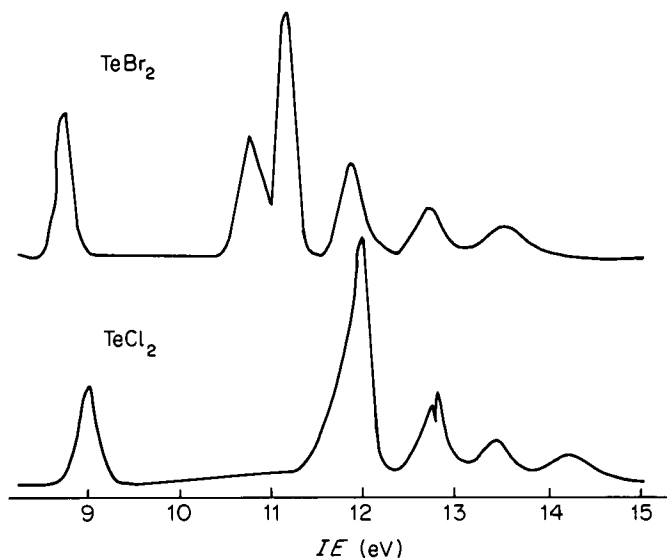
FIGURE 7. He I photoelectron spectra of $TeCl_2$ and $TeBr_2$. *Reproduced by permission of North-Holland Physics Publishing from Reference 65*

XCl$_2$, X = Te, Se, S and O   XBr$_2$, X = Te, Se and S
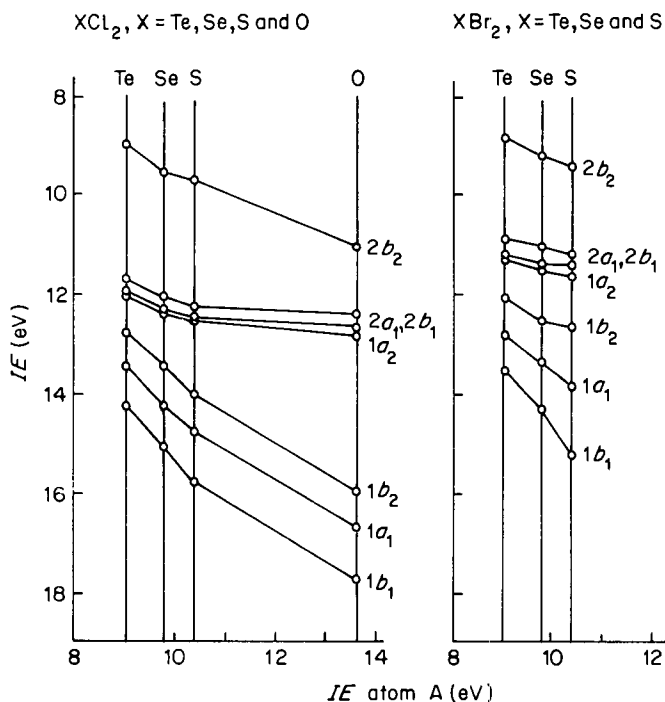
FIGURE 8. Correlation diagram of the experimental ionization energies of XCl$_2$ (X = Te, Se, S and O) and XBr$_2$ (X = Te, Se and S) molecules versus the first atomic ionization energies. *Reproduced by permission of North-Holland Physics Publishing from Reference 65*

lations are also reported]. The agreement between the experimental and theoretical data confirms the validity of the geometry of Se$_2$Cl$_2$ optimized by the VEOMP calculations: C_2 symmetry with Se—Se and Se—Cl bond lengths of 2.40 and 2.20 Å, respectively, a Cl—Se—Se bond angle of 98° and a dihedral angle of 90°.

The He I spectra of TeCl$_2$ and TeBr$_2$, measured by Jonkers and coworkers[65], are shown in Figure 7. The assignment, supported by both non-relativistic and relativistic Hartree–Fock–Slater (HFS) calculations, is analogous to that for SeCl$_2$ and SeBr$_2$. In Figure 8 the trends found in the He I spectra of XCl$_2$ and XBr$_2$ molecules are presented.

C. Pseudohalide Derivatives

The transient molecules ASeCN (A = Cl, Br) were prepared and detected by UPS for the first time by Jonkers and coworkers[66], by passing the corresponding molecular halogens over freshly prepared silver selenocyanate (AgSeCN) deposited in the tip of the spectrometer inlet system. The photoelectron spectrum was assigned on the ground of comparison with the already known UPS data for the ASCN (A = Cl, Br) molecules[67] and with the results of HFS transition-state calculations. From a simple MO approach with the molecules constructed from three fragments, i.e. two separate atoms and one cyanide

Carla Cauletti and Giuseppe Distefano

TABLE 10. Ionization energies (eV) for AXCN (A = Cl, Br; X = S, Se)

Band label	CISCN[a]	BrSCN[a]	Assignment	CISeCN[b]	BrSeCN[b]	Assignment
	(10.45)	(10.26)				
1	10.52	10.32	$3a''(\pi_{AS})$	10.19	9.99	$3a''(\pi_{ASe})$
2	12.67	11.89	$8a'(n_A)$	12.43	11.69	$8a'(n_A)$
3	13.05	12.39	$7a'(\pi_A)$	~12.9	12.24	$2a''(\pi_A)$
4	13.28	12.65	$2a''[n_A, \pi_{C\equiv N}$ (in-plane)]	12.82	12.56	$7a'[\pi_{C\equiv N}$ (in-plane)]
5	13.66	13.43	$6a'(p\sigma_{SCN})$	13.49	13.25	$6a'(n_N)$
6	14.47	14.00	$1a'(\pi_b)^c$	13.85	13.54	$1a''[\pi_{C\equiv N}$ (out-of-plane)]
7	15.44	14.93	$5a'(\pi_b)^c$	14.90	14.41	$5a'(\pi_b)^c$
8	17.55	17.18	$4a'(\sigma_{S-C})$	16.95	16.76	$4a'(\sigma_{Se-C})$

[a] From Reference 67.
[b] From Reference 66.
[c] Bonding orbital delocalized on the whole molecule.

group, taking into account only the valence p orbitals for Se and X atoms and the 2σ, 3σ and 1π fragment orbitals (FROs) for the CN group, eight orbitals are expected to give rise to bands in the He I spectrum. The halogen atom contributes two lone pairs and one unpaired electron, the selenium atom one lone pair and two unpaired electrons and the cyanide fragment one lone pair $(2\sigma = n_N)$, two filled π and one half-filled 3σ FRO. The selenium atom shares one of its unpaired electrons with the halogen atom and the other with the CN fragment (3σ) giving rise to two MO ionization phenomena, while six more or less lone-pair or π-type ionizations are expected. Table 10 reports the observed IEs and the proposed assignment for both ASeCN and ASCN. The overall UP spectra and even various features of the corresponding bands in both series show detailed agreement. Spectral comparison between CIXCN and BrXCN (X = S or Se) indicates that bands 1, 6, 7 and 8 show shifts due to significant central atom character, in agreement with the proposed assignments.

The same authors[66,68] measured the He I and He II spectra of the stable compound $Se(CN)_2$, which are shown in Figure 9 and whose assignment parallels that for SeA_2 (A = Cl, Br)[65], with the obvious difference that the halogen lone pairs are replaced by π_{CN} FROs and two nitrogen lone-pair ionizations (n_N) appear.

At variance with the ASeCN molecules, methyl selenocyanate (MeSeCN) is a stable compound. Its photoelectron spectrum was studied[18] together with that of the thio analogue, (MeSCN), investigated by UPS also by other workers[69]. The spectra of the two compounds look very similar (see Figure 10), the only appreciable difference being a parallel shift by about 0.3 eV of all bands to lower ionization energy in the selenium derivative, consistent with the lower electronegativity of Se compared with S. The assignment, supported by CNDO and *ab initio* calculations and comparison with related simpler molecules, therefore follows the same general lines. The first band, significantly decreasing in intensity with respect to the following bands in He II, arises from the ionization of an essentially non-bonding orbital, i.e. the halogen lone pair $(\pi_X; X = S, Se)$. The calculations suggest a certain degree of conjugation with a $\pi_{C\equiv N}$ component. The second band corresponds to a p-type orbital of X, which is close to bisecting the CXC angle. The shape and intensity of the third band (a very intense adiabatic transition,
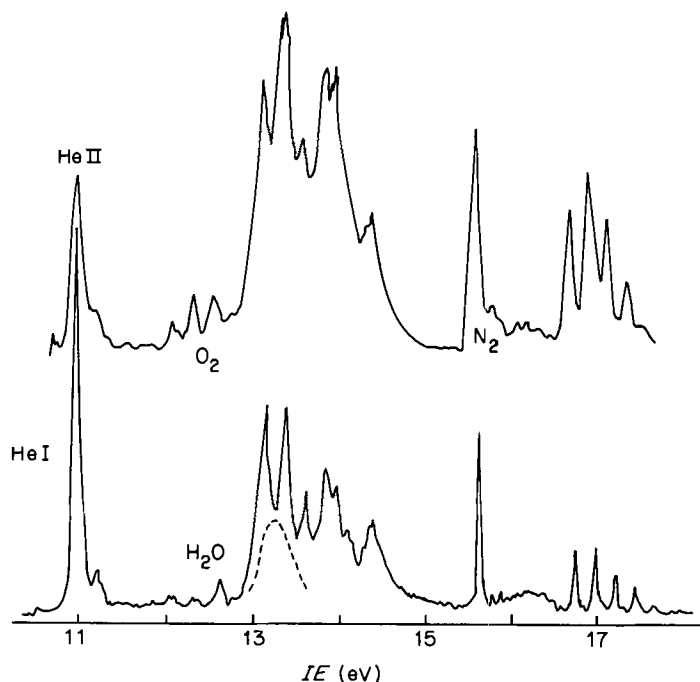
FIGURE 9. Photoelectron spectra of $Se(CN)_2$. *Reproduced by permission of Taylor and Francis from Reference 66*

followed by a broad structure with an irregular vibrational progression) suggest that it should be attributed to two ionization processes, namely of the two π orbitals of the XCN group, mainly formed by C and N atomic contribution. The fourth band is due to ionization of a σ-bonding orbital of the system C—X—C—N.

It is interesting to study the effect on the MOs of changing A in the series AXCN (A = Cl, Br, CH_3; X = S, Se). Figure 11 shows a correlation diagram between ClSeCN, BrSeCN and MeSeCN. Apart from the obvious appearance of the halogen lone-pair ionizations in the first two compounds, the following points deserve attention:

(i) the HOMO does not shift much along the series (10.19 eV for A = Cl, 9.99 eV for A = Br, 9.68 eV for A = Me), despite the opposite inductive effect of Cl and Br versus Me. This is probably due to the destabilizing interaction of the selenium lone pair with the halogen lone pairs, which partly counterbalances the electron-withdrawing effect of the halogen.

(ii) the same does not occur for the second MO (the fourth of the halogen derivatives) which ionizes at 12.82 eV in ClSeCN and 12.56 eV in BrSeCN, moving to 11.76 eV in MeSeCN. This is in agreement with the nature of this orbital, lying in the plane of molecule.

(iii) the most affected MO is the fifth one of MeSeCN (seventh of ClSeCN and BrSeCN, *I E* 14.90 eV in ClSeCN, 14.41 eV in BrSeCN and 13.37 eV in MeSeCN), consistent with the significant contribution of AOs of all the three groups.
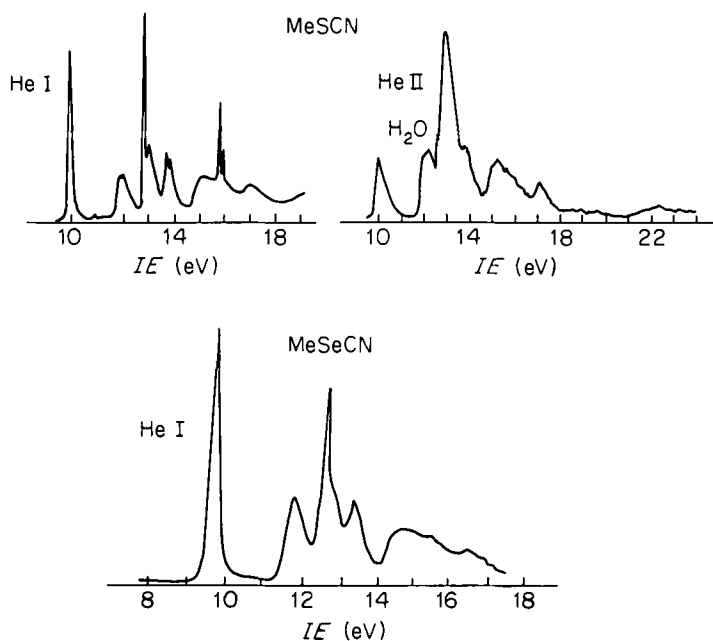
FIGURE 10. Photoelectron spectra of MeSCN (*reproduced by permission of the Royal Society of Chemistry from Reference 18*) and MeSeCN (*reproduced by permission of Elsevier Science Publishers from Reference 69*)
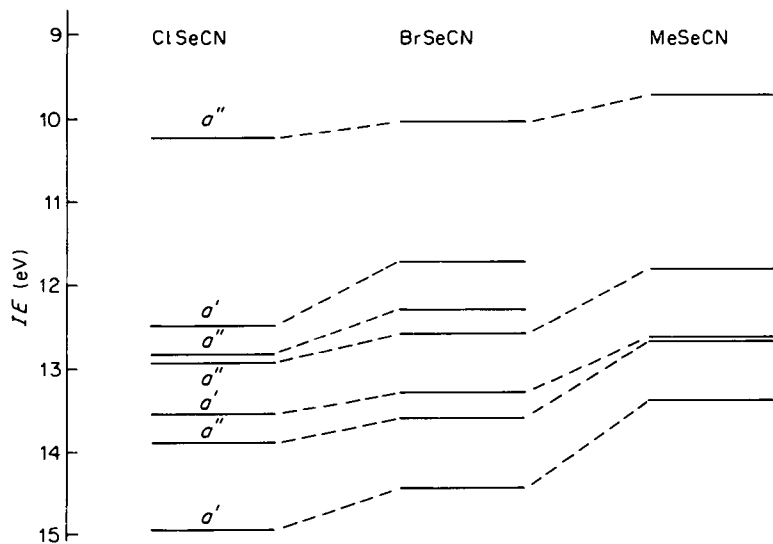
FIGURE 11. Correlation diagram of the ionization energies of the ASeCN (A = Cl, Br and Me) molecules. ClSeCN and BrSeCN from Reference 66; MeSeCN from Reference 18

TABLE 11. Vertical ionization energies (eV)
for PF_2X (X = —NCS, —NCSe)

X = —NCS[a]	X = —NCSe[b]	Assignment
10.2	9.8	π_{NCX}
11.9	11.7	n_P
13.9	13.6	π_{NCX}
15.5	15.2	$\sigma_{P—N}$
16.4	16.4	π_F
18.0		$\sigma_{P—F}$

[a] From Reference 71.
[b] From Reference 70.

Andreocci and collaborators[18] also measured the UP spectra of phenyl-substituted selenocyanates and isoselenocyanates, together with those of the corresponding thio analogues. Unfortunately, the dominant features of the spectra, corresponding to ionizations of phenyl-based orbitals, completely masked the ionizations of the —XCN and —NCX groups, preventing any detailed assignment.

The moderately stable (in the vapour phase) difluoro(isoselenocyanato)phosphine, $PF_2(NCSe)$, was studied by UPS, IR spectroscopy and NMR[70]. The photoelectron spectrum was assigned by analogy with those of $PF_2(NCO)$ and $PF_2(NCS)$[71] (see Table 11). The first and third bands, peaked at 9.8 and 13.6 eV, respectively, arise from $(\pi)^{-1}$ ionizations of the NCSe moiety, the second band, at 11.7 eV, from ionization of the phosphorus lone pair, the fourth band, at 13.6 eV, is related to the P—N bond and the fifth band, at 15.2 eV, is related to a fluorine lone pair.

III. CHALCOGEN HETEROCYCLOPENTADIENES AND THEIR DERIVATIVES

A. Monocyclic Compounds

1. Experimental data

The filled $1a_2$, $2b_1$ and $1b_1$ and empty $3b_1$ and $2a_2$ π MOs of the pentaatomic heteroaromatic rings furan (1), thiophen (2), selenophen (3) and tellurophen (4) can be considered to derive from the interaction between those of cis-butadiene and the p_π AO of the heteroatom X. By symmetry, the latter can participate only in the b_1 MOs (see Figure 13). Therefore, the influence of X is expected to be much larger on these than on the a_2 MOs.

A comparison of the UPS data for the first two bands of the four compounds shows[72,73] that the energy of one is constant, whereas that of the other changes with the heteroatom. They have therefore been assigned to the $1a_2$ and $2b_1$ MOs, respectively (see Table 12). This assumption, which was also based on the non-bonding shape of the first band in the spectrum of tellurophen, and on the variation of the IE values with the heteroatom electronegativity (or IE value)[72,73], leads to a reversal of the energy sequence of the π $1a_2$ and π $2b_1$ MOs in tellurophen with respect to the other congeners where the HOMO is the $1a_2$ MO (see Figure 12).

This assignment has been confirmed by the data of the α-monosubstituted derivatives[74]. In fact, methyl or halogen substitution at $C_{(2)}$ (see Table 12) causes an increase in the

TABLE 12. Experimental π_3 and π_2 ionization energy values and their difference (Δ) for furan, thiophen, selenophen and tellurophen and for their 2-methyl derivatives (eV)[a]

Compound	π_3 ($1a_2$)	π_2 ($2b_1$)	$\Delta(\pi_2 - \pi_3)$
Furan	8.88	10.31	1.43
2-Methylfuran	8.37	10.13	1.76
Thiophen	8.87	9.52	0.65
2-Methylthiophen	8.43	9.23	0.80
Selenophen	8.88	9.14	0.26
2-Methylselenophen	8.40	8.96	0.56
Tellurophen	8.88	8.40	0.48
2-Methyltellurophen	8.43	8.20	0.23

[a] The ionization energies were taken from References 72–77.

separation of the first two bands in **1–3** and a decrease in **4**, in agreement with the expectation that electron-releasing substituents in the α-position exert a more pronounced destabilizing effect on the energy of the $1a_2$ MO (because of its larger wavefunction coefficient) than on the $2b_1$ MO.

More conclusive support for the reversed sequence in **4** has been obtained[74] from an examination of the correlation between the corresponding IE values for the various congeners. In fact, slopes close to one, very high correlation coefficients and low values of standard errors were obtained when the IE values of $1a_2$ and $2b_1$ bands of a series of substituted furans (selenophens or tellurophens) were plotted against the corresponding values for substituted thiophens. The very poor correlations obtained by plotting the IE_1 ($2b_1$) of tellurophens against IE_1 ($1a_2$) of thiophens and the IE_2 ($1a_2$) of tellurophens versus IE_2 ($2b_1$) of thiophens confirmed the change of ordering[74].
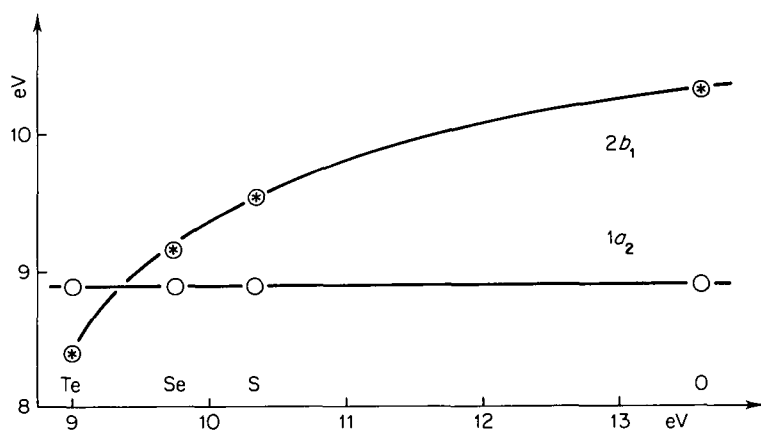
FIGURE 12. Plots of the $\pi 2b_1$ and $\pi 1a_2$ ionization energies of furan, thiophen, selenophen and tellurophen versus the ionization energy of the corresponding heteroatom

The first two bands in the UP spectrum of **3** partly overlap, indicating that the corresponding MOs are close in energy. The vibrational structures are only partly resolved so that there were some doubts[72,73] about the assignment of IE_1 and IE_2 and their precise vertical values.

A contribution toward the solution of this problem has been obtained[74] by plotting the IE_1 and IE_2 values for α-substituted selenophens against the corresponding values for the other congeners. Average interpolated values (for α-substituent = H) of 8.88 (π $1a_2$) and 9.14 (π $2b_1$) eV were obtained, which are in excellent agreement with the values and the assignment reported[72].
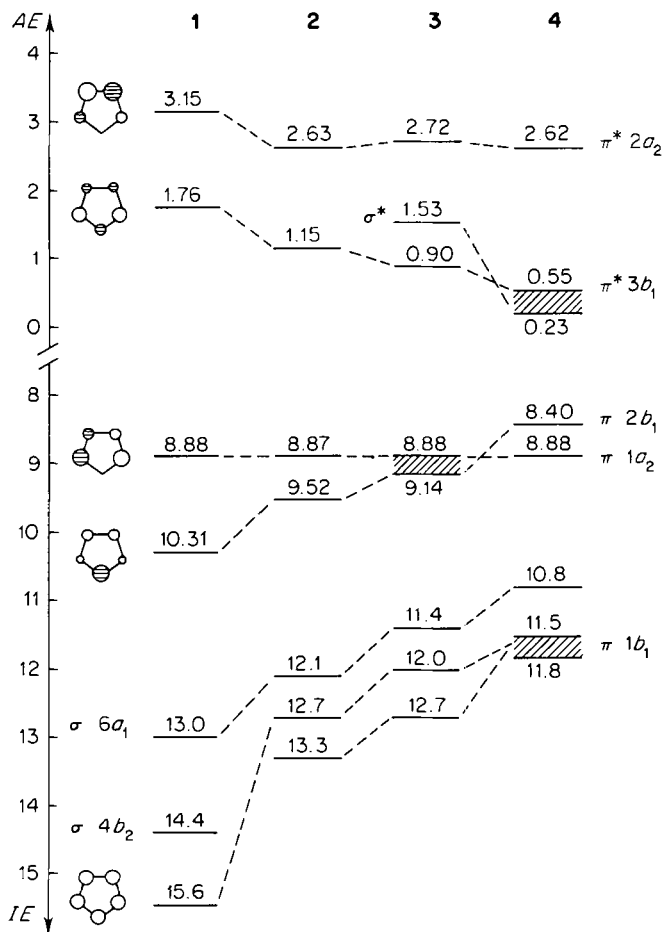
FIGURE 13. Ionization energy (eV) and attachment energy correlation diagram for furan (**1**), thiophen (**2**), selenophen (**3**) and tellurophen (**4**) *Reproduced by permission of North-Holland Physics Publishing from Reference 81*

The assignments of the next bands of **3** and **4** have been attempted[74] by comparing their UP spectra with those of the corresponding tetrahydro derivatives[80]. On this basis, it has been suggested that ionization from the $1b_1 \pi$ MO contributes to the fourth band in both spectra. The third and the remaining component of the fourth band in **4** and the fifth band in **3** have been ascribed to σ_{X-C} ionizations.

According to this assignment, the IE value of the innermost π MO of the five-membered congener compounds decreases with increasing heteroatom electronegativity (see Figure 13).

2. Comparison with theoretical computations

Several attempts have been made to confirm the empirical assignments on the basis of theoretical calculations.

Findlay's minimal basis set STO-3G and open-shell RHF calculations indicate[82] that the ordering of the uppermost MOs of **3** is $2b_1 < 1a_2$, the reverse of that found for thiophen and furan and the experimentally established order. In these *ab initio* computations, the total energy for selenophen is found to decrease by $76.5 \, kJ \, mol^{-1}$ on going from an sp to an spd basis set. Nevertheless, the 4d orbitals have been considered to assume the role of polarization functions, i.e. to increase the variational flexibility of the system rather than to make a significant contribution to the ground-state bonding[82].

Similarly, the MS X_α computations of De Alti and Decleva[83] do not reproduce the near degeneracy, in **3**, or the reversal, in **4**, of the first two IE values, although they correctly reproduce the constancy of the $\pi \, 1a_2$ MO and the destabilization of the $\pi \, 1b_1$ and the $\sigma \, 6a_1$ and $\sigma \, 4b_2$ MOs from **1** to **4**.

According to the X_α computations, the compositions of the $1b_1$ and $2b_1$ orbitals change with the heteroatom. The former is largely heteroatom in character in furan, whereas it becomes mostly ring in the other molecules. The latter exhibits the reverse behaviour, so that the two orbitals exchange their nature. This may be reasonably attributed to the difference in the relative energies of the b_1 ring and p_π heteroatom levels along the series. The $6a_1$ and $4b_2 \, \sigma$ MOs show a prevailing heteroatom character deduced experimentally[74].

The inversion in the energy sequence of the two uppermost $\pi \, IEs$ of tellurophen, with respect to the other members in the series and their near degeneracy in **3**, are correctly accounted for by application of a one-particle Green's function technique within the framework of the CNDO approximation[84] and by a successive MS X_α approach[81]. The former computations also predict the ordering of the succeeding IEs ($6a_1 < 1b_1 \approx 4b_2$) to be the same in both **3** and **4**, which is consistent with the analogies in their UP spectra[72,74] and the band shifts with respect to their tetrahydro derivatives[74,80].

3. Electron affinity values

The experimental electron affinities (EAs) of **1–4**, determined by electron transmission spectroscopy (ETS)[81]† , are presented in Table 13 together with the corresponding data computed by a Green's function technique[84] and the X_α method[81]. Reasonable agreement between the theoretical and experimental EAs is apparent. The energies of the $2a_2 \, (\pi^*)$ MO are nearly the same in **2–4**, but considerably smaller than in **1**. The $3b_1 \, (\pi^*)$ MO is increasingly stabilized in the heavier congeners, that is, with *decreasing* heteroatom

---

†For a brief description of the ETS technique, see Section VIII.

TABLE 13. Electron affinities (eV) of heterocyclopentadienes

Molecule	MO	EA^a (Green's function)	EA^b (MS X$_\alpha$)	EA^b (exptl.)
Furan	$2a_2$	− 3.06	− 3.19	− 3.15
	$3b_1$	− 1.95	− 1.82	− 1.76
Tiophen	$2a_2$	− 2.84	− 2.81	− 2.63
	$3b_1$	− 1.47	− 1.57	− 1.15
Selenophen	$2a_2$	− 2.69	− 2.76	− 2.72
	$3b_1$	− 1.19	− 1.53	− 0.90
Tellurophen	$2a_2$	− 2.59	− 2.67	− 2.62
	$3b_1$	− 0.95	− 1.02	− 0.55

^{a} From Reference 84.
^{b} From Reference 81.

electronegativity (see Figure 13)[†]. Both the $3b_1$ and $2a_2$ (π*) MOs can mix with heteroatom d orbitals of proper symmetry and be stabilized. This interaction is absent in furan where d orbitals at low energy are not available.

A correct evaluation of the effective d–π* mixing has been obtained by X$_\alpha$ computations. This method, in fact, solves numerically the Schrödinger equation in partial waves. In the LCAO methods the contributions from d orbital basis functions can arise through lack of convergence of the lower angular momentum functions[86–88].

According to the results of the calculations, the d–π* mixing is negligible in furan, while the two Π anion states of 2–4 have some heteroatom d orbital character, in agreement with the observed stabilization. It is to be noted, however, that the largest d orbital character is calculated for the $^2A_2$ anion state of thiophen (ca. 16% of the atomic sphere charge density), suggesting that geometric parameters affect the observed attachment energies (AEs, the negative of the electron affinities). The large increase in the chalcogen—carbon bond length (O—C, 1.362 Å[89]; S—C, 1.714 Å[90]; Se—C, 1.885 Å[91]; Te—C, 2.055 Å[92]) can reduce the antibonding interaction between the heteroatom lone pair orbital and the adjacent carbon atoms, and also that between $C_{(2)}$ and $C_{(5)}$ (see the orbital sketches in Figure 13), resulting in a stabilization of the $3b_1$ and $2a_2$ MOs, respectively[81]. This effect is apparent only when vacant orbitals are considered probably because of their more diffuse nature with respect to filled orbitals.

The X$_\alpha$ calculations predict in 2–4 a $\Sigma^2 B_2$ anion state with a very large heteroatom d character close in energy to the $\Pi^2 B_1$ anion state. The corresponding resonance is observed between the two σ resonances in the spectrum of 3 and at the lowest energy in the spectrum of 4. It is not observed, however, in the spectrum of thiophen[85], probably because it overlaps with the π resonance. In fact, the spectra of thiazole and isothiazole display an additional resonance centred at about 1.6 eV[85].

[†] The IE values have been taken from References 72–79, 83 and 84 and the EA values from References 81 and 85. In the energy region shown in the figure there are some other σ IEs deriving from MOs mainly localized at the ring and therefore almost insensitive to the change in heteroatom. They have been omitted for clarity.

B. Bicyclic Derivatives

1. Benzo derivatives

The assignment of the UP spectra of benzo[b]selenophen (5) and benzo[b]tellurophen has been made[93] on the basis of semiempirical PPP calculations and the analysis of relative band intensities observed by changing the ionizing radiation from He I to He II. The first three bands have been found to correspond to the uppermost π orbitals by analogy with the assignment of the spectra of the corresponding oxygen and sulphur derivatives[94-97]. The variation of the ionization energy values $(IE_1 - IE_3)$ with the electronegativity of the ionization energy of the heteroatom is similar, but smaller, than that observed for the simple pentaatomic compounds. This smaller sensitivity has been ascribed to the larger number of carbon atoms present per heteroatom and to the lack of symmetry[93].
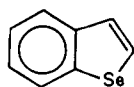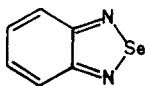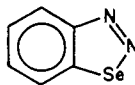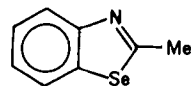
(5)   (6)   (7)   (8)

The photoelectron spectrum of 2, 1, 3-benzoselenadiazole (6) is remarkably similar to that of the corresponding thiadiazole, both in overal shape and in the position of the maxima. The same situation occurred with selenophen and thiophen, and has been related to the similar electronegativity of the heteroatoms and to the similarity of their orbital energies[98]. Analogously, the spectra of 1, 2, 3-selenadiazole[99,100], 1, 2, 3-benzoselenadiazole (7)[100] and 2-methylbenzoselenazole (8)[101] very closely resemble those of the corresponding sulphur compounds[102,103]. The assignment of the first few bands has been reported[99,101].

2. Thienothiophenes and selenolo analogues

A more detailed analysis of the electronic effects of the heteroatom on the orbital energies of five-membered heterocycles has been reported by Gleiter and coworkers[104]. They compared the UP spectra of thieno[2, 3-b]thiophen (9) and thieno[3, 2-b]thiophen (12) with the selenolo analogues 10–14.
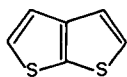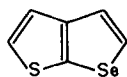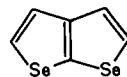
(9)   (10)   (11)
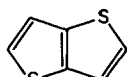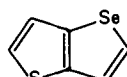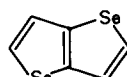
(12)   (13)   (14)

The UP spectra of the series 9–10–11 all appear very similar, as do the UP spectra of the series 12–13–14. HMO calculations reproduce the significant trends observed (see Table 14).

TABLE 14. Measured vertical ionization energies
(IEs) and Hückel MO theory orbital energies (ε)
(eV) of **9–14**[a]

Compound	Assignment	ε	IE
9	$4b_1$	-8.48	8.32
	$3a_2$	-8.60	8.41
10	$8a''$	-8.32	8.28
	$7a''$	-8.49	8.28
11	$4a_2$	-8.16	8.16
	$5b_1$	-8.45	8.16
12	$4a_u$	-8.25	8.10
	$3a_u$	-8.94	8.61
13	$8a''$	-8.19	8.08
	$7a''$	-8.61	8.39
14	$5a_u$	-8.09	8.05
	$4a_u$	-8.50	8.20

[a] *Reproduced by permission of the American Chemical
Society from Reference 104. Copyright (1977) American
Chemical Society.*

Replacement of sulphur by selenium has been considered as a minor perturbation. Its effects have in fact been described by simple perturbation theory applied to the MOs of **9** and **12** computed according to the Hückel method. The HOMO of **9** has a small localization at the sulphur atoms, while the next MO has a large amplitude in these positions. The two orbitals are therefore destabilized to different extents by substitution of selenium for sulphur. This gives rise to a reversal of the ordering in the series **9–10–11**. Similar shifts are shown by the two highest occupied orbitals in **12**. They, however, have the same symmetry and interact considerably, but the crossing (along the series **12–14**) is not allowed. Their shape corresponds to the initial stages of an 'avoid crossing'[104].

IV. SELENIDES AND TELLURIDES

A. Alkyl Chalcogenides

The Group IV hydrides have the valence shell structure $(1a_1)^2$ $(1b_2)^2$ $(2a_1)^2$ $(1b_1)^2$. Ionization from the $1b_1$ orbital results[13,14] in a sharp and intense peak, characteristic of non-bonding electrons, followed by a short vibrational progression. The second $(2a_1)$ and third $(1b_2)$ band systems show long progressions, in agreement with the strong H—X bonding character for these orbitals (see Figure 1).

The $(1a_1)^{-1}$ photoelectron bands are all extremely weak because they are related to orbitals which have mainly s AO character. For these orbitals the photoionization cross-section near the ionization threshold is very much less than that of p AOs.

The IE values (see Table 15) exhibit a clear dependence on the atomic number of the heteroatom. In particular, IE_1 and IE_4 are fairly close to the first and the second IE values[105] of the corresponding heteroatom.

There is a sudden loss of vibrational structure around the maximum of the second band of H_2S, H_2Se and H_2Te. It may be due, at least in part, to predissociation into $X^+ + H_2$, which also is found at these energies[106]. In contrast, the $^2A_1$ state of H_2O^+ does not predissociate. The formation of O^+ ions from H_2O occurs at much higher energy than that

TABLE 15. X lone pair and X—C vertical IE values (eV) of alkyl chalogenides, R_2X (X = O, S, Se, Te)[a]

R	$X_{lp}(b_1)$	$\sigma_{(X—C)}(a_1)$	$\sigma_{(X—C)}(b_2)$
Oxygen derivatives			
H	12.62	14.74	18.51
Me	10.04	11.91	13.43
SiH_3	11.17	11.2	14.5
GeH_3	10.40	10.9	13.5
$CH_2—CH_2—$ | $CH_2—CH_2—$	9.65	11.4	13.0
Sulphur derivatives			
H	10.47	13.33	15.47
Me	8.71	11.28	12.68
SiH_3	9.70	11.15	11.71
GeH_3	9.25	10.66	11.30
$CH_2—CH_2—$ | $CH_2—CH_2—$	8.42	10.9	$\geqslant 11.9$
Selenium derivatives			
H	9.88	12.93	14.62
Me	8.40	11.0	12.0
SiH_3	9.18	10.85	11.29
GeH_3	8.84	10.44	10.88
$CH_2—CH_2—$ | $CH_2—CH_2—$	8.14	10.5	$\geqslant 11.4$
Tellurium derivatives			
H	9.14	12.00	13.25
Me	7.89	10.35	11.32
SiH_3	8.63	10.23	10.83
GeH_3	8.34	9.93	10.56
$CH_2—CH_2—$ | $CH_2—CH_2—$	7.73	10.0	10.7

[a] R = H, from Reference 14; R = MH₃, from Reference 107; R = C₄H₈, from Reference 108.

of the $^2A_1$ state and the $^2A_1$ band exhibits vibrational structure extending over the whole band[13,14].

Analogously, the sharp, intense band at lowest IE in each of the $(MH_3)_2X$ molecules (M = C, Si, Ge; X = O, S, Se, Te) has been assigned to the $1b_1$ MO, the X_{np} lone pair orbital[107]. The trend of IE₁ parallels that observed[14] for the corresponding hydrides (see Table 15).

The second and the third bands correspond to the $3a_1$ and $2b_2$ bonding orbitals, respectively. They shift to lower values with increasing atomic number of X and M. All are smaller than the corresponding hydride values, indicating an electron-releasing capability of the MH_3 groups.

The variation of the first IE with M is C < Ge < Si in each series, rather than C > Si ≥ Ge, as might have been expected on the basis of electronegativity changes. This effect has been ascribed to π-donation from the X lone pair towards the nd AOs of M.
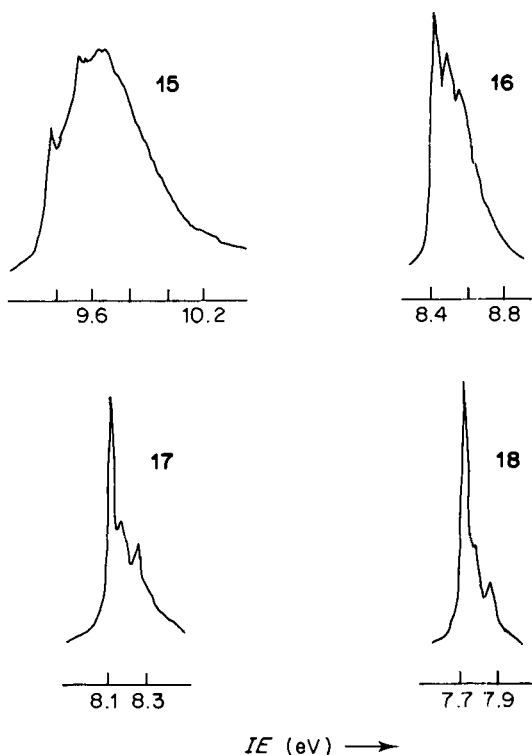
FIGURE 14. First band of the He I photoelectron spectra
of $(CH_2)_4X$ (X = O, S, Se and Te). *Reproduced by permission
of North-Holland Physics Publishing from Reference 80*

The X_{lp} and the two X—C bonding orbitals of the $(CH_2)_4X$ derivatives (**15–18**) are
pushed to even higher energy with respect to the corresponding MOs of the dimethyl

(**15**)   (**16**)   (**17**)   (**18**)
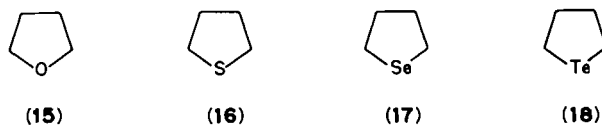
derivatives. However, their relative ordering in each compound and by changing X are
mantained[108] (see Table 15).

The most peculiar aspect of the spectra of these cyclic compounds is the shape of the first
band. The characteristic non-bonding aspect observed in the previous series is still present
in **18** and, to a lesser extent, in **17**, while the band assumes an increasingly bonding
structure on going towards tetrahydrofuran (see Figure 14).

The X_{lp} orbital can interact by symmetry with the in-phase combination of the pseudo π
orbitals of the CH_2 groups. For overlap and energy reasons this interaction gradually
increases on going from **18** to **15**, causing a gradual broadening of the first band. This is
confirmed by the plot of the IE_1 values against those of the corresponding hydrides[14].
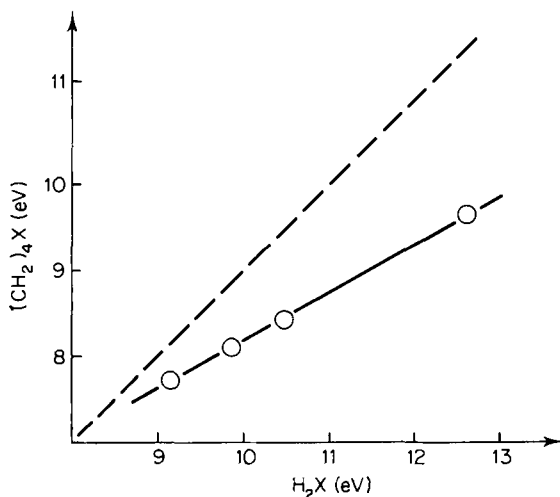
FIGURE 15. Plot of the first ionization energy of $(CH_2)_4X$
$(X = O, S, Se$ and Te) versus the corresponding one of H_2X.
Reproduced by permission of North-Holland Physics Publishing from Reference 80

The two sets of data are linearly related, but the slope is significantly less than one. The distance of $(CH_2)_4O$ from the 45° line is the greatest, in agreement with the increasingly bonding character of the lone pair orbital on going from **18** to **15** (see Figure 15).

B. Open-chain and Cyclic Ethylene Derivatives

1,4-Dithiin (**19**) and the related compounds 1,4-thiaselenin (**20**) and 1,4-thiatellurin (**21**) posses four π MOs whose energy patterns are shown in Figure 16[110].

(19)   **(20)**   **(21)**

The first two bands, π_4 and π_3, are related to the in-phase (π^+) and out-of-phase (π^-) combinations of the heteroatom lone pairs, respectively. They exhibit the 'reverse ordering' $(\pi^+$ above $\pi^-)$[109] due to through-bond interaction. According to *ab initio* calculations, in fact, π_4 and π_3 interact with the in-phase combinations of the filled and empty ethylenic orbitals, respectively, being destabilized (π_4) and stabilized (π_3). The small perturbation of π_4 along the series can be related to the different degree of mixing with the ethylenic bonds. The energy and the trend of π_3 are very similar to the first IE of the free heavier chalcogen atom[105].

π_2 is related to the out-of-phase combination of the $\pi\,C{=}C$ orbitals. The decrease in its *ionization energy in the series* **19** > **20** > **21** *is in agreement with the decrease in the* inductive effect of the chalcogen atom due to the change in the order of electronegativities: 3.5 (O), 2.5 (S), 2.4 (Se), 2.1 (Te)[11].

19   20   21
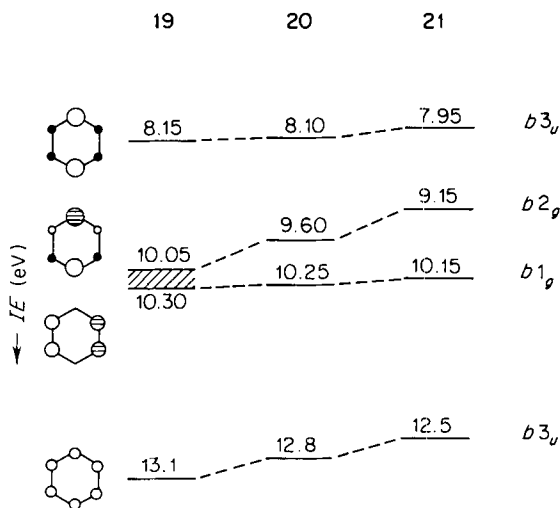
FIGURE 16. Partial energy level diagrams (eV) showing the evolution of the π MOs in 1,4-dithiin (19), 1,4-thiaselenin (20) and 1,4-thiatellurin (21). Three σ levels at energies intermediate between the π_1 and π_2 levels have been omitted for clarity

The UP spectra of some 1-acceptor-2-donor-substituted ethylenes have been analysed to study the 'push–pull' interaction and its effect on the electronic structure[112].

The first three bands of 22–25 have been ascribed in order of increasing IE value, to ionization from the HOMO, a π MO delocalized over all the molecule, from the out-of-phase combination of the chalcogen lone pair (n^-), and from a carbon—chalcogen σ MO.

(22)   (23)

(24)   (25)
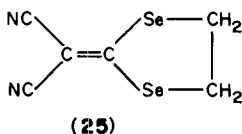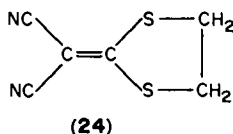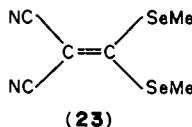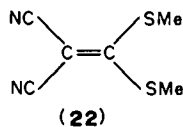
The spectra of the seleno derivatives are similar to those of the corresponding thio analogues, but the considered IE values are generally smaller, in agreement with the difference in the IEs of the sulphur and selenium atoms (see Table 16). The shifts are larger (0.4–0.5 eV) for IE_2 and IE_3, whose corresponding MOs have prevailing chalcogen character[112], than for the HOMO (0.3 eV from 22 to 25). The close similarity ($\Delta = 0.06$ eV) of the IE_1 of 24 and 25 is probably related to the different sizes of the sulphur and selenium atoms, which cause a grater deviation from planarity of the pentaatomic ring in 24 than in 25. This allows additional mixing of the sulphur outer shell p_z orbitals with other orbitals.

TABLE 16. Experimental ionization energies and their differences
(eV) for some push–pull ethylenes[a]

Compound	$IE_1(\pi)$	ΔIE_1	$IE_2(n^-)$	ΔIE_2	$IE_3(\sigma)$	ΔIE_3
22	9.16 ⎫		9.89 ⎫		11.20 ⎫	
	⎬	0.31	⎬	0.50	⎬	0.47
23	8.85 ⎭		9.39 ⎭		10.73 ⎭	
24	8.88 ⎫		9.94 ⎫		11.55 ⎫	
	⎬	0.06	⎬	0.40	⎬	0.40
25	8.82 ⎭		9.54 ⎭		11.15 ⎭	

[a] *Reproduced by permission* of Acta Chemica Scandinavica *from Reference 112.*

C. Alkyl Phenyl Chalcogenides

Photoelectron spectroscopy and theoretical studies[113–115] on alkyl phenyl ethers and thio ethers have suggested that in phenyl chalcogenides a balance of electronic and steric factors may exist which leads to the prevalence of one of the two limiting forms designed as planar (I) and perpendicular (II). In the former, the conjugation between the ring π orbitals and the X_{lp} orbital is more extensive than in the latter, producing a larger splitting of relevant MOs.

             (I)   (II)

Schweig and Thon[114] have shown that by increasing the source temperature from 20 to 500 °C the population of rotamer II in thioanisole increases significantly. Mellor and collaborators[115] followed the approach of changing the size of R. They found that the importance of the less conjugated rotamers of phenyl alkyl sulphides and ethers increases in the order H < Me < Et < i-Pr < t-Bu[115]. In both cases, however, the bands of the two rotamers are not clearly discernible in the spectra, so that arguments must reside on the appearance of shoulders.

Much more propitious to this kind of investigation are the alkyl phenyl selenides studied by Baker and coworkers[116]. The following example illustrates their approach.

The steric effects are clearly apparent comparing the spectra of 26–28.

      (26)   (27)   (28)
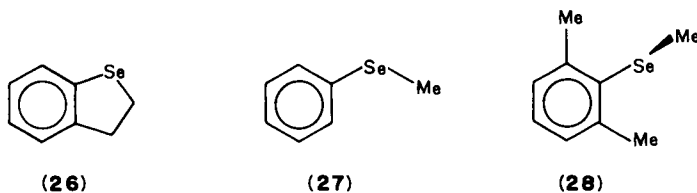
In each compound the first band corresponds to the HOMO which has prevailing Se_{4p} character. It shows a doublet structure (intensity ratio 1:1) in the spectrum of 27. The lowest IE component (8.0 eV) corresponds to the HOMO of the planar rotamer I and the

second (8.3 eV) to the rotamer with reduced conjugation. The single band observed for **26** must correspond to form I, the only rotamer allowed by the constrained structure. Its low IE value (7.6 eV) is in fact compatible only with a conjugated system.

The *ortho* disubstitution in **28** makes II the only form allowed. The IE_1 value, 8.7 eV, clearly shows the absence of p-π conjugation.

On going through the series PhXMe (X = O, S, Se, Te) the ratio between the planar and perpendicular conformers gradually decreases. In fact, at room temperature no perpendicular conformer can be seen in the spectrum of anisole[115], the I:II ratio is about 1.5:1 in thioanisole[114] and 1:1 and < 1:2 when X = Se[116] and Te[117], respectively.

This trend is probably related to the balance of several geometric and electronic factors. In fact, the C—X—C angle is much larger when X = O than for the heavier chalcogens favouring the planar rotamer, while the increasing bond length acts in the opposite direction. The n–π overlap decreases when the size of the heteroatom increases, while the n-π energy matching is the best for X = S (benzene, 9.24 eV; the X_{1p} IE values of the dimethyl derivatives are listed in Table 15). Finally, the $\pi \rightarrow \sigma^{*}_{X-C}$ charge-transfer interaction (which favours rotamer II) is energetically favoured in the heavier chalcogenides, where the empty orbital is stabilized by mixing with the heteroatom d orbitals (see Section III.A.3).

Other studies have been carried out on phenyl chalcogenides. The IE_1 of p-$NO_2C_6H_4XMe$ (X = O, S, Se) have been correlated with structure and MO characteristics. The v_{max} value in the UV–visible spectra has been found to increase with increasing value of the first IE[118,119]. This finding is in agreement with the fact that the HOMO is mainly localized on the ring-chalcogen part of the molecule and therefore it is sensitive to the nature of X, whereas the lowest unoccupied MO (LUMO) is localized at the NO_2 group in all cases, and therefore its energy is nearly constant. MO calculations on o-, m- and p-$MeSeC_6H_4Y$ (Y = OMe and NH_2) indicate that the substituent with the lowest IE of the lone pair (SeMe) makes the largest contribution to the HOMO, and that a substituent with high IE contributes more to the second HOMO than to the HOMO[120].

Five bands, two arising from the benzene-like π MOs, two from the two (in-phase and out-of-phase) CO lone pair n^+ and n^- and one from the π MO localized mainly at the heteroatom (π_X) are present in the low IE region of the UP spectra of phthalic anhydride and its chalcogen analogues (**29–32**)[121].

(**29**) X = O
(**30**) X = S
(**31**) X = Se
(**32**) X = Te
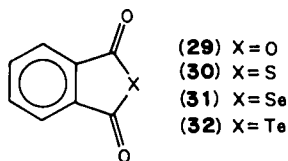
The benzene-like π MOs are nearly insensitive to X. Their IE values range from 10.25 and 10.63 eV in **29** to 10.02 and 10.28 eV in **32** indicating that the CO—X—CO groups have a similar electronic effect on the benzene ring. In contrast, the π_X MOs change in a parallel way with the $2b_1$ MO of the related pentaatomic heterocycles going from 11.73 eV in **29** to 8.59 eV in **32**[74,121].

The two lone-pair MOs n^+ and n^- are similarly destabilized because of their effective mixing with the σ_{X-C} orbitals and the changing inductive effect. The electronic distribution at the CO groups also depends on the mesomeric interaction with the p_π AO of X. Other observables, such as the $v_{C=O}$ stretching frequencies and the ^{13}C NMR chemical shifts, depend on the electronic distribution in the CO groups. It has been found that these three properties (IE_n, v and δ) vary in a parallel manner[121].

D. Cyclic Phenyl Chalcogenides

Replacement of an oxygen atom with a heavier chalcogen causes changes in the electronic and geometric structures, the effects of which are visible in the UP spectra. In the previous section we have seen that in phenyl alkyl chalcogenides steric hindrance can cause rotation about the ring—X bond. In cyclic derivatives, relief of strain about the chalcogen atoms can occur by a different conformational change, as shown by the following examples.

From the value of appropriate IEs, Pfister-Guillouzo and collaborators[122] obtained information on the preferred conformation of some organometallic zirconium compounds. They suggested that in $(RC_5H_4)_2Zr(Me)SePh$ the benzene ring plane forms a large angle (ca. 90°) with the plane defined by the Zr, Se and $C_{(Ph)}$ atoms, while in $(RC_5h_4)_2Zr(SePh)_2$ the corresponding angles are small (ca. 0°) and therefore a significant $n_{Se}-\pi_{ring}$ conjugation is present.

In the cyclic derivative 33, the question arises of whether the heterocycle is planar or not.

(33)
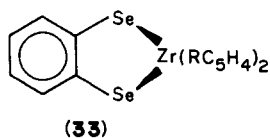
A qualitative interaction diagram between the selenium unshared pairs and the two uppermost degenerate π benzene orbitals indicated[122] that only in a conformation folded along the Se—Se line the two uppermost π MOs can be nearly degenerate as found experimentally. This result is in agreement with an EHT calculation and the solid-state structure[123].

The UP spectra of the homonuclear and heteronuclear chalcanthrenes (34) have been recently analyzed[124-126]. The six bands present in the low-energy region of the spectra

X, Y = O, S, Se, Te

(34)
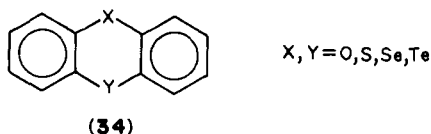
derive from the interaction of two π MOs of each benzene ring and the heteroatom lone-pair orbitals. Two of the resulting MOs (IE_3 and IE_4) are localized only on the benzene ring (in a perfectly planar conformation), and their energy is only slightly modified from the benzene value (9.24 eV) by the inductive effect of the heteroatoms. The IEs obtained, in fact, range from 9.5 and 9.7 eV in dibenzo-p-dioxin (X = Y = O) to 9.12 and 9.30 eV in telluranthrene (X = Y = Te)[126] (see Table 17).

The two outermost MOs are the antibonding combinations between $\pi_{X,Y}^+$ and $\pi_{X,Y}^-$ orbitals and appropriate combinations of the benzene π orbitals. If the chalcanthrenes where planar or had the same angle of fold Φ along the line connecting the two heteroatoms, these MOs would become progressively destabilized with increasing size of the heteroatoms (as is well established, see Section III). The HOMO, on the other hand, is only slightly destabilized in phenoxachalcogenins (34, X = O, Y = O, S, Se, Te) [7.78 (O), 7.72 (S), 7.74 (Se), 7.61 (Te)eV[124]] and, in the homonuclear chalcanthrenes (34, X = Y), the HOMO energy does not decrease monotonically along the series [7.78 (O), 7.94 (S), 7.93 (Se), 7.52 (Te)eV[127]] (see Table 17).

Dipole moment analyses showed that the folding is small and nearly constant in phenoxachalcogenins, whereas it can not be neglected and increases with the mass of the

TABLE 17. Experimental ionization energies (eV) and angles of fold (°) for chalcanthrenes (34)[a]

| Heteroatoms | | IE_1 | IE_2 | IE_3 | IE_4 | $\Delta IE_{1,2}$ | Φ |
X	Y	$(\pi^+_{X,Y})$	$(\pi^-_{X,Y})$	(π_{ring})	(π_{ring})		
O	O	7.78	8.76	9.5	9.7	0.98	163.8
O	S	7.72	8.71	9.4	9.6	0.99	163.4
O	Se	7.74	8.67	9.33	9.5	0.93	162.6
O	Te	7.61	8.66	9.24	9.4	1.05	172.2
S	S	7.94	8.43	9.30	9.45	0.49	142.4
Se	Se	7.93	8.18	9.26	9.4	0.25	139.0
Te	Te	7.52	7.72	9.12	9.30	0.20	124.6
S	Se	7.93	8.32	9.27	9.45	0.39	135.0
S	Te	7.70	8.25	9.23	9.4	0.55	133.3
Se	Te	7.67	8.07	9.21	9.5	0.40	134.0

[a] From References 124–126.

heteroatoms in homonuclear chalcanthrenes[124–126]. The folding causes a reduction of the $n_{X,Y}$–π_{ring} interaction, decreasing the energy of the HOMO.

In a non-planar conformation, the separation of MOs into π and σ is no longer strictly valid and the $\pi^-_{X,Y}$ MOs can also mix with formally σ orbitals. This is reflected, for example, in the energy separation (Δ) between IE_1 and IE_2. Δ is ca. 1 eV in phenoxachalcogenins, whereas it decreases from 1 to 0.2 eV in the homonuclear chalcanthrenes[125].

The conformation of diphenylchalcogenides (PhXPh) and some chalcanthrenes has been investigated by means of UPS and theoretical computations also by Traven and coworkers[127,128]. In the latter compounds, the Φ values are different from those determined in solution[124–126], even though the general trend is maintained.

V. DISELENIDES AND DITELLURIDES

A. Methyl and Phenyl Dichalcogenides

Dichalcogenides represent an ideal series for studying the interactions between p orbitals of adjacent atoms as the geometry and general characteristics of the system are changed[129].

For aliphatic dichalcogenides the first two bands in the UP spectra correspond to the symmetric and antisymmetric combinations of the X_{1p} orbitals n^+ and n^-. When the dihedral angle C—X—X—C (ω) deviates from 90°, the energy separation between the n^+ and n^- orbitals (ΔIE) will increase. In fact, ΔIE has been found in disulphides to be about 0.2–0.3 eV when R = Me, Et and Pr and 0.65 eV in di-t-butyl derivatives[130–132]. The value of ω has been computed to be close to 90° and to 98°[129] or 110°[131,132], respectively.

Dimethyl diselenide assumes a stable skew conformation with a dihedral angle ω of 87.5°[133]. Accordingly, the ΔIE value is small (0.23 eV)[134]. EHMO calculations indicate that this Δ value derives in part from through-space splitting and spin–orbit coupling (ca. 0.07 and 0.06 eV, respectively) and in part (ca. 0.1 eV) from interaction of the n^+ and n^- orbitals with the low-lying σ_{Se-C} and σ_{Se-Se} orbitals, respectively[134]. According to calculations, these through-bond mixings are larger than the corresponding interactions in dimethyl disulphide. The n^+/n^- splitting does not change in diisopropyl diselenide (as inferred from Figures 1 and 2 in Ref. 135).

In agreement with the shift to lower IE values observed for π, non-bonding and σ_{X-C}

orbitals when selenium is substituted for sulphur, the σ_{X-X} orbital is equally destabilized. It goes from 11.28 eV in dimethyl disulphide to 10.67 eV in dimethyl diselenide[134].

In this class of compounds, the conformation with a dihedral angle of 90° between the two electron lone pairs on the chalcogen atoms minimize lone pair–lone pair repulsion. Alternatively, the n–n repulsion is reduced if the lone electron pairs are delocalized on the substituents as in diphenyl dichalcogenides, Ph—X—X—Ph. Their splitting in fact is about 0.4–0.5 eV in diphenyl diselenide and ditelluride (see Table 18), which corresponds to an ω value of about 70°[134,136].

In the diphenyl dichalcogenides the $n^{\pm}$ orbitals mix with the $\pi_s^{\pm}$ combinations of appropriate symmetry, giving rise to the $IE_{1,2}$ and $IE_{5,6}$ bands[136]. The modest splittings $\Delta IE_{1,2}$ and $\Delta IE_{5,6}$ (unresolved) and the similarity of their average values $\overline{IE}_{1,2}$ and $\overline{IE}_{5,6}$ to the corresponding IEs in PhXMe[114–117] indicate that very little interaction takes place between the two phenyl groups through the dichalcogen bridge.

In addition, the splittings between the π_{ring} (asymmetric or non-interacting) MOs 3 and 4 and the π MOs 5 and 6 can be taken as a measure of the X–ring interaction, which, in turn, depends on conformation. Their absolute energy values and splittings are very similar to those reported for the planar conformer of the PhXMe systems[114–117] (see Table 18). One can therefore infer that the combination of the two PhX moieties to give Ph_2X_2 will not substantially influence the interaction between the chalcogen $\pi_{\text{lone pair}}$ and the π_{ring} orbitals and hence will not change the conformation of each PhX—fragment.

B. *Peri* Dichalcogenides

The naphthalene-1,8-dichalcogenides (35a–f) have received renewed interest as potential electron donors in one-dimensional organic charge-transfer conductors[137,138].
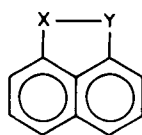
	X,Y	X,Y
	(a) S,S	(d) Se,Se
	(b) S,Se	(e) Se,Te
	(c) S,Te	(f) Te,Te

(35)

TABLE 18. IE values, average values and their splitting for some diphenyl dichalcogenides (eV) (from Reference 136). The values in parentheses refer to ionization from the corresponding MOs of the planar conformation of the PhXMe derivatives

Band	Ph—S—S—Ph			Ph—Se—Se—Ph			Ph—Te—Te—Ph		
	IE	$\overline{IE}$	ΔIE	IE	$\overline{IE}$	ΔIE	IE	$\overline{IE}$	ΔIE
1 (n)	8.21			8.06			7.68		
	(8.07)[a]	8.33	0.24	(8.0)[b]	8.30	0.48	(7.6)[c]	7.88	0.40
2 (n)	8.45			8.54			8.08		
3 (π_a)									
	9.36			9.31			9.22		
4 (π_a)	(9.3)[a]			(9.3)[b]			(9.2)[c]		
			0.80			0.52			0.28
5 (π_s)			(0.85)			(0.6)			(0.3)
	10.16			9.83			9.50		
6 (π_s)	(10.15)[a]			(9.9)[b]			(9.5)[c]		

[a] From Reference 115.
[b] From Reference 116.
[c] Estimated from Figure 2 in Reference 117.

Compounds **35a** and **35b** have been found to be planar by Raman studies[139] and X-ray diffraction data[137], respectively, so that coplanar chalcogen–chalcogen lone pair (through-space) interaction is expected to be large.

The first four photoelectron bands of the UP spectrum have been assigned to π MOs on the basis of perturbational arguments and semiempirical calculations[137,138]. The spectra are very similar for all the derivatives, showing in the low IE region one isolated band at 7.03–7.14 eV followed by three partially overlapped bands at 8.7–9.3 eV. The n^- orbital is destabilized by 1 eV[138] or 2 eV[137] with respect to n^+ by through-space interaction. Its coupling with the naphthalene HOMO gives rise to the first band and to one component of the second structure.

The HOMO of **35a–f** is destabilized by more than 1 eV with respect to the naphthalene HOMO. Therefore, the destabilizing effect of the *peri* dichalcogenide substitution is similar to that of two amino groups[137].

The constancy of the first IE values and the similarity of the spectra indicate that the electron-releasing inductive effect of the heavier chalcogens is counteracted by the reduced second-order perturbation, and that all compounds **35** are planar or nearly planar.

VI. SELENOKETENES, SELENOCARBONYLS AND SELENOFULVALENES

Some of the compounds presented in this section are short-lived or unstable species which have been generated *in situ* from appropriate precursors, at high temperature, inside or close to the ionization chamber of the spectrometer. Most of these studies, which have often been accompanied by high-level theoretical calculations, have been performed by the research teams of Bock and of Schweig.

A. Selenoketenes

Gas-phase thermal decomposition of 1,2,3-selenadiazole afforded the short-lived selenoketene **36a** (yield 95%, $T = 800$ K[99,140,141]) which has been identified by mass spectrometry and by comparing its UP spectrum with those of thioketene **36b**[142,143] and ketene **36c**[144] and with the results of *ab initio* SCF calculations.

$$\begin{array}{c} H \\ \diagdown \\ C{=}C{=}X \\ \diagup \\ H \end{array} \qquad \begin{array}{l} X \\ \textbf{(a)} \text{ Se} \\ \textbf{(b)} \text{ S} \\ \textbf{(c)} \text{ O} \end{array}$$

(36)
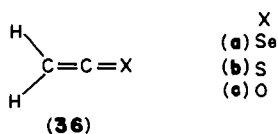
In particular, the in-phase and out-of-phase combination of the selenium $4p_\pi$ and $\pi_{C=C}$ orbitals give rise to IE_3 (11.7 eV) and IE_1 (8.7 eV), respectively. IE_2 (10.7 eV) corresponds to the in-plane $\pi_{C=Se}$ MO. The succeeding three bands have been assigned to the σ_{C-C-Se} (14.1), σ_{CH_2} (15.3) and σ_{C-CH_2} (17.0 eV) MOs (see Table 19).

The MO ordering is equal to that found for thioketene[142,143], while the relative ordering of IE_4 and IE_5 is reversed with respect to ketene[140,144]. Substitution of selenium for sulphur destabilizes corresponding MOs by 0.2–0.6 eV. Shifts as large as 3.5 eV have been reported for the comparison between the selenium and oxygen derivatives. The largest shifts are associated with MOs whose localization at the heteroatom greatly depends on the nature of X.

Analogously, the products of the gas-phase thermal decompositions of cyclohexene-1,2,3-selenodiazole and cyclooctene-1,2,3-selenodiazole have been identified as cyclopentylideneselenoketene (**37**) and cycloheptylideneselenoketene (**38**), respectively[145]; **37** is formed in high yield (ca. 100%), while cyclooctyne is the main product of the second reaction.

TABLE 19. Experimental ionization energies (eV) of selenoketene (36a), thioketene (36b) and ketene (36c) with assignments

Assignment		36a[a]	36b[b]	36c[c]
$\pi_{X/C=C}$	(b_1)	8.72	8.89	9.8
$\pi_{C=X}$	(b_2)	10.75	11.32	14.2
$\pi_{X/C=C}$	(b_1)	11.6	12.14	15.0
σ_{CCX}	(a_1)	14.15	14.55	16.8
σ_{CH_2}	(b_2)	(15.3)	(15.5)	16.3
σ_{C-CH_2}	(a_1)	(17.0)	(17.5)	18.2

[a] From References 99, 140 and 141.
[b] From References 142 and 143.
[c] From Reference 144.
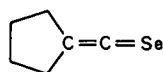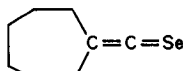
(37)   (38)

The spectrum of 37 has been assigned by analogy with those of the corresponding thio and oxa derivatives. The sequence of the three uppermost MOs is the same as that of 36a. The cycloalkyl substituent destabilizes the MOs by 0.8–1.0 eV. Only the first IE value has been reported for 38.

6-Fulveneketene (39c), 6-fulvenethione (39b)[146,147] and 6-fulveneselone (39a)[99,147] have been generated in situ at high temperature from appropriate precursors by means of 'variable-temperature photoelectron spectroscopy'[148]. The UP spectra are very similar to

X
(a) Se
(b) S
(c) O

(39)
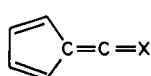
each other, mainly those of 39b and 39a. As expected, a constant shift to lower values of the IEs has been observed on going from 39c to 39a (see Table 20).

TABLE 20. Experimental ionization energies (eV) of 6-fulveneketene (39c), 6-fulvenethione (39b) and 6-fulveneselone (39a)[a]

Ionization energy		39a	39b	39c
IE_1	(b_1)	8.36	8.37	8.56
IE_2	(a_2)	8.46	8.57	9.06
IE_3	(b_1)	10.78	11.07	12.12
IE_4	(b_2)	10.78	11.07	12.70
IE_5	(a_1)	12.50	12.60	13.00
IE_6	(b_1)	13.00	13.15	

[a] Reproduced by permission of Verlag der Zeitschrift fur Naturforschung from Reference 147.

The π MOs of **39** can be considered to derive from the symmetry-allowed interaction between the orbitals of *cis*-butadiene and corresponding ketenes. In particular, IE_1, IE_3 and IE_6 in **39b** and **39a** derive from the mixing of the in-phase combination of the π orbitals of the ring with IE_1 and IE_3 of thioketene or selenoketene. IE_2 corresponds to the out-of-phase combination of the ethylenic orbitals, while IE_4 derives from the in-plane $\pi_{C=X}$ MO[147]. This assignment has been obtained experimentally, with the help of semiempirical calculations[99,147].

The thermal decomposition of 1,2,3-benzoselenadiazole at intermediate temperature (below about 600 °C) and low pressure produces a short-lived intermediate which, from its UP spectrum, has been identified as benzo[1,2b]selenirene (**40**)[147], an isomer of the stable final product **39a**.

The assignment of the spectrum has been made on the basis of that of benzocyclopropane (**41**)[149,150] and semiempirical calculations on the latter and on (the unknown) benzothioirene.

(40)   **(41)**
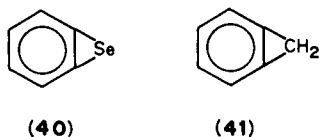
It is interesting that selenium exerts on the benzene π orbitals of **40** a σ electron-withdrawing effect (0.2 eV) larger than that exerted by the CH_2 groups in **41**, and a π donor effect.

B. Selenocarbonyl Derivatives

1. Selenoaldehydes

Selenoformaldehyde, $H_2C=Se$ (**42**), has been prepared (together with other decomposition products) by pyrolysis of its trimer *s*-triselenane (1100 K, 10^{-4} mbar) in a very short pipe close to the target chamber of the spectrometer[151].

The first three bands in its spectrum have been assigned to the corresponding MOs (n_{Se}, $\pi_{C=Se}$ and σ_{Se-C} in order of increasing IE values) on the basis of ΔE^{SCF} restricted Hartree–Fock calculations, taking into account the different electron correlations in the various states. The 'suggested values' thus obtained[151] are compared with the experimental values in Table 21.

TABLE 21. Experimental IE values (eV) for selenoformaldehyde compared with the corresponding data for thioformaldehyde and formaldehyde and with the results of theoretical calculations

Assignment		$H_2C=Se^a$		$H_2C=S^b$		$H_2C=O^c$	
		Exptl.	Theor.	Exptl.	Theor.	Exptl.	Theor.
n_X	(b_2)	8.95	8.8	9.34	9.08	10.9	10.81
$\pi_{C=X}$	(b_1)	11.10	11.1	11.78	11.49	14.5	14.62
σ_{X-C}	(a_1)	13.25	12.9	13.90	13.75	16.2	16.20
σ_{CH_2}	(b_2)	15.1		15.15	15.78	~17.0	17.36

[a] From Reference 151.
[b] From Reference 154.
[c] From References 156 and 157.

Carla Cauletti and Giuseppe Distefano

TABLE 22. Ionization energies (eV) and CNDO/S orbital assignment of tetramethylthiourea (43) compared with ionization energies of tetramethyl selenourea (44)[a]

43		44
IE (eV)	Assignment and electron density (%)	IE(eV)
7.80	n_S(92)	7.35
8.15	π_S(77)	7.70
8.60	π_N − (61)	8.60
11.25	σ_{S-C}(C = 22, S = 48)	11.05
12.10	π_{N_2CS}(N = 30, C = 24, S = 7)	11.95

[a] *Reproduced by permission of* Acta Chemica Scandinavica *from Reference 160.*

The formation of **42** and the assignment of its UP spectrum have been confirmed, producing selenoacetaldehyde, MeC(H)=Se, and selenocarbonyl difluoride, F_2C=Se, by thermal monomerization of [MeC(H)Se]$_3$ and (F_2C=Se)$_2$ at 1000 and 1140 K, respectively[151].

As expected, methyl substitution destabilizes the $\pi_{C=Se}$ MO more than the HOMO, mainly deriving from the Se_{4p} AO (0.8 and 0.45 eV, respectively). Fluorine substitution, instead, stabilizes the n MO (by 0.85 eV) but does not influence the energy of the $\pi_{C=Se}$ orbital, in line with expectation based on the 'perfluoro effect'[152].

Further support for the interpretation of the UP spectrum of the main product obtained from the thermal decomposition of *s*-triselenane has been obtained by the comparison[151] of the bands of its spectrum with the corresponding bands in the spectra of the chemically equivalent compounds thioformaldehyde[153,155] and formaldehyde[156,157]. Table 21 compares the uppermost *IE* values by changing the heteroatom. The lowering of the *IE* values with increasing effective nuclear charge (Se < S ≪ O) is self-evident.

2. Selenoketones

The assignment of the spectrum of tetramethylthiourea (**43**), initially proposed by Pfister-Guillouzo and collaborators[158,159] on the basis of experimental evidence, was subsequently confirmed with the help of semiempirical calculations[160] to be n_S, π_S, π_{N^-}, σ_{S-C} and π_{N_2CS} in order of increasing *IE* values (see Table 22).
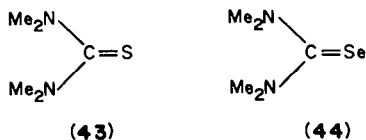
The calculations indicate that the localization at the sulphur atom is large for the first two MOs, moderate for the fourth and fifth MOs and negligible for the third MO. Accordingly, the MOs of tetramethylselenourea (**44**) are destabilized by about 0.45, 0.2 and 0.0 eV, in that order, with respect to the corresponding MOs of **43**. Therefore, both the n_{Se}

and π_{Se} ionizations in the amino-substituted selenocarbonyl group are small (7.35 and 7.70 eV, respectively[160]).

As observed for **43** and **44**, even the n_X and π_X ionizations of the C=X group of compounds **45** are lowered by 0.4–0.5 eV on going from the thio- to the corresponding selenoketones[161].

(45)
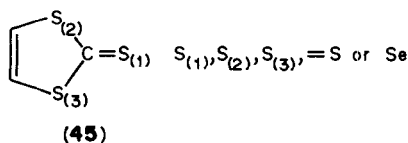
The absolute IE values of the selenocarbonyl group in compounds **45** are 0.35–0.50 eV higher than the corresponding values of **44** because of the smaller electron-releasing capability of the chalcogen substituents with respect to the dimethylamino groups. The first six ionization events from these compounds have been assigned on the basis of semiempirical calculations, perturbational arguments and the comparison of the energy trends of corresponding bands along the series[161].

C. Selenofulvalenes

Schweig and coworkers[162] have found that in the series **46a–c** the ionizations related to MOs largely localized on the heteroatoms are distinctly more affected by selenium for sulphur substitution than the rest of them.

(46)

	X,Y
(a)	S,S
(b)	S,Se
(c)	Se,Se
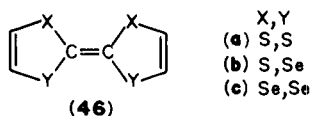
Surprisingly, the HOMO is stabilized by the selenium atoms (**46a** = 6.70, **46b** = 6.75, **46c** = 6.90 eV). We think that a possible explanation could be based on the shape of the HOMO[162] shown below.

(47)
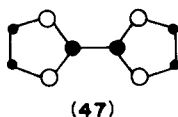
The two antibonding interactions between each heteroatom and the adjacent carbon atoms could be relieved by the increased X—C bond lengths. The resulting stabilization should overwhelm the destabilization connected with the smaller electronegativity of selenium.

Similarly, the stabilization of the HOMO observed on going from tetramethyltetrathiafulvalene (6.40 eV) to tetramethyltetraselenafulvalene (6.58 eV) has been ascribed to a reduction of the X—C resonance integral, $\beta_{X\ C}$, from -1.8 to -1.5 eV[163]. The spectra of both compounds have been interpreted on the basis of molecular orbital calculations based on a zero differential overlap (ZDO) model and semiempirical calculations. The assignment of the first four ionizations agrees with those of **46a** and **46c**[162], whilst the fifth and sixth ionizations are reversed.

Carla Cauletti and Giuseppe Distefano

TABLE 23. Ionization energies (eV) for $(MeO)_3P$ and $(MeO)_3PX$ (X = O, S, Se)[a]

Compound	$n_P(a)$	$n_O(a)$	$n_O(e)$	$\sigma/n_O(e)$	$\sigma/n_O(a)$
$(MeO)_3P$	9.22	10.54	11.11 11.3	12.3	13.0
	$n_X(e)$	$n_O(a)$	$n_O(e)$	$\sigma_{PX}(a)$	$\sigma/n_O(a+e)$
$(MeO)_3PO$	10.82	11.36	11.9 12.1	12.4	12.9
$(MeO)_3PS$	9.16	11.15	11.56 11.8	12.0	12.7
$(MeO)_3PSe$	8.67	10.93	11.5	—[b]	—[b]

[a] From Reference 164.
[b] Overlapping peaks.

VII. GROUP 5A DERIVATIVES

A. Phosphoroselenoic Acid O,O,O-Trimethyl Ester

$(MeO)_3PX$ (X = O, S, Se) have been investigated by UPS[164] in the framework of an extensive study on some phosphite esters[164,165]. On passing from $(MeO)_3P$ to the adducts with oxygen, sulphur and selenium the phosphorus lone pair is stabilized by ca. 3 eV as it becomes the dative $P \rightarrow X$ σ bond, σ_{PX} (see Table 23). Each of the acceptors X features a doubly degenerate lone-pair MO, $n_X(e)$, at low IE and a singly degenerate MO, $n_X(a)$, comprising largely s-character, at appreciably high IE. The acceptor $n_X(e)$ lone-pair MO replaces the phosphorus lone-pair MO as the lowest IE peak when coordination to $(MeO)_3P$ occurs.

B. Phosphine Derivatives

Despite the low molecular symmetry (C_s), the UP spectra of the compounds $R_2P(X)Y$ and $RP(X)Y_2$ (R = Me or F; X = O, S or Se; Y = Cl or Br)[166] were assigned empirically, by comparison with related molecules. Figure 17 shows the He I spectra of the species $MeP(X)Cl_2$, together with that of $MePCl_2$. The assignment and the correlations between the various MOs are also indicated. Table 24 reports the IEs for some series of sixteen-electron compounds. In Figure 17 and Table 24 the symbols R, V and T indicate orbitals with radial (R), horizontal (T, tangential) and vertical (V) orientations relative to the bond axes (see Figure 18). The first band of $R_nP(X)Y_{3-n}$ compounds is assigned to an MO exhibiting predominant lone-pair character on X (n_X) in each case. On coordination to X all original R_2PY[69,167,168] and RPY_2[167,168] energies are appreciably stabilized by the strong electron-withdrawing effect of the acceptor X and partially by hyperconjugation. In the spectra of the compounds $MeP(X)Y_2$ and $Me_2P(X)Y$, the energy range beyond the n_X bands may be further subdivided into n_Y (sharper intense band, 11–13 eV) and Me regions (broad featureless band, ca. 14–16 eV) joined by bands due to orbitals possessing large P—R, P—Y and P—X σ-bonding contributions.

A marked low-energy shift of the first band only takes place for the transition X = O $\rightarrow$ S (second to third period); n_{Se} is less shifted relative to n_S and thus reflects the trend in p valence ionization energy.
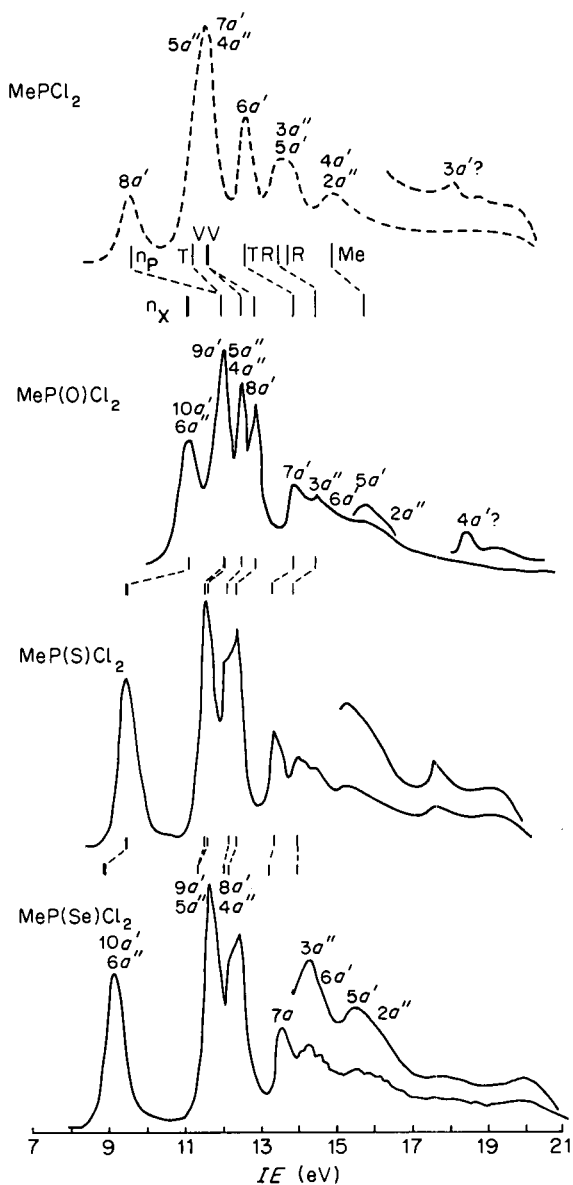
FIGURE 17. He I photoelectron spectra of $MePCl_2$ and $MeP(X)Cl_2$ (X = O, S and Se). The figures and letters on the bands refer to the numbering and symmetry of MOS. *Reproduced by permission of the Royal Society of Chemistry from Reference 166*

TABLE 24. Ionization energies for some phosphine derivatives[a]

Compound	IE(eV)							
MeP(O)Cl$_2$[b]	11.43	12.33T	12.82V	13.17V	14.23T	14.75R	15.23?R	16.15
MeP(S)Cl$_2$[b]	9.73	11.89T	12.47V	12.65V	13.66T	14.32R	15.6	17.9
MeP(Se)Cl$_2$[b]	9.16	11.64T		12.47V	13.6T	14.25R	15.62	19.94
Me$_2$P(O)Cl[b]	10.77	12.0T	13.28V	14.12R	15.0	15.53	18.12	
Me$_2$P(S)Cl[b]	9.12	11.53T	12.69V	13.5R	14.55	17.39	19.2	
Me$_2$P(Se)Cl[b]	8.64	11.31T	12.57V	13.67R	14.08	19.6		
MePCl$_2$[c]	9.86	11.89TVV	12.91T	14.0R	15.06	18.58		
Me$_2$PCl[c]	9.15	11.0T	11.74V	12.72R	13.9	15.3	16.98	

[a] For the meaning of symbols T, V and R, see text.
[b] From Reference 166.
[c] From References 167 and 168.
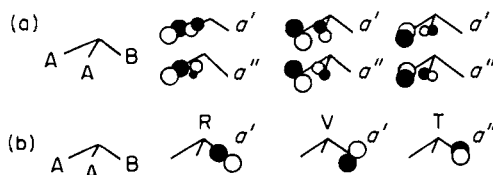
FIGURE 18. Substituent group orbitals for two (a) or one (b) decoupled substituents (A$_2$ and B) in A$_2$PB phosphines (A = Me, B = Y; A = Y, B = Me). *Reproduced by permission of the Royal Society of Chemistry from Reference 166*

Differing n_Y shifts are expected along the series due to the degree of interaction between n_Y and the $\sigma_{P \ X}$, $\sigma_{P \ Me}$, and $\sigma_{P \ Y}$ orbitals, which is additionally governed by the energy separation $\alpha_Y \leftrightarrow \alpha_X$ and the inductive perturbation. Again, the *IE* difference is larger on going from X = O to X = S than from X = S to X = Se.

C. Me$_2$YXMe

In the UPS study on Me$_2$YXMe (Y = P, As; X = S, Se), Böhm and coworkers[169] emphasize the dependence of the interaction between the lone pair MO of Y and X on the molecular conformation. In fact, such an interaction is not possible either in *A* or *C* conformation where the lone pairs of X and Y lay in the plane XYC$_1$ and perpendicular to
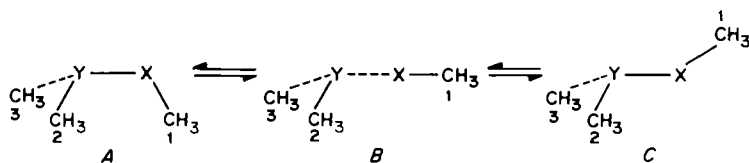
it, respectively. However, it may occur in conformation *B*, at an extent depending on the dihedral angle θ between the XYC$_1$ and XYC$_{2(3)}$ planes. The photoelectron spectra,

Me$_2$PSMe

Me$_2$PSeMe

Me$_2$AsSMe

Me$_2$AsSeMe
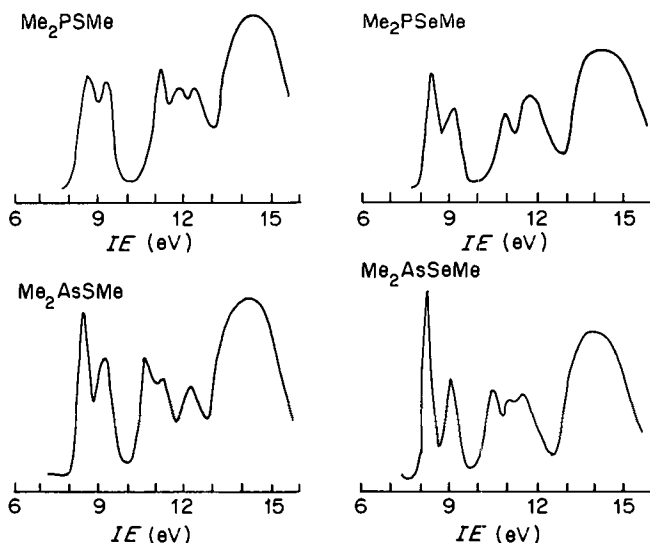
FIGURE 19. He I photoelectron spectra of the Me$_2$YXMe (Y = P, As; X = S, Se) molecules. *Reproduced by permission of VCH Verlagsgesellschaft from Reference 169*

showing two bands between 8 and 9.5 eV (see Figure 19), which account for the ionization of the out-of-phase and in-phase combination of the two lone pairs, indicate for these molecules a *B*-type conformation. INDO calculations suggest that the conjugation is maximum for θ between 80 and 90°.

VIII. APPENDIX: ELECTRON TRANSMISSION SPECTROSCOPY

From a theoretical and chemical point of view, the electron affinities (*EA*s), associated with electron capture into the normally unoccupied MOs, are as important as the ionization energies. Information on the anion states, however, is scarce. In part this derives from experimental difficulties connected with measuring the electron affinities of molecules which possess stable anions.

One of the most powerful tools of *EA* measurements is electron transmission spectroscopy (ETS)[170-172]. In this technique, an electron beam, selected in energy by a trochoidal monochromator and aligned by a magnetic field, is passed through a gas-filled collision chamber. Electrons of appropriate energy and angular momentum can be temporarily trapped in unoccupied MOs. A retarding voltage is responsible for the rejection of those scattering electrons which have lost a given value of axial velocity. ETS, therefore, makes it possible to determine the energies at which an electron is temporarily trapped in normally unoccupied MOs, from the sharp variations in the electron scattering cross-section.

The most important difference with respect to UPS is that in UPS all the cation states whose energy difference from the neutral ground state is smaller than the energy of the radiation used can be detected, whereas in ETS there is an energy region which cannot be examined. In fact, anion states more stable than the neutral ground state cannot be detected. (see Scheme 1).
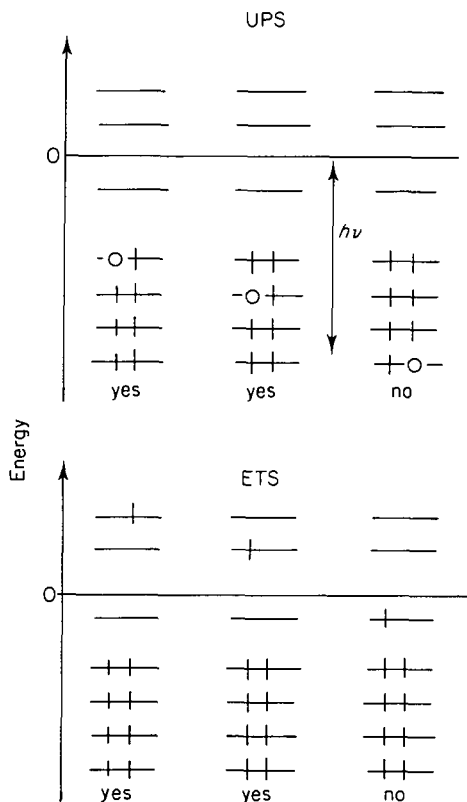
SCHEME 1

IX. REFERENCES

1. A. D. Baker, *Acc. Chem. Res.*, **3**, 17 (1970).
2. A. Hammett and A. F. Orchard, in *Electronic Structure and Magnetism of Inorganic Compounds*, Vol. 1, Chemical Society, London, 1972, p. 1.
3. A. D. Baker, C. R. Brundle and M. Thompson, *Chem. Soc. Rev.*, **3**, 355 (1972).
4. S. Evans and A. F. Orchard, in *Electronic Structure and Magnetism of Inorganic Compounds*, Vol. 2, Chemical Society, London, 1973, p. 1.
5. A. Hammett and A. F. Orchard, in *Electronic Structure and Magnetism of Inorganic Compounds*, Vol. 3, Chemical Society, London, 1974, p. 218.
6. A. F. Orchard, in *Electronic States of Inorganic Compounds: New Experimental Techniques* (Ed. P. Day), Reidel, Dordrecht, 1975, p. 267.
7. R. G. Egdell and A. W. Potts, in *Electronic Structure and Magnetism of Inorganic Compounds*, Vol. 6, Chemical Society, London, 1980, p. 1.
8. D. W. Turner, C. Baker, A. D. Baker and C. R. Brundle, *Molecular Photoelectron Spectroscopy*, Wiley–Interscience, London, 1970.
9. J. H. D. Eland, *Photoelectron Spectroscopy*, 2nd ed., Butterworths, London, 1974.
10. J. W. Rabalais, *Principles of Ultraviolet Photoelectron Spectroscopy*, Wiley–Interscience, New York, 1977.

11. R. E. Ballard, *Photoelectron Spectroscopy and Molecular Orbital Theory*, Adam Hilger, Bristol, 1978.
12. T. Koopmans, *Physica*, **1**, 104 (1934).
13. J. Delwiche, P. Natalis and J. E. Collin, *Int. J. Mass Spectrom. Ion Phys.*, **5**, 443 (1970).
14. A. W. Potts and W. C. Price *Proc. R. Soc. London, Ser. A*, **326**, 181 (1972).
15. S. M. Goldberg, C. S. Fadley and S. Kono, *J. Electron Spectrosc. Relat. Phenom.*, **21**, 285 (1981).
16. S. T. Manson, A. Msezane, A. F. Starace and S. Shahabi, *Phys. Rev. A*, **20**, 1005 (1979).
16a. U. Gelius and K. Siegbahn, *Faraday Discuss. Chem. Soc.*, **54**, 257 (1972).
17. P. H. Connington and N. S. Ham, *J. Electron Spectrosc. Relat. Phenom.*, **31**, 175 (1983).
18. M. V. Andreocci, M. Bossa, C. Furlani, M. N. Piancastelli, C. Cauletti and T. Tarantelli, *J. Chem. Soc., Faraday Trans. 2*, 105 (1979).
19. C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).
20. G. G. Hall, *Proc. Roy. Soc. London, Ser. A*, **205**, 541 (1951); **213**, 102, 113 (1952).
21. A. Golebiewski and H. S. Taylor, *Annu. Rev. Phys. Chem.*, **18**, 353 (1952).
22. E. Clementi, *Chem. Rev.*, **68**, 341 (1968).
23. J. A. Pople and D. L. Beveridge, *Approximate Molecular Orbital Theory*, McGraw-Hill, New York, 1970.
24. J. A. Pople, D. P. Santry and G. A. Segal, *J. Chem. Phys.*, **43**, S129 (1965).
25. J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **43**, S136 (1965); **44**, 3289 (1966).
26. D. P. Santry and G. A. Segal, *J. Chem. Phys.*, **47**, 158 (1967).
27. J. A. Pople, D. L. Beveridge and P. A. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967).
28. N. C. Baird and M. J. S. Dewar, *J. Chem. Phys.*, **50**, 1262 (1969).
29. N. C. Baird, M. J. S. Dewar and R. Sustmann, *J. Chem. Phys.*, **50**, 1275 (1969).
30. M. J. S. Dewar and E. Haselbach, *J. Am. Chem. Soc.*, **92**, 590 (1970).
31. N. Bodor, M. J. S. Dewar, A. Harget and E. Haselbach, *J. Am. Chem. Soc.*, **92**, 3854 (1970).
32. M. J. S. Dewar and G. Klopman, *J. Am. Chem. Soc.*, **89**, 3089 (1967).
33. C. Fridh, L. Åsbrink and E. Lindholm, *Chem. Phys. Lett.*, **15**, 408 (1972).
34. A. Streitwiesser, Jr., *Molecular Orbital Theory for Organic Chemistry*, Wiley, New York, 1961.
35. R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).
36. A. Modelli and G. Distefano, *Z. Naturforsch., Teil A*, **36**, 1344 (1981), and references cited therein.
37. R. N. Dixon and S. E. Hull, *Chem. Phys. Lett.*, **3**, 367 (1969).
38. O. Edqvist, E. Lindholm, L. E. Selin and L. Åsbrink, *Phys. Scr.* **1**, 25 (1970).
39. J. Berkowitz, *J. Chem. Phys.*, **62**, 4074 (1975).
40. J. M. Dyke, L. Golob, N. Jonathan and A. Morris, *J. Chem. Soc., Faraday Trans. 2*, 1026 (1975).
41. D. G. Streets and J. Berkowitz, *J. Electron Spectrosc. Relat. Phenom.*, **9**, 269 (1976).
42. A. W. Potts and I. Novak, *J. Electron Spectrosc. Relat. Phenom.*, **28**, 267 (1983).
43. A. W. Potts and T. A. Williams, *Chem. Phys. Lett.* **42** 550 (1976).
44. M. G. White, R. A. Rosenberg, S. T. Lee and D. A. Shirley, *J. Electron Spectrosc. Relat. Phenom.*, **17**, 323 (1979).
45. M. Wu and T. P. Fehlner, *J. Am. Chem. Soc.*, **98**, 7578 (1976).
46. D. C. Frost, S. T. Lee and C. A. McDowell, *J. Chem. Phys.*, **59**, 5484 (1973).
47. S. Cradock and W. Duncan, *J. Chem. Soc., Faraday Trans. 2*, 1262 (1975).
48. S. Cradock and W. Duncan, *Mol. Phys.*, **27**, 837 (1974).
49. Reference 8, p. 66.
50. J. H. D. Eland and C. J. Danby, *Int. J. Mass. Spectrom. Ion Phys.*, **1**, 111 (1968).
51. J. B. Coon, R. E. De Wames and C. M. Lloyd, *J. Mol. Spectrosc.*, **8**, 285 (1962).
52. T. Wentink, *J. Chem. Phys.*, **30**, 109 (1959).
53. A. W. Potts, *J. Electron Spectrosc. Relat. Phenom.*, **11**, 157 (1977).
54. Reference 8, p. 84.
55. D. R. Lloyd and P. J. Roberts, *Mol. Phys.*, **26**, 225 (1973).
56. I. H. Hillier and V. R. Saunders, *Mol. Phys.*, **22**, 193 (1971).
57. For a review, see J. M. Dyke, N. Jonathan and A. Morris, in *Electron Spectroscopy, Theory, Technique and Applications*, Vol. 3, Academic Press, New York, 1979, p. 189.
58. A. B. Cornford, D. C. Frost, F. G. Herring and C. A. McDowell, *J. Chem. Phys.*, **55**, 2820 (1971).
59. B. Solouki, P. Rosmus and H. Bock, *Chem. Phys. Lett.*, **26**, 20 (1974).
60. R. J. Colton and J. W. Rabalais, *J. Electron Spectrosc. Relat. Phenom.*, **3**, 345 (1974).
61. D. M. Leeuw, R. Mooyman and C. A. de Lange, *Chem. Phys.*, **38**, 21 (1979).

62. E. Nagy-Felsobuki and J. B. Peel, *J. Chem. Soc., Faraday Trans. 2*, 148 (1980).
63. E. Nagy-Felsobuki and J. B. Peel, *Chem. Phys.*, **45**, 189 (1980).
64. B. Solouki and H. Bock, *Inorg. Chem.*, **16**, 665 (1977).
65. G. Jonkers, R. Mooyman and C. A. de Lange, *Chem. Phys.*, **50**, 11 (1980).
66. G. Jonkers, R. Mooyman and C. A. de Lange, *Mol. Phys.*, **43**, 655 (1981).
67. D. C. Frost, C. B. MacDonald, C. A. McDowell and N. P. C. Westwood, *J. Am. Chem. Soc.*, **103**, 4423 (1981).
68. G. Jonkers, C. A. de Lange, L. Noodleman and E. J. Baerends, *Mol. Phys.*, **46**, 609 (1982).
69. B. J. M. Neijzen and C. A. de Lange, *J. Electron Spectrosc. Relat. Phenom.*, **18**, 179 (1980).
70. S. Cradock, E. A. V. Ebsworth, M. L. McConnell, D. W. H. Rankin and M. R. Todd, *J. Chem. Soc., Dalton Trans.*, 1925 (1977).
71. S. Cradock and D. W. H. Rankin, *J. Chem. Soc., Faraday Trans. 2*, 940 (1972).
72. G. Distefano, S. Pignataro, G. Innorta, F. Fringuelli, G. Marino and A. Taticchi, *Chem. Phys. Lett.* **22**, 132 (1973).
73. W. Schäffer, A. Schweig, S. Gronowitz, A. Taticchi and F. Fringuelli, *J. Chem. Soc., Chem. Commun.*, 541 (1973).
74. F. Fringuelli, G. Marino, A. Taticchi, G. Distefano, F. P. Colonna and S. Pignataro, *J. Chem. Soc., Perkin Trans.* **2**, 276 (1976).
75. P. J. Derrick, L. Åsbrink, O. Edqvist, B.-Ö. Jonsson and E. Lindholm, *Int. J. Mass Spectrom. Ion Phys.*, **6**, 161 (1971).
76. P. J. Derrick, L. Åsbrink, O. Edqvist, B.-Ö. Jonsson and E. Lindholm, *Int. J. Mass Spectrom. Ion Phys.*, **6**, 177 (1981).
77. J. A. Sell and K. Kuppermann, *Chem. Phys. Lett.*, **61**, 355 (1979).
78. W. von Niessen, W. P. Kraemer and L. S. Cederbaum, *J. Electron Spectrosc. Relat. Phenom.*, **8**, 179 (1976).
79. T. Munakata, K. Kuchitsu and Y. Harada, *J. Electron Spectrosc. Relat. Phenom.*, **20**, 235 (1980).
80. S. Pignataro and G. Distefano, *Chem. Phys. Lett.*, **26**, 356 (1974).
81. A. Modelli, M. Guerra, D. Jones, G. Distefano, K. J. Irgolic, K. French and G. C. Pappalardo, *Chem. Phys.*, **88**, 455 (1984).
82. R. H. Findlay, *J. Chem. Soc., Faraday Trans. 2*, 1397 (1975).
83. G. De Alti and P. Decleva, *Chem. Phys. Lett.*, **77**, 413 (1981).
84. V. Galasso, *J. Mol. Struct. Theochem.*, **3**, 231 (1982).
85. A. Modelli, G. Distefano and P. D. Burrow, unpublished results.
86. K. H. Johnson, *Adv. Quantum Chem.*, **7**, 143 (1973).
87. J. C. Slater, *Adv. Quantum Chem.*, **6**, 1 (1972).
88. R. Roberge and D. R. Salahub, *J. Chem. Phys.*, **70**, 1117 (1979).
89. B. Bak. D. Christensen, W. B. Dixon, L. Hansen-Nygaard, J. Rastrup-Andersen and M. Scottlander, *J. Mol. Spectrosc.*, **9**, 124 (1962).
90. B. Bak, D. Christensen, L. Hansen–Nygaard and J. Rastrup–Andersen, *J. Mol. Spectrosc.*, **7**, 58 (1961).
91. N. M. Pozeev, O. B. Akulinin, A. A. Schapkin and N. N. Magdesieva, *Dokl. Akad. Nauk SSSR, Phys. Chem. Sect.*, **185**, 384 (1969).
92. R. D. Brown and J. C. Crofts, *Chem. Phys.*, **1**, 217 (1973).
93. J.-F. Muller, *Helv. Chim. Acta*, **58**, 2646 (1975).
94. J. H. Eland, *Int. J. Mass. Spectrom. Ion Phys.*, **2**, 417 (1969).
95. P. A. Clark, R. Gleiter and E. Heilbronner, *Tetrahedron*, **29**, 3085 (1973).
96. J. P. Maier and D. W. Turner, *J. Chem. Soc., Faraday Trans. 2*, 196 (1973).
97. M. H. Palmer and M. S. F. Kennedy, *J. Chem. Soc., Perkin Trans.* **2**, 1893 (1974).
98. M. H. Palmer and M. S. F. Kennedy, *J. Mol. Struct.*, **43**, 203 (1978).
99. R. Schulz and A. Schweig, *Angew. Chem., Int. Ed. Engl.*, **19**, 69 (1980).
100. H. Bock, S. Aygen, P. Rosmus and B. Solouki, *Chem. Ber.*, **113**, 3187 (1980).
101. C. Guimon, G. Pfister–Guillouzo, G. Salmona and E. J. Vincent, *J. Chim. Phys. Phys.-Chim. Biol.*, **75**, 859 (1978).
102. M. H. Palmer, R. H. Findlay, J. Neil, A. Ridyard, A. Barrie and P. Swift, *J. Mol. Struct.*, **39**, 189 (1977).
103. R. A. W. Johnston and F. A. Mellon, *J. Chem. Soc., Faraday Trans. 2*, 1155 (1973); M. H. Palmer and M. S. F. Kennedy, *J. Mol. Struct.*, **43**, 203 (1978).

104. R. Gleiter, M. Kobayashi, J. Spanget–Larsen, S. Gronowitz, A. Konar and M. Farnier, *J. Org. Chem.*, **42**, 2230 (1977).
105. R. C. Weast (Ed.), *Handbook of Chemistry and Physics*, Chemical Rubber Co., Cleveland, OH, 1971.
106. V. H. Diebeler and S. R. Liston, *J. Chem. Phys.*, **49**, 482 (1968).
107. S. Cradock and R. A. Whiteford, *J. Chem. Soc., Faraday Trans. 2*, 281 (1972).
108. S. Pignataro and G. Distefano, *Chem. Phys. Lett.*, **26**, 356 (1974).
109. E. Heilbronner, *Isr. J. Chem.*, **10**, 143 (1972); E. Heilbronner and A. Schmelzer, *Helv. Chim. Acta*, **58**, 936 (1975).
110. F. P. Colonna, G. Distefano and V. Galasso, *J. Electron Spectrosc. Relat. Phenom.*, **18**, 75 (1980).
111. V. Shomaker and D. P. Stevenson, *J. Am. Chem. Soc.*, **63**, 37 (1941)
112. D. Betteridge, L. Henriksen, J. Sandstroem, I. Wennerbeck and M. A. Williams, *Acta Chem. Scand., Ser. A*, **31**, 14 (1977).
113. N. L. Allinger, J. J. Maul and M. J. Hickey, *J. Org. Chem.*, **36**, 2747 (1971).
114. A. Schweig and N. Thon, *Chem. Phys. Lett.*, **38**, 482 (1976).
115. P. S. Dewar, E. Ernstbrunner, J. R. Gilmor, M. Godfrey and J. M. Mellor, *Tetrahedron*, **30**, 2455 (1974).
116. A. D. Baker, G. Horozoglu Armen, Y. Guang–di, D. Liotta, N. Flannagan, C. Barnum, M. Saindane, G. C. Zima and J. Grossman, *J. Org. Chem.*, **46**, 4127 (1981).
117. G. Tschmutova and H. Bock, *Z. Naturforsch., Teil B*, **31**, 1611 (1976).
118. C. A. Tschmutova, N. N. Vtyurina and H. Bock, *Dokl. Akad. Nauk SSSR*, **244**, 1138 (1979).
119. F. Bernardi, G. Distefano, A. Mangini, S. Pignataro and G. Spunta, *J. Electron Spectrosc. Relat. Phenom.*, **7**, 457 (1975).
120. C. A. Tschmutova, N. N. Vtyurina, T. V. Komina, I. G. Gazizov and H. Bock, *Zh. Obshch. Khim.*, **49**, 192 (1979).
121. A. Bigotto, V. Galasso, G. Pellizer, G. Distefano, G. C. Pappalardo, J. Bergman and L. Engman, *Spectrochim. Acta. Part A*, **38**, 185 (1982).
122. C. Guimon, G. Pfister–Guillouzo, Ph. Meunier, B. Gautheron, G. Tainturier and S. Pouly, personal communication.
123. B. Gautheron, G. Tainturier, S. Pouly, F. Theobald, H. Vivier and A. Laarif, *Organometallics*, **3**, 1495 (1984).
124. F. P. Colonna, G. Distefano, V. Galasso, K. J. Irgolic, C. E. King and G. C. Pappalardo, *J. Organomet. Chem.*, **146**, 235 (1978).
125. G. Distefano, V. Galasso, K. J. Irgolic and G. C. Pappalardo, *J. Chem. Soc., Perkin Trans. 2*, 1109 (1983).
126. G. Distefano, V. Galasso, K. J. Irgolic and G. C. Pappalardo, unpublished results.
127. O. G. Rodin, V. F. Traven, V. V. Redchenko, M. Yu. Eismont and B. I. Stepanov, *Zh. Obshch. Khim.*, **53**, 2537 (1983).
128. V. F. Traven, O. G. Rodin, M. Yu. Eismont and B. I. Stepanov, in *Proceedings of the European Workshop on UV Molecular Photoelectron Spectroscopy, Rimini, Italy, 1983*, p. 138.
129. A. D. Baker, M. Brisk and M. Gellender, *J. Electron Spectrosc. Relat. Phenom.*, **3**, 227 (1974).
130. H. Bock and G. Wagner, *Angew. Chem., Int. Ed. Engl.*, **11**, 150 (1972).
131. G. Wagner and H. Bock, *Chem. Ber.*, **107**, 68 (1974).
132. M. F. Guimon, C. Guimon and G. Pfister–Guillouzo, *Tetrahedron Lett.*, 441 (1975).
133. P. D'Antonio, C. George, A. H. Lowerey and J. Karle, *J. Chem. Phys.*, **55**, 1071 (1971).
134. G. Tschmutowa and H. Bock, *Z. Naturforsch., Teil B*, **31**, 1616 (1976).
135. T. Hirabayashi, S. Mohamand and H. Bock, *Chem. Ber.*, **115**, 483 (1982).
136. F. P. Colona, G. Distefano, V. Galasso, K. J. Irgolic, G. C. Pappalardo and L. Pope, *J. Chem. Soc., Perkin Trans. 2*, 281 (1981).
137. D. J. Sandman, G. P. Ceasar, P. Nielsen, A. J. Epstein and T. J. Holmes, *J. Am. Chem. Soc.*, **100**, 202 (1978), and references cited therein.
138. H. Bock, G. Brähler, D. Dauplase and J. Meinwald, *Chem. Ber.*, **114**, 2622 (1981).
139. H. E. van Wart and H. A. Sheraga, *J. Phys. Chem.*, **80**, 1823 (1980).
140. H. Bock, S. Aygen, P. Rosmus and B. Solouki, *Chem. Ber.*, **113**, 3187 (1980).
141. H. Bock, B. Solouki, S. Aygen, T. Hirabayashi, S. Mohamand, P. Rosmus and J. Wittmann, *J. Mol. Struct.*, **60**, 31 (1980).
142. H. Bock, B. Solouki, G. Bert and P. Rosmus, *J. Am. Chem. Soc.*, **99**, 1663 (1977).

143. P. Rosmus, B. Solouki and H. Bock, *Chem. Phys.*, **22**, 453 (1977).
144. D. Hall, J. P. Maier and P. Rosmus, *Chem. Phys.*, **24**, 373 (1977).
145. R. Shulz and A. Schweig, *Z. Naturforsch., Teil B*, **39**, 1536 (1984).
146. R. Shulz and A. Schweig, *Tetrahedron Lett.*, 59 (1979).
147. H. Bock, S. Aygen and B. Solouki, *Z. Naturforsch., Teil B*, **38**, 611 (1983).
148. V. Eck, C. Müller, R. Shulz, A. Schweig and H. Verner, *J. Electron Spectrosc., Relat. Phenom.*, **17**, 67 (1969).
149. G. Bieri, F. Burger, E. Heilbronner and J. P. Maier, *Helv. Chim. Acta*, **60**, 2213 (1977).
150. F. Brogli, E. Giovannini, E. Heilbronner and R. Schuster, *Chem. Ber.*, **106**, 961 (1973).
151. H. Bock, S. Aygen, P. Rosmus, B. Solouki and E. Weissflog, *Chem. Ber.*, **117**, 187 (1984).
152. C. R. Brundle, N. A. Kuebler, M. B. Robin and H. Basch, *J. Am. Chem. Soc.*, **94**, 1451 (1972).
153. B. Solouki, P. Rosmus and H. Bock, *J. Am. Chem. Soc.*, **98**, 6054 (1976).
154. H. Bock, T. Hirabayashi and S. Mohamand, *Chem. Ber.*, **115**, 492 (1982).
155. E. Block, E. R. Corey, R. E. Penn, T. L. Renken, P. F. Sherwin, H. Bock, T. Hirabayashi, S. Mohamand, and B. Solouki, *J. Am. Chem. Soc.*, **104**, 3119 (1982).
156. W. Domcke and L. S. Cederbaum, *J. Chem. Phys.*, **64**, 612 (1976).
157. K. Kimura, S. Katsumata, Y. Achiba, T. Yamazaki and S. Iwata, *Handbook of He I Photoelectron Spectra of Fundamental Organic Molecules*, Japan Scientific Society Press, Tokyo, 1981, p. 144.
158. C. Guimon, G. Pfister–Guillouzo, M. Arbelot and M. Chanon, *Tetrahedron*, **30**, 3831 (1974).
159. C. Guimon, D. Gonbeau, G. Pfister–Guillouzo, L. Åsbrink and J. Sandstroem, *J. Electron Spectrosc. Relat. Phenom.*, **4**, 49 (1974).
160. G. Borch, P. Klaeboe, P. H. Nielsen and L. M. Pedersen, *Acta Chem. Scand., Ser. A*, **32**, 259 (1978).
161. J. Spanget–Larsen, R. Gleiter, M. Kobayashi, E. M. Engler, P. Sju and D. O. Cowan, *J. Am. Chem. Soc.*, **99**, 2855 (1977).
162. A. Schweig, N. Thon and E. M. Engler, *J. Electron Spectrosc. Relat. Phenom.*, **12**, 335 (1977).
163. R. Gleiter, M. Kobayashi, J. Spanget–Larsen, J. P. Ferraris, A. N. Bloch, K. Bechgaard and D. O. Cowan, *Ber. Bunsenges. Phys. Chem.*, **79**, 1218 (1975).
164. A. H. Cowley, M. Lattman, R. A. Montag and J. G. Verkade, *Inorg. Chim. Acta*, **25**, L151 (1977).
165. A. H. Cowley, M. Lattman, R. A. Montag and J. G. Verkade, *Inorg. Chem.*, **23**, 3378 (1984).
166. S. Elbel and H. tom Dieck, *J. Chem. Soc., Dalton Trans.*, 1762 (1976).
167. S. Elbel and H. tom Dieck, *Z. Naturforsch.*, **316**, 178 (1976).
168. G. K. Barker, M. F. Lappert, J. B. Pedley, G. J. Sharp and N. P. C. Westwood, *J. Chem. Soc., Dalton Trans.*, 1765 (1975).
169. M. C. Böhm, M. Eckert–Maksić, R. Gleiter, J. Grober and D. Le Van, *Chem. Ber.*, **114**, 2300 (1981).
170. L. Sanche and G. J. Schulz, *Phys. Rev. A*, **5**, 1672 (1972).
171. G. J. Schulz, *Rev. Mod. Phys.*, **45**, 378, 423 (1973).
172. K. D. Jordan, and P. D. Burrow, *Acc. Chem. Res.*, **11**, 341 (1978).

CHAPTER **2**

The application of Mössbauer spectroscopy to the study of organotellurium compounds

FRANK J. BERRY

Department of Chemistry, University of Birmingham, Birmingham B15 2TT, UK

I. INTRODUCTION

The discovery in 1958 by Rudolf Mössbauer of recoil-free nuclear resonance fluorescence[1] gave rise to the technique which is now known as Mössbauer spectroscopy. Since the late 1950s, Mössbauer spectroscopy has developed from an elegant experiment in nuclear physics to a technique which has made important contributions in many areas of science. As an experimental method of scientific investigation it successfully complements other techniques such as visible-light spectroscopy, infrared spectroscopy, nuclear magnetic resonance and the various diffraction methods but, because it has several advantages which give it a special power in a number of important situations and applications, Mössbauer spectroscopy has developed as a particularly useful technique in solid-state and structural chemistry. This chapter initially outlines the basic theory of Mössbauer spectroscopy and the type of instrumentation which is involved, and then considers the application of the technique to the study of various types of organotellurium compounds.

II. MÖSSBAUER SPECTROSCOPY

Several texts[2-8] which deal in detail with the theory and practice of Mössbauer spectroscopy, and also a shorter article[9], are recommended to the reader requiring further information on this technique.

A. Mössbauer Effect

Atomic resonant fluorescence was predicted and discovered shortly after the turn of the century. The process may be envisaged in simple terms as involving the decay of an atom in an excited electronic state to the ground state by the emission of a photon which can then be absorbed by another atom during electronic excitation. The subsequent de-excitation and re-emission of the photon in random directions gives rise to scattering or resonant fluorescence.

Nuclear resonant absorption might be considered in analogous terms. The decay of many radioactive nuclei in an excited state occurs by the emission of gamma-rays and the possibility that these might excite another stable nucleus of the same isotope and give rise to nuclear resonant absorption and fluorescence was recognized early in the 1920s. Although the initial attempts to detect these resonant processes were unsuccessful, the inhibiting role of nuclear recoil and Doppler broadening effects were accurately identified.

Subsequent experiments in the quest were inspired by the awareness that the emitted gamma-rays would be an unusually good source of monochromatic radiation but the degradation of the gamma-ray energies by nuclear recoil and thermal energy constraints persisted as insuperable problems.

Mössbauer successfully eliminated these destructive effects by considering the behaviour of the recoiling nucleus when it was no longer isolated but was fixed in a crystal lattice. When, under these circumstances, the recoil energy is less than the lowest quantized lattice vibrational energy the gamma-ray is emitted without loss of energy due to the recoil of the nucleus. Such recoilless emission is optimized for low-energy gamma-rays from nuclei strongly bound in a crystal lattice at low temperatures and, if incident on another identical matrix containing the same isotope in the ground state, will be resonantly absorbed and subsequently re-emitted in a random direction, i.e. by resonant fluorescence. It is also relevant to note that the energy distribution, or line width, of the gamma-ray depends on the lifetime of the excited nuclear state such that the ease with which the Mössbauer effect can be observed for a particular isotope, and the likelihood of recording chemically significant data, is strongly related to the gamma-ray line width. It will be appreciated from the foregoing that whether or not an isotope of an element exhibits the Mössbauer effect depends on inherent properties of the nucleus which cannot be changed. Selenium, for example, has no Mössbauer active isotopes whereas the tellurium-125 isotope is Mössbauer sensitive with the resonance process being first observed[10,11] in 1962.

B. Tellurium-125 Mössbauer Spectroscopy

1. General principles

a. Sources. The energy levels of an atomic nucleus are modified by the electronic environment of that nucleus. Mössbauer spectroscopy is a means by which these energy levels may be examined and the results interpreted in terms of the local environment of the nucleus. Hence, to probe the energy states of the tellurium-125 nucleus by the Mössbauer effect it is necessary to have a source containing the tellurium-125 nucleus in an excited state. The three convenient nuclear decay schemes which populate the $I = +3/2$ excited state of ^{125}Te emanate from ^{125}Sb, ^{125m}Te and ^{125}I and are depicted in Figure 1. The radioactive excited ^{125}Te nucleus emits a gamma-ray of energy 35.48 keV when decaying from the first excited nuclear state, $I = +3/2$, to the ground state, $I = 1/2$, and it is this 35.48 keV gamma radiation which is used in ^{125}Te Mössbauer spectroscopy. Hence the preparation of a good source is an essential prerequisite of ^{125}Te Mössbauer spectroscopy. It will be seen from Figure 1 that the decay of ^{125}Sb by β-emission with a half-life of 2.7 years involves a complex decay scheme which includes the metastable ^{125m}Te isotope. The complexity is a disadvantage but the method has been used successfully when the ^{125}Sb has been diffused into a copper or rhodium[13] matrix to minimize the nuclear recoil. The ^{125m}Te, state, with a half-life of 58 days, can also be populated by neutron irradiation and single line sources have been obtained from matrices of PbTe[14], ZnTe[15], electrodeposited Te/Pt[16] and TeO$_3$[17,18], but there are recorded instances of radiation damage affecting the emission line. ^{125}I decays with a half-life of 60 days by electron capture directly to the 35.48 keV level and is therefore the most efficient precursor with a very satisfactory source being conveniently made by the diffusion of ^{125}I into copper foil[19].

The present author has been involved in tellurium-125 Mössbauer studies using an ^{125}I/Cu source, a Pb^{125m}Te source prepared by neutron irradiation of a Pb^{125}Te sample in a thermal neutron flux and both ^{125}Sb/Cu and ^{125}Sb/Rh sources. The relatively short half-lives of the ^{125}I and ^{125m}Te isotopes are a considerable disadvantage in the use of ^{125}I/Cu and Pb^{125m}Te, sources and, given the narrow line widths and relatively large
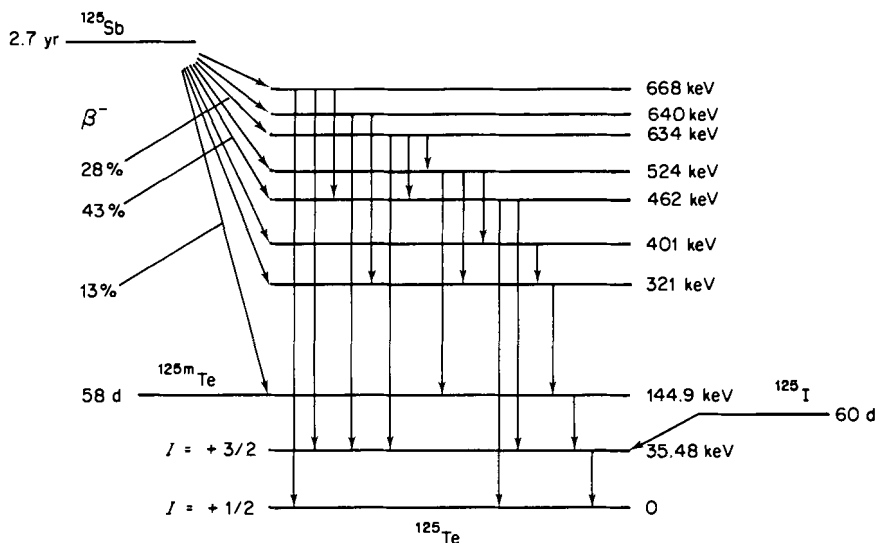
FIGURE 1. Nuclear decay schemes for ^{125}Sb, 125^{m}Te and ^{125}I which populate the 35.48 keV level of tellurium-125

recoil free fractions obtained from ^{125}Sb/Cu and ^{125}Sb/Rh, the sources produced from ^{125}Sb seem to be the most favourable. It is relevant to note, however, that a source[16] prepared from ^{125m}Te which had been radiochemically milked from the parent ^{125}Sb and deposited on platinum gave large recoil fractions and narrow line widths and may have been the best source yet used in ^{125}Te Mössbauer spectroscopy. Such a preparation avoids the high-level background from the ^{125}Sb but retains the advantageously long half-life of the parent. It must be appreciated, however, that the radiochemical manipulations which are required in preparing such a source are a significant disadvantage.

The 35.48 keV excited state of ^{125}Te has a half-life[20] of $1.535 + 10^{-9}$ s, the transition is highly converted $\alpha_T = 12.7$, and the gamma-rays are sometimes difficult to resolve from the intense $K\alpha$ (27.4 keV) and $K\beta$ (31.00 keV) X-rays, although copper filters can be used to reduce the background radiation, as will be discussed later.

b. Instrumentation. The investigation of tellurium-containing materials by Mössbauer spectroscopy involves the exposure of the samples, called the absorber, to the radiation from the source. An absorber containing tellurium atoms in the same chemical environment as the source will, as a consequence of the presence of ^{125}Te nuclei with 6.99% natural abundance, absorb this 35.48 keV radiation and become raised from the nuclear ground state to the nuclear first excited state. However, the energy states of nuclei depend on the interaction between the nuclei and their electronic environments. Hence, when the environments of the tellurium nuclei in the source and absorber are different, as will occur for example when the source and absorber are different chemical compounds, the nuclear energy levels will no longer coincide and absorption can only occur when the energy of the gamma-ray emitted by the source is modulated by the application of a Doppler velocity (Figure 2). This is achieved by oscillating the source backwards and forwards with respect

Nuclear excited state

Nuclear ground state

Detector

Material under
examination
(absorber)

^{125}Sb source

− ve
velocity

+ ve
velocity
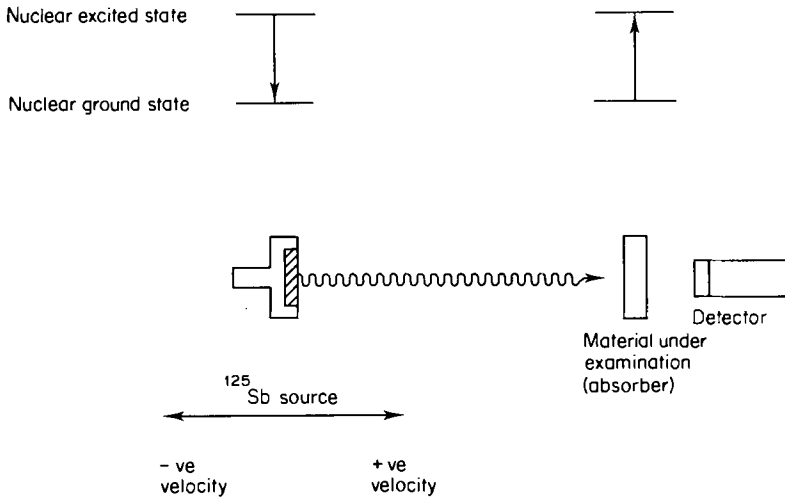
FIGURE 2. Energy of the gamma ray emitted by the source modified by oscillating the source backwards and forwards with respect to the stationary absorber. Reproduced with permission from *Phys. Bull.*, **34**, 517 (1984)

to the stationary absorber and resonant absorption occurs when the energy of the incident gamma-ray just matches the nuclear transition energy of the ^{125}Te nuclei in the absorber. A range of velocities are scanned until maximum absorption occurs and a Mössbauer spectrum is composed of a plot of gamma-ray counts against the velocity of the source with respect to the absorber measured in millimetres per second (Figure 3).

Counts

− ve   O   +ve
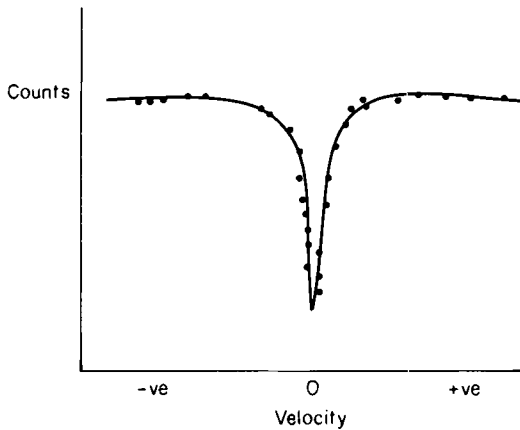
Velocity

FIGURE 3. Simple representation of a Mössbauer spectrum which is composed of a plot of gamma-ray counts against the velocity of the source with respect to the absorber measured in millimetres per second

Oscilloscope
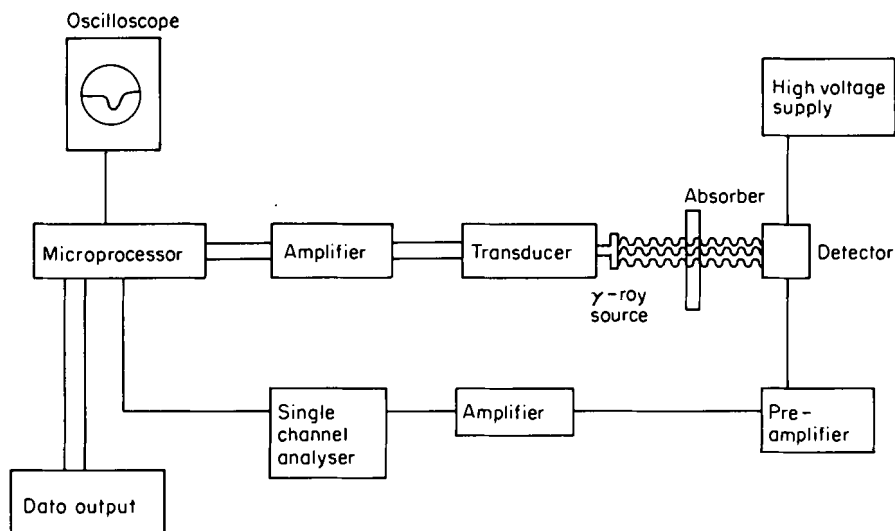
FIGURE 4. Schematic representation of a microprocessor controlled Mössbauer spectrometer

The Doppler velocities of ca. $10 \, mm \, s^{-1}$ can be generated by electromechanical transducers, electronic drives and loudspeaker devices and, in the modern Mössbauer spectrometer (Figure 4), are controlled by a microprocessor which also collects the data. The detection of the 35.48 keV gamma-ray can be achieved indirectly through the escape peak using a thin NaI/Th scintillation detector or a gas-filled proportional counter, or directly using a high-resolution germanium or lithium-drifted germanium detector. The persent author has found that a Xe/CO_2 proportional counter, coupled with a copper critical absorber to reduce background radiation under the 6 keV escape peak, gives good results with most tellurium-containing absorbers. The detector is set to monitor the gamma-rays by means of the single-channel analyser. The microprocessor receives and stores the amplified impulses from the detector and the accumulating spectrum may be monitored on the oscilloscope screen. When the spectrum is of satisfactory quality it is read out on to punched or magnetic tape and finally fitted by a computer which produces the spectrum and Mössbauer parameters.

The 35.48 keV gamma-rays used in ^{125}Te Mössbauer spectroscopy are sufficiently high in energy that the fraction of recoil-free emission or absorption events is low. The recoil-free fraction can be increased, however, if the source and the absorber are cooled to liquid nitrogen (77 K) or liquid helium (4.2 K) temperatures and in ^{125}Te Mössbauer spectroscopy it is necessary to cool at least the absorber to increase the recoilless fractions. Indeed, the examination of organotellurium compounds is best performed at liquid helium temperature with both the source and absorber at 4.2 K. Such experiments in which both the source and the absorber are held at temperatures as low as a few millikelvin still require the source to be vibrated, and it will be appreciated that the construction of cryogenic facilities to perform such measurements is not without its problems. However, a number of cryostats for performing measurements at 77 or 4.2 K, such as is illustrated in Figure 5, are now commercially available.

Cryostats with a variable temperature control are used in many studies, such as those involving the investigation of phase transitions, and, for investigations where it is desirable

Drive

Drive Tube

Exchange Gas

Pump He Bath

He Fill

N_2 Fill

Vacuum

Baffles

Liquid He

Liquid N_2

Guide Spring

Source

Heater

Solenoid

Absorber

Detector
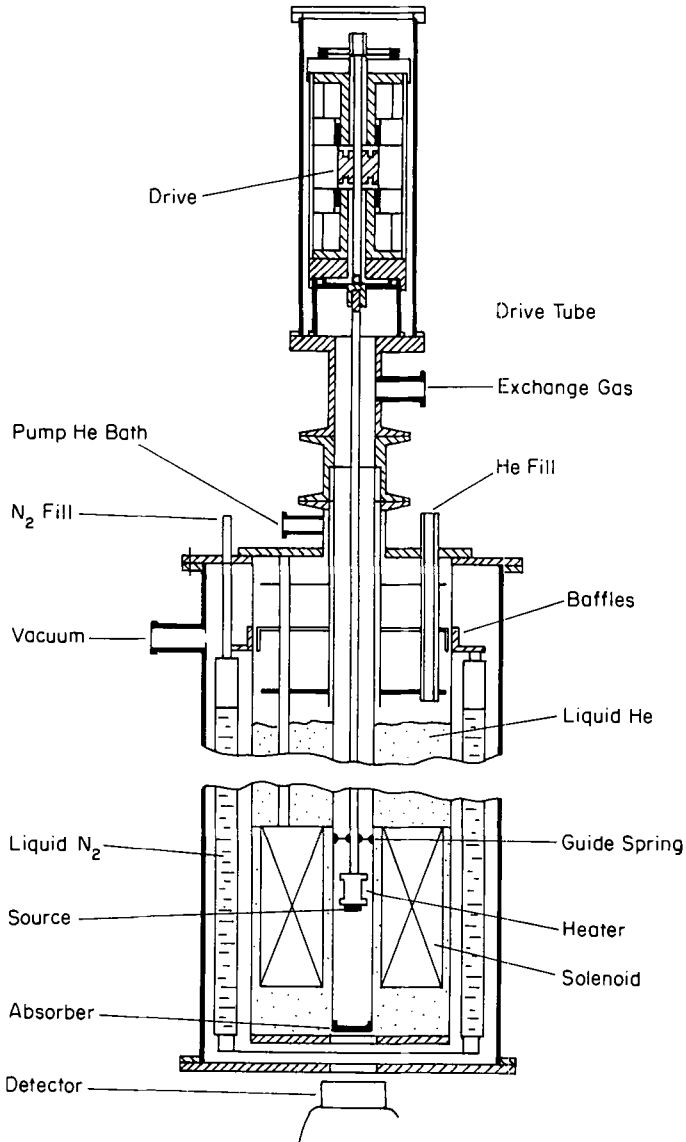
FIGURE 5. Helium cryostat with vertical beam geometry. Both source and absorber can be cooled. The system is equipped with a superconducting solenoid. If the magnet coil is not in use, the drive tube is extended to bring the source closer to the absorber in order to obtain a larger solid angle. Reproduced by permission of North-Holland Publishing Company, Amsterdam, from Shenoy and Wagner (Eds.), *Mössbauer Isomer Shifts*, 1978

to apply a large external magnetic field to the absorber, superconducting magnets are required which are capable of producing magnetic flux densities of up to 10 T.

2. Tellurium-125 Mössbauer parameters

The information contained in the ^{125}Te Mössbauer spectrum is mainly extracted by the computation of two Mössbauer parameters—the chemical shift, δ, and the quadrupole splitting, Δ. These parameters and their temperature dependence, together with line width data and an appreciation of any magnetic interactions which may influence the spectral patterns, enable information relating to bonding, structural and time-dependent effects to be examined.

a. Chemical isomer shifts. At the velocity required to excite the absorber nucleus from the ground state to the first excited state there is resonant absorption of the incident gamma radiation and the count rate drops (Figure 3). The magnitude of the applied velocity is known as the chemical isomer shift, δ.

Chemical isomer shifts, which are sometimes called chemical shifts, isomer shifts or centre shifts, arise because the nucleus has a finite volume which may be larger or smaller in the excited state than in the ground state. The change in density of the positive charge on the nucleus which therefore alters during the gamma-ray transition gives rise to a change in the coulombic interaction, known as the electric monopole interaction, between the positive nuclear charge and the electron density at the nucleus. Hence the spacings of the nuclear energy levels depend on the electron density at the nucleus and changes in this density give rise to shifts in the position of the resonance line. The situation is described schematically in Figure 6.

The horizontal lines represent the nuclear energy levels and the transition energy between the nuclear ground and first excited state in a bare nucleus is designated by E_n. The electronic environment of the nucleus in the source might lift the nuclear energy levels
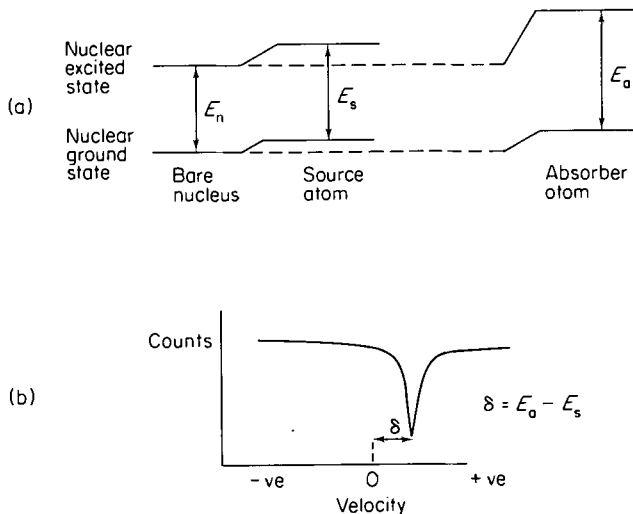
FIGURE 6. Schematic representation of chemical isomer shifts in Mössbauer spectroscopy

such that the transition energy for the source is E_s. When the absorber nucleus is in a different chemical environment the displacement of the energy levels will differ from those in the source such that the transition energy E_a will also differ. The application of a Doppler velocity to the source to attain resonance therefore results in a shift of the position of the resonance line in the spectrum. The applied velocity is known as the chemical isomer shift, δ.

To a first approximation, the electron density about the nucleus is appreciably large only for s-electrons. By making certain assumptions[3] it can be shown that the chemical isomer shift δ can be described by the expression

$$\delta = \text{constant} \times \frac{\Delta R}{R}\left(|\Psi_s(0)|_a^2 - |\Psi_s(0)|_s^2 \right)$$

where ΔR is the change in the nuclear radius during its transition from the excited to the ground state and R is the radius of the ground state. The value of $\Delta R/R$ is characteristic of each Mössbauer transition and may be of either sign, such that a positive $\Delta R/R$ indicates that the nucleus shrinks on de-excitation. After some controversy it is now accepted that $\Delta R/R$ is positive for the ^{125}Te 35.48 keV γ-ray transition[21].

The terms $|\Psi_s(0)|_a^2$ and $|\Psi_s(0)|_s^2$ refer to the s electron densities at the nuclei in the absorber and source, or reference, respectively. Since $\Delta R/R$ is positive for the ^{125}Te transition the chemical isomer shift increases with increasing s electron density at the absorber tellurium nucleus. Although the term $|\Psi_s(0)|^2$ includes contributions from all the occupied s electron orbitals in the atom, it is also sensitive to p and d orbital electron density as a result of shielding and penetration effects. Mössbauer spectroscopy therefore provides a means of monitoring s-electron density at the nucleus which is dependent on p, d and f electron disposition.

It will now be appreciated that the chemical isomer shift, δ, is an important means by which atomic oxidation states, which have sometimes in the past been difficult to determine, may now be directly investigated. Similarly, covalency effects and the shielding of one set of electrons by another which also influences the electronic environment of the nucleus may also be reflected in changes in δ. The chemical isomer shift data can sometimes be used to assess quantitatively the electron-withdrawing power of substituent electronegative groups in addition to the degree of π-bonding and back-donation from metal atoms to ligands in coordination complexes. The interpretation of the isomer shift data in terms of the Townes and Dailey theory[22] will be discussed later.

b. Quadrupole splittings. The principles outlined during the discussion of the electric monopole interaction which gives rise to chemical isomer shifts assumed that the nuclear charge distribution is spherical. However, nuclei in energy states with a nuclear angular momentum quantum number $I > 1/2$ have non-spherical charge distributions which are characterized by a nuclear quadrupole moment, Q, i.e. the nuclear charge distribution may be elongated along the intrinsic axis of symmetry labelled the z-axis, in which case the nuclear quadrupole moment Q is positive, or it may be compressed along this axis, in which case Q is negative. The interaction of the nuclear charge density with asymmetric extranuclear electric fields, i.e. non-symmetric arrays of electronic charge, ligands on ions, which are characterized by a tensor quantity called the electric field gradient (EFG), is called the electric quadrupole interaction. The axes of the electric field gradient are labelled such that $V_{zz} > V_{xx} > V_{yy}$ and the EFG is normally expressed in terms of the principal component V_{zz}, which is usually written as eq, and an asymmetry parameter η, which is described by

$$\eta = \frac{V_{xx} - V_{yy}}{V_{zz}}$$
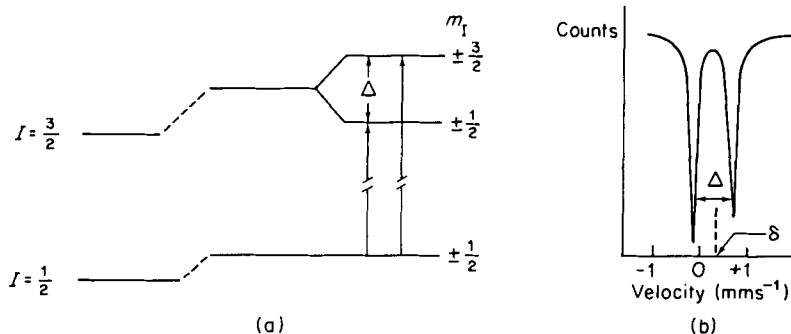
FIGURE 7. The Mössbauer quadrupole splitting in tellurium-125: (a) the excited state, $I = 3/2$, splits into two; (b) the resulting Mössbauer spectrum

The electric quadrupole interaction involves the nuclear quadrupole moment aligning itself either with or across the electric field gradient, i.e. the coupling of eQ with eq, which is expressed as the quadrupole coupling constant e^2qQ, and gives rise to a splitting of the nuclear energy levels. Hence, in ^{125}Te the excited state has $I = 3/2$ and in the presence of an asymmetric electric field splits into two substates characterized by $M_I \pm 1/2$ and $M_I = \pm 3/2$, as is shown schematically in Figure 7. The transitions from the degenerate ground state ($I = 1/2$) to the excited state produce a two-line spectrum in which the separation between the two lines, measured in millimetres per second, is a measure of the quadrupole splitting Δ. The centroid of the two peaks represents the chemical isomer shift δ.

Hence the quadrupole splitting obtained from the Mössbauer spectrum involves both a nuclear quantity, the quadrupole moment, and an electronic quantity, the electric field gradient, and, for Mössbauer transitions between nuclear states with spin 1/2 and 3/2, may be expressed in terms of the quadrupole coupling constant for the $I = 3/2$ state:

$$\Delta = \tfrac{1}{2}e^2qQ\left(1 + \frac{\eta^2}{3}\right)^{1/2}$$

The electric field gradient contains contributions from several different components. One of the major contributions may be described as that due to the electronic environment about the nucleus and is called the valence term (q_{val}). This may be envisaged as arising from the valence electrons of the Mössbauer atom itself and originates from asymmetry in the electronic structure which may derive from the unfilled or partly filled electronic shells occupied by the valence electrons. Another contribution to the electric field gradient originates from surrounding charged entities and is called the lattice contribution (q_{lat}). This arises from the asymmetry in the arrangement of atoms around the Mössbauer nuclei and is most important in ionic systems. Other contributions to the electric field gradient include the effects of molecular orbitals and any polarisation of the core electrons of the Mössbauer atom.

The quadrupole splitting therefore reflects the symmetry of the bonding environment and the local structure in the vicinity of the Mössbauer atom. There have been several attempts to formulate semi quantitative treatments of the electric field gradient which have recently been well summarized[8]. One of these, based on the theory of Townes and Dailey[22], is particularly well suited for the treatment of tellurium-containing compounds. The method assumes that the electric field gradient arises entirely within the valence shell of the tellurium atom, that the bonding involves only the p orbitals or has a constant s
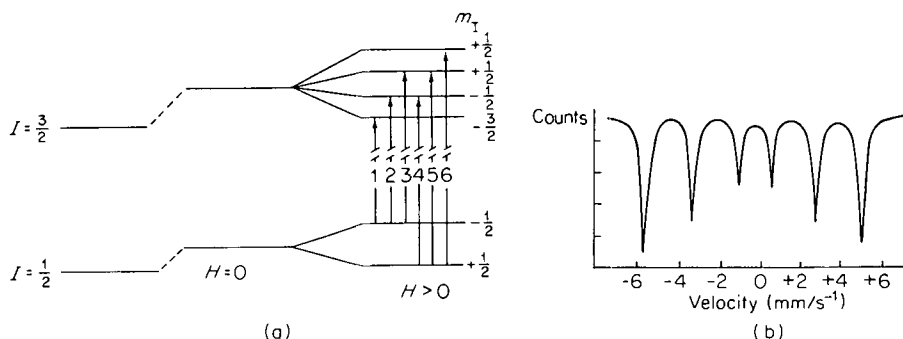
FIGURE 8. Effect of magnetic splitting on the nuclear energy levels of iron-57: (a) splitting of the nuclear energy levels in a magnetic field; (b) the resulting Mössbauer spectrum

character, and that π-bonding interactions can be ignored. From the Mössbauer quadrupole splitting and quadrupole coupling constants the p orbital imbalance, designated as U_p, can be derived which gives information about the electron population of the p orbitals. The method also allows the calculation of a quantity, h_p, which is pertinent to isomer shift calculations and which describes the number of holes in the shell.

c. Magnetic splitting. When a nuclear state with spin quantum number I is placed in a magnetic field its energy levels split into $2I + 1$ levels. Hence metallic iron gives a six-line Mössbauer spectrum (Figure 8). The spacing of the levels is directly proportional to the magnetic field at the nucleus and Mössbauer spectroscopy is therefore a simple method by which the magnitude and direction of the field may be measured.

Although the gamma-ray transition in ^{125}Te is also between nuclear states with spin 1/2 and 3/2 the magnetic splitting of the ^{125}Te resonance is less helpful than in, for example, ^{57}Fe or ^{119}Sn Mössbauer spectroscopy because of the poorer resolution which is obtained. The magnetic splitting has not been used in the interpretation of ^{125}Te Mössbauer spectra recorded from organotellurium compounds.

3. Other features of tellurium-125 Mössbauer spectra

a. Time-dependent effects. The hyperfine interactions observed in Mössbauer spectra occur on characteristic time scales and the spectrum observed from a specific system depends on whether the nuclear environment or the position of the nucleus is changing relative to these times. These time-dependent effects can influence both the spectral line shapes and the observed Mössbauer parameters. Time-dependent changes in the nuclear environment are often called relaxation processes and may relate to time-dependent structural changes or to changes involving the electronic configuration. It is also relevant to note that any dynamic properties of Mössbauer nuclei arising from the lattice dynamics of the solid in which the nucleus is situated, or from the motion of a localized part of the system such as molecular motion or the motion of the whole system within its environment, may also be reflected in changes in the Mössbauer spectra. Studies of these types of phenomena usually require the monitoring of the spectral changes as a function of temperature.

b. Absorbers. Since Mössbauer spectroscopy depends on nuclear recoil-free events, it is restricted to the investigation of materials in the solid state. Although liquids and gases are not amenable to investigation it is possible to freeze both pure liquids and solutions to give solids which can be examined. Hence samples for Mössbauer spectroscopy are usually presented as single crystals, crystalline powders, amorphous powders, glasses or frozen liquids.

If the material under examination contains a low concentration of ^{125}Te it may be possible to improve the signal-to-noise ratio, and hence the ability to obtain useful spectra, by using samples enriched in ^{125}Te.

c. Reference standards. For each Mössbauer isotope a specific reference standard is used to serve as a zero-point reference for all the chemical isomer shift data recorded from that element. In tellurium-125 Mössbauer spectroscopy the chemical isomer shifts are usually referred to ^{125}I/Cu, mainly because this source was used in many early Mössbauer studies and because most chemical isomer shift values have normally been referred to this standard. However, an alternative standard[16] is tetragonal tellurium dioxide, which has some advantages since it is one of the most readily obtainable pure well characterized compounds of tellurium and gives an excellent quadrupole split absorption.

d. Limitations. The chemical isomer shifts recorded in ^{125}Te Mössbauer spectra span a rather narrow range of about $3 \, mm \, s^{-1}$, which is less than the natural line width[20] of $5.02 \, mm \, s^{-1}$. However, good quality spectra have been obtained by careful experimental methods and the use of a good source[13,16] such that differences of only $0.1 \, mm \, s^{-1}$ may be shown to be significant. The low resolution of the spectra frequently precludes the interpretation of data in terms of a heterogeneity of tellurium sites and the detection of different tellurium-containing materials in a multi-phased sample is usually difficult.

III. APPLICATION TO THE STUDY OF ORGANOTELLURIUM COMPOUNDS

The initial ^{125}Te Mössbauer investigations of organotellurium compounds were performed in the mid-1970s and involved the examination[23-27] of a variety of alkyl and aryl derivatives of tellurium-(II) and -(IV). The early Mössbauer studies were summarized[28] in 1976 and the most recent developments were reviewed[29] in 1983.

A. Organo-tellurides(II) and -ditellurides (II)

1. Dialkyl and diaryl tellurides and ditellurides

The diorgano-tellurides and -ditellurides give ^{125}Te Mössbauer spectra which are characterized by small positive chemical isomer shifts and large quadrupole splittings (Figure 9, Table 1).

Investigations of the structural properties of simple aryltellurium(II) compounds have shown them to be covalently bonded molecules with bond angles within the range expected for sp^3 or p^3 hybridized tellurium. For example, the C—Te—C bond angle in[31] $(p\text{-Tol})_2\text{Te}$ is $101.0 \pm 2.7°$ whereas the C—Te—Te bond angle in $(p\text{-ClC}_6\text{H}_4)_2\text{Te}_2$ is[32] $94.4°$ and in Ph_2Te_2 is[33] $99°$ (Figure 10).

Since the nuclear radius term is positive for the ^{125}Te transition[21], the chemical isomer shift data become more positive as the s electron density, $|\psi_s(0)|^2$, at the tellurium nucleus increases. Such an increase can occur by the removal of 5p electron density from the tellurium atom, which results in a deshielding of the 5s electrons from the nucleus. On the
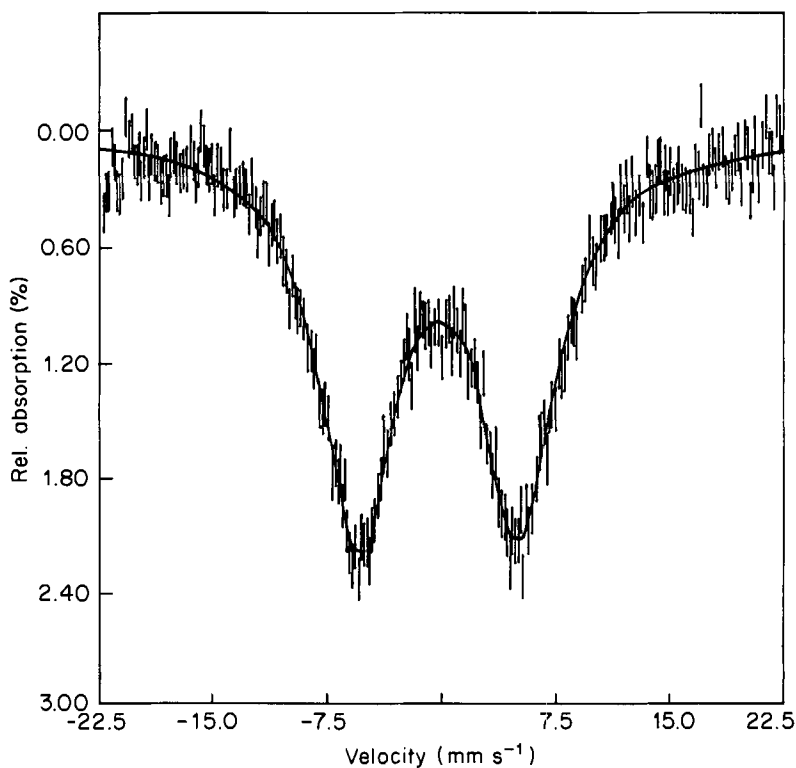
FIGURE 9. ^{125}Te Mössbauer spectrum of i-Pr$_2$Te$_2$ measured at 4.2 K. Reproduced with permission from *J. Organomet. Chem.*, **255**, 61 (1983)

TABLE 1. ^{125}Te Mössbauer parameters recorded from some organo-tellurides and -ditellurides at 4.2 K

Compound	$\delta^a \pm 0.08$ (mm s^{-1})	$\Delta \pm 0.1$ (mm s^{-1})	Ref.
Me$_2$Te	0.06	10.5	25
t-Bu$_2$Te	0.19	10.5	30
Ph$_2$Te	0.18	10.5	25
p-Tol$_2$Te	0.7	10.1	23
p-An$_2$Te	0.3	11.3	23
Me$_2$Te$_2$	0.26	12.3	30
i-Pr$_2$Te$_2$	0.37	11.0	30
i-Bu$_2$Te$_2$	0.32	11.0	30
p-TolTe$_2$	0.6	9.9	23
Ph$_2$Te$_2$	0.37	10.7	25
p-AnTe$_2$	0.3	10.3	23
$(p$-EtOC$_6$H$_4)_2$Te$_2$	0.28	10.6	25
$(p$-C$_6$H$_5$OC$_6$H$_4)_2$Te$_2$	0.3	10.3	23
$(neo$-Hex$)_2$Te$_2$	0.38	10.5	30

^{a} δ with respect to I/Cu.
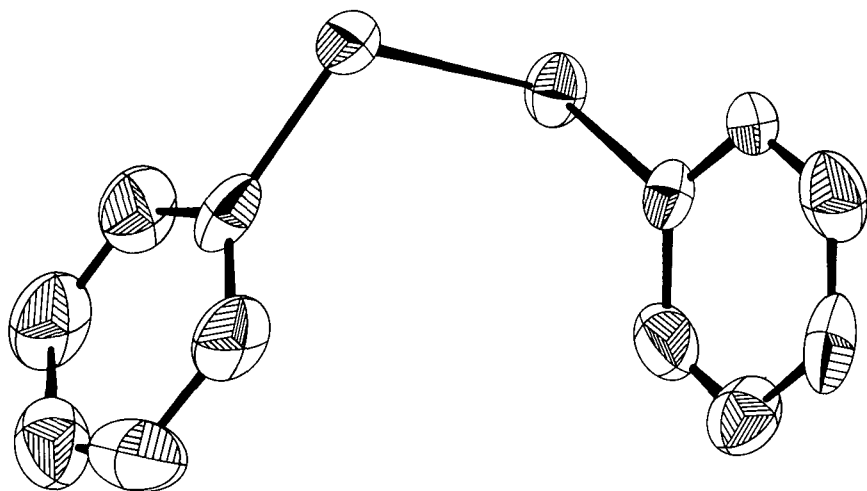
FIGURE 10. Structure of diphenyl ditelluride. Reproduced with permission from *Acta Crystallogr., Sect. B*, **28**, 2438 (1972)

other hand, the removal of s electrons leads to a direct decrease in the s electron density at the nucleus. Hence the small positive chemical isomer shifts of the tellurides and ditellurides described in Table 1 may be associated with compounds with relatively small s electron densities at the tellurium nuclei.

The large [125]Te Mössbauer quadrupole splittings of the diorgano-tellurides and -ditellurides are amenable to interpretation in terms of the Townes and Dailey theory[22,25], for which the basic tenets, as it is generally applied, are that the electric field gradient derives predominantly from any imbalance in the tellurium 5p orbital populations and that the lattice terms, the d orbital contributions, and Sternheimer shielding and anti-shielding factors[12] can all, to a first approximation, be conveniently ignored. The quadrupole coupling constants, e^2qQ, are then linearly related to the p orbital imbalance, U_p, through the expression

$$\frac{e^2qQ}{e^2q_oQ} = -U_p$$

$$\Delta = \tfrac{1}{2}e^2qQ\left(1 + \frac{\eta^2}{3}\right)^{1/2}$$

where η is the asymmetry parameter and e^2q_0Q is the quadrupole coupling constant for one 5p electron on tellurium, which is assumed to remain constant with changes in oxidation state and has[34] a value of ca. $+ 24$ mm s^{-1}. The p orbital imbalance is defined as

$$U_p = -U_z + \frac{U_x + U_y}{2}$$

The p-orbital populations U_x, U_y, and U_z can be related to the bonding orbital populations through a consideration of the hybrid orbitals which describe the bonding to the tellurium atom and, by using this approach[25], the large quadrupole splittings of the diorgano-tellurides and -ditellurides may be considered as reflecting a considerable

imbalance in the tellurium $5p$ orbital population. The method[25] accommodates the structural properties[31-33] of the compounds and the Mössbauer chemical isomer shift data[23,25,30] which indicate that the tellurium $5s$ electrons participate in the bonding such that the bonding may be viewed as intermediate between pure p^3 and sp^3 to generate bond angles θ in the range $90° < \theta < 109.5°$ and concludes[25] that

$$\frac{e^2qQ}{e^2q_0Q}(1 - \cos\theta) = 2 - U_c$$

$$\eta = 3\cos\theta$$

where θ is the C—Te—C bond angle and U_c is the Te—C bond orbital population. By assuming that the bonding is essentially p in character, i.e. $\theta = 90°$ with only limited s character in the Te—C bonds, the lone pairs on the tellurium atom may be visualized as occupying the $5s$ and the $5p_z$ orbitals, the latter being directed out of the bonding plane. Since this would correspond to an excess of p electron density along the z-axis, V_{zz}, the principal component of the electric field gradient tensor, may be assumed to be negative. Under such circumstances, e^2qQ would be positive since Q, the quadrupole moment of the $I = 3/2$ excited state, is negative. For the tellurides the quadrupole splitting Δ is the same, within the errors, for the different alkyl and aryl groups and the average value for the quadrupole splitting of 10.6 mm s^{-1} corresponds to an orbital population of ca. 1.1 for the Te—C bond. The ditellurides have very similar splittings to the tellurides, indicating a similar covalency of the Te—C and Te—Te bonds and, since the bond orbital population for the latter is presumably 1.0, this is consistent with a value of 1.1 for the Te—C bond.

Given that the large ^{125}Te Mössbauer quadrupole splittings recorded from the diorgano-tellurides and -ditellurides arise from the p-orbital imbalance between the Te—C bonds and the lone pairs of electrons on the tellurium atom, it would be reasonable to except that increasing electronegativity in the organic groups would result in $5p$ electron density being removed from the tellurium and to be reflected in increases in quadrupole splitting. It might also be expected that, depending on the relative s–p character of the Te—C bond, the Mössbauer chemical isomer shift might also be influenced. It is interesting, therefore, that the data compiled in Table 1 show that the Mössbauer chemical isomer shifts and quadrupole splittings are essentially similar for all the diorgano-tellurides and -ditellurides. However, it is notable that dimethyl ditelluride has a larger quadrupole splitting, which is consistent with enhanced electron withdrawal by the methyl group and an increased removal of $5p$ electron density from tellurium. This molecule would also presumably have a larger asymmetry parameter, which would further enhance the magnitude of the quadrupole splitting.

In these respects it is interesting to note the Mössbauer parameters more recently recorded[35] from bis(trifluoromethyl) and bis(pentafluorophenyl) tellurides, which contain significantly more electronegative organic ligands (Table 2). The ^{125}Te Mössbauer chemical isomer shifts are not too dissimilar from those of the dialkyl and diaryl tellurides (Table 1) and, given the small range of isomer shifts for ^{125}Te, the similarity in the chemical isomer shift data is not too surprising. On the other hand, the quadrupole splitting data recorded from $(CF_3)_2Te$ and $(C_6F_5)_2Te$ are significantly larger than those of the dialkyl and diaryl tellurides. These larger quadrupole splittings are indicative of a considerable p orbital imbalance on the tellurium atom and reflect the high electronegativity of the CF_3 and C_6F_5 ligands.

It is interesting that there appear[30] to be no simple relationships between the ^{125}Te Mössbauer parameters recorded from dialkyl tellurides and ditellurides in the solid state, or as frozen liquids, and the ^{125}Te NMR data recorded from the species in solution. Although the absence of any such correlation may reflect the different environments about tellurium in the solid state and in solution, it must be acknowledged that there is no

Frank J. Berry

TABLE 2. ^{125}Te Mössbauer para-
meters   recorded^{35} from
bis(trifluoromethyl)   and
bis(pentafluorophenyl)   tellurides
at 4.2 K

Compound	$\delta^a \pm 0.08$ (mm s^{-1})	$\Delta \pm 0.08$ (mm s^{-1})
$(CF_3)_2Te$	-0.14	14.02
$(C_6F_5)_2Te$	$+0.14$	13.40

^{a} δ relative to I/Cu.

evidence from the crystal structure data of any intermolecular attractions in the solid state in either the tellurides or the ditellurides which might lead to such a difference.

Hence the large quadrupole splittings of the tellurides and ditellurides correspond to a considerable imbalance in the 5p orbital population in the Te—C bonds and to the presence of lone pairs of electrons on the tellurium atoms. The data are indicative of considerable covalent character in the Te—C and Te—Te bonds and suggest that the tellurium atoms have a significant number of holes in the 5p shells. Such a situation would be expected to give rise to increased s electron densities at the tellurium nuclei and consequently to large and positive chemical isomer shifts. Hence the small chemical isomer shifts, when considered in conjunction with the quadrupole splitting data, imply that the Te—C and Te—Te bonds possess some s character and that the bonding in these compounds is intermediate between p^3 and sp^3. It is also pertinent to record that the Mössbauer data are consistent with the C—Te—C and C—Te—Te bond angles, which are indicative of the presence of stereochemically active lone pairs in these compounds.

2. Bis(organyltelluro)methanes

Another group of compounds closely related to the diorganotellurides are the bis(organyltelluro)methanes of composition $(RTe)_2CH_2$. In a study of bis(methyltelluro)- and bis(phenyltelluro)-methanes, the ^{125}Te Mössbauer quadrupole splittings were shown^{36} to be large, Δ 10.4 and 11.1 mm s^{-1}, respectively, and the chemical isomer shifts small and positive. The data are similar to those recorded from the simple diorganotellurides and give no evidence for the second tellurium atom in the Te—CH$_2$—Te linkage having any significant effect on the electronic environment at tellurium. The Mössbauer parameters appear to be dominated by the bonds of each tellurium to two carbon atoms, indeed the data recorded^{36} from the ethyl and isopropyl derivatives show no measurable differences.

3. Cyclic derivatives

It is also relevant to comment on the compound of formula CH_2Te_2, which was previously described^{37} as a three-membered cyclic species called ditelluromethane (Figure 11a) and which has more recently^{38} been shown to be the six-membered cyclic compound 1,2,4,5-tetratelluracyclohexane (Figure 11b). The ^{125}Te Mössbauer parameters^{38}, δ 0.42 mm s^{-1}, Δ 9.3 mm s^{-1}, indicate the presence of only one tellurium site in the compound and are similar to those of the diorganoditellurides (Table 1).

(a)   (b)
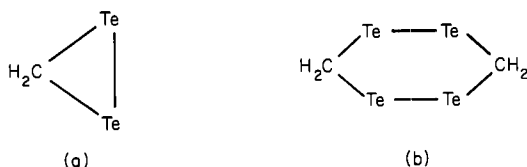
FIGURE 11. Schematic representation of (a) ditelluro-
methane and (b) 1, 2, 4, 5-tetratelluracyclohexane

B. Organotellurium(IV) Halides

1. Diorganotellurium(IV) dihalides

The diorganotellurium(IV) dihalides were among the first organotellurium(IV) compounds to be examined by ^{125}Te Mössbauer spectroscopy. The Mössbauer parameters recorded from selected series of diorganotellurium(IV) dihalides are collected in Table 3 and a representative spectrum is illustrated in Figure 12.

Several structural studies of the crystalline diorganotellurium(IV) dihalides Ph_2TeBr_2[39], Me_2TeCl_2[40], $(p\text{-}ClC_6H_4)_2TeI_2$[41], $\alpha\text{-}Me_2TeI_2$[42], and Ph_2TeF_2[43] have shown the tellurium atoms to occupy distorted trigonal bipyramidal coordination (Figure 13). In these structures the halogen atoms occupy *trans* axial positions and the organic groups are situated in the equatorial plane in which the third position is occupied by a lone pair of electrons which may sometimes be involved in intermolecular bonding through bridging

TABLE 3. ^{125}Te Mössbauer parameters recorded from some diorganotellurium(IV) dihalides at 4.2 K

Compound	$\delta^a \pm 0.08$ (mm s^{-1})	$\Delta \pm 0.1$ (mm s^{-1})	Ref.
Me_2TeCl_2	0.58	9.4	25
Me_2TeBr_2	0.65	8.5	25
Me_2TeI_2	0.52	7.6	25
Ph_2TeF_2	0.52	10.4	26
$p\text{-}An_2TeF_2$	0.54	10.0	26
$(p\text{-}EtOC_6H_4)_2TeF_2$	0.36	10.1	26
Ph_2TeCl_2	0.5	9.2	23
$p\text{-}An_2TeCl_2$	0.68	9.1	26
$(p\text{-}EtOC_6H_4)_2TeCl_2$	0.7	9.1	23
Ph_2TeBr_2	0.5	8.1	23
$p\text{-}An_2TeBr_2$	0.72	7.8	26
$(p\text{-}EtOC_6H_4)_2TeBr_2$	0.52	7.6	25
$(CH_2)_4TeBr_2$	0.54	7.1	25
$(C_6F_5)_2TeBr_2$	0.73	5.3	25
$p\text{-}An_2TeI_2$	0.51	6.1	26
$p\text{-}Tol_2TeI_2$	0.6	6.3	23

^{a} δ with respect to I/Cu.
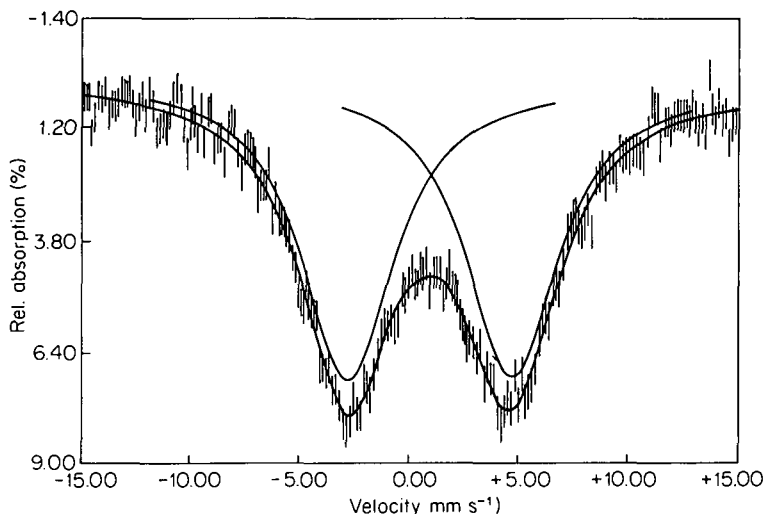
FIGURE 12. ^{125}Te Mössbauer spectrum recorded from $(p\text{-EtOC}_6\text{H}_4)_2\text{TeCl}_2$ at 4.2 K. Reproduced with permission from *Can. J. Chem.*, **54**, 3234 (1976)

halogens. Indeed the structures of all the diorganotellurium(IV) dihalides examined so far are essentially similar despite their various descriptions as distorted trigonal bipyramidal, distorted tetrahedral and distorted octahedral, depending on the significance which has been attributed to intermolecular associations through bridging halogens and the mixing of 5s with p electrons. Low-frequency infrared and Raman spectra of many diaryltellurium(IV) dihalides are also consistent with Ψ-trigonal bipyramidal structures[44].

The chemical isomer shifts of the diorganotellurium(IV) dihalides are more positive than those of the diorganotellurides and are consistent with the halogen ligands removing predominantly p electron density from the tellurium and the conversion of tellurium(II) to tellurium(IV). However, within a given series of dihalides the chemical isomer shift does not change significantly with increasing electronegativity of the halogen. For example, the compounds $p\text{-An}_2\text{TeX}_2$ (X = F, Cl, Br, I; $p\text{-An} = p\text{-MeOC}_6\text{H}_4$) all have the same chemical isomer shifts within the limits of experimental accuracy. On first inspection this may seem unusual, since it would be reasonable to expect that, within a series of dihalides, the chemical isomer shift would change as the electronegativity of the halogens increases from iodine through bromine and chlorine to fluorine such that increasing amounts of 5p electron density are removed from the vicinity of the tellurium nucleus. However, the relatively small value of $\Delta R/R$ for the ^{125}Te Mössbauer transition gives rise to a small range of chemical isomer shifts and it must be appreciated that δ increases[34] by only *ca.* $+0.4\,\text{mm s}^{-1}$ on the removal of one tellurium 5p electron. This, together with the broad natural line width of the ^{125}Te Mössbauer transition and the consequently relatively large errors in δ, means that the chemical isomer shift is not a particularly sensitive probe to small changes in the tellurium 5p orbital populations. It is also possible that the s–p hybrid character of the bonds changes as the electronegativity of the halogens varies and that this effect is also reflected in the consistency of the chemical isomer shift data.

The quadrupole splittings of the dihalides lie in the order F > Cl > Br > I, and the trend is well illustrated by a consideration of the data for the *p*-methoxyphenyl derivatives. The order is consistent with an increasing imbalance in the p orbital electron population about
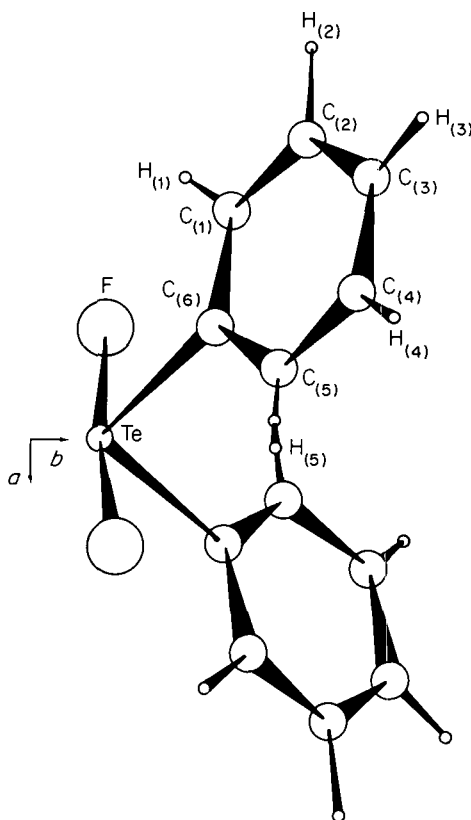
FIGURE 13. Distorted trigonal bipyramidal
structure of diphenyltellurium(IV) difluoride. Re-
produced with permission from *J. Chem. Soc.,
Dalton Trans.*, 2306 (1980)

tellurium as the electronegativity of the halogen increases. The trend may be rationalized if
the bonding in these compounds is envisaged as primarily involving the p-orbitals such
that V_{zz}, the principal component of the electric field gradient tensor, lies along the X—
Te—X bond axis and is positive. Thus in the difluorides the fluorine ligand may be viewed
as removing considerable electron density from the tellurium $5p_z$ orbital leading to an
electron deficit along that axis compared with the xy equatorial plane. As the
electronegativity of the halogen ligand decreases the occupation of the tellurium $5p_z$
orbital would be expected to increase and hence give rise to a decrease in the quadrupole
splitting.

Although the data recorded for most halides show the Mössbauer parameters to be
independent of the nature of the organic group, it is interesting to note the order of
quadrupole splittings in the series of dibromides: $Me_2TeBr_2 > Ph_2TeBr_2 > p\text{-}An_2TeBr_2$
$> (p\text{-}EtOC_6H_4)_2TeBr_2 > (CH_2)_4TeBr_2 > (C_6F_5)_2TeBr_2$. These differences may arise from
variations in the σ donor character of the organic ligands although contributions arising
from changes in the s–p hybrid character of the Te—C bonds, or variations in the degree

of intermolecular bonding from one compound to another, may also be relevant. Hence the smaller quadrupole splitting in $(C_6F_5)_2TeBr_2$ may reasonably be associated with the lower σ donor capacity of the C_6F_5 group compared with the C_6H_5 entity which results in a decreased 5p electron density in the xy plane, and consequently produces a smaller p-orbital imbalance. It is important to note that if V_{zz} lay through the lone pair in the equatorial plane a decrease in donor character of the organic ligand would lead to an increase, rather than a decrease, in quadrupole splitting.

The range of quadrupole splittings recorded from the diorganotellurium(IV) dihalides illustrates the sensitivity of this Mössbauer parameter to changes in the p orbital population with Δ_0, the unit quadrupole splitting for one 5p electron, being estimated[25] to be ca. 12 mm s^{-1}.

Given that X-ray crystallography has shown[43] diphenyltellurium(IV) difluoride to be a Ψ-trigonal bipyramid, and therefore similar to the structures of other diorganotellurium(IV) dihalides, and recalling that the ^{125}Te Mössbauer parameters of the diaryltellurium(IV) dihalides have been found[25,26] to be essentially independent of the nature of the organic group for any specific halide, it is interesting that the Mössbauer parameters recorded[26] from the difluorides are characterized by low chemical isomer
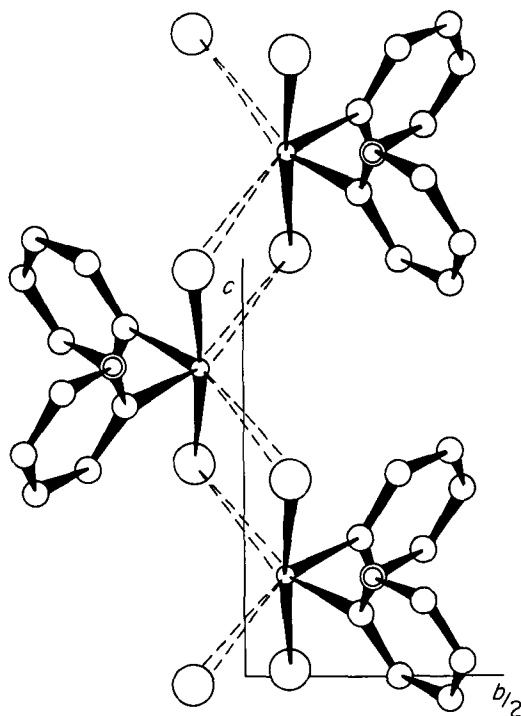
FIGURE 14. Projection of a part of the structure of diphenyltellurium(IV) difluoride down [100] showing the weak intermolecular interactions (hydrogen atoms are not shown for clarity). Reproduced with permission from *J. Chem. Soc., Dalton Trans.*, 2306 (1980)

shifts and large quadrupole splittings. The results are indicative of compounds which, although adopting essentially similar structures to those of the heavier dihalides, have subtle differences in bonding and structure, e.g. the low chemical isomer shifts may indicate a greater stereochemical activity of the 5s electrons in the difluorides. Although the larger quadrupole splittings of the difluorides may easily be associated with the dominating effect of electronic, rather than ligand, asymmetry in these compounds, it is also likely that the larger value of Δ reflects the lower degree of intermolecular association in the difluorides which is achieved by, for example in Ph_2TeF_2, two long bridging contacts from tellurium to fluorine of 3.208 Å (Figure 14)[43]. The ^{125}Te Mössbauer parameters of these compounds may therefore also be considered in terms of the extent of intermolecular association as measured by the ratio of the crystallographically determined tellurium—halogen intermolecular distance to that of the intramolecular distance, i.e. ratios of 1.60:1 for Ph_2TeF_2, 1.39:1 for Me_2TeCl_2, 1.47:1 for Ph_2TeBr_2, 1.41:1 for $(p\text{-}ClC_6H_4)_2TeI_2$ and 1.34:1 for Me_2TeI_2. The difluoride is clearly the dihalide with least intermolecular association. It is also clear that intermolecular association is more significant in alkyl than in the corresponding aryl compounds and this is presumably a reflection of the closer packing in the former species due to the smaller size of the alkyl group. It is also interesting to note that the chemical isomer shifts for the tellurium tetrahalides TeX_4 (X = Cl, Br, or I)[45] and the antimony halides SbX_3 (X = F, Cl, Br or I)[46] are, like those of the diaryltellurium(IV) dihalides, essentially similar within each series of compounds. This relative constancy of s electron density at the tellurium, and antimony, nuclei within a given series of compounds is further evidence that the stereochemical activity of the lone pair and the degree of intermolecular association in the diaryltellurium(IV) dihalides vary in a complex way with changes in the electronegativity of the halogen and in the coordination about the tellurium atom.

Finally, it is pertinent to note that ^{125}Te Mössbauer data have been used[47] to show that the compound dimethyltellurium tetraiodide, Me_2TeI_4, is an adduct of Me_2TeI_2 with iodine linked by intermolecular I—I bonds and weak Te—I bonds and that the compound does not contain tellurium(VI).

2. Organotellurium(IV) trihalides

The ^{125}Te Mössbauer parameters recorded from some aryltellurium(IV) trihalides are collected in Table 4.

TABLE 4. ^{125}Te Mössbauer parameters recorded from some aryltellurium(IV) trihalides at 4.2 K

Compound	$\delta^a \pm 0.08$ (mm s^{-1})	$\Delta \pm 0.1$ (mm s^{-1})	Ref.
p-AnTeF$_3$	0.56	8.6	26
$(p$-EtOC$_6$H$_4)$TeF$_3$	0.6	8.6	26
p-AnTeCl$_3$	0.9	9.2	23
$(p$-EtOC$_6$H$_4)$TeCl$_3$	0.91	9.4	25
PhTeBr$_3$	0.91	7.8	25
$(p$-EtOC$_6$H$_4)$TeBr$_3$	1.0	8.0	23
PhTeI$_3$	0.9	3.9	23
$(p$-EtOC$_6$H$_4)$TeI$_3$	1.0	5.2	23

$^a \delta$ with respect to I/Cu.

Frank J. Berry
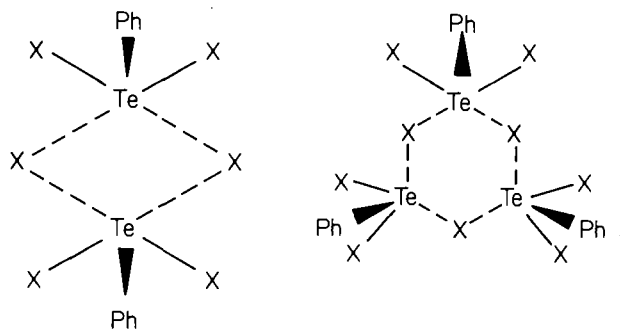
FIGURE 15. Illustration of typical structures found in
aryltellurium(IV) trihalides. Reproduced with permission from *J.
Chem. Soc., Dalton Trans.*, 551 (1972)

The aryltellurium(IV) trihalides have been described[48], on the basis of infrared and
Raman spectroscopic data, as associated structures as shown in Figure 15.

The trihalides $RTeX_3$ (X = Cl, Br, I) have more positive chemical isomer shifts than
those of the corresponding dihalides which are consistent with the removal of predomi-
nantly p electrons by the bonded halogens. However, the chemical isomer shifts of the
difluorides and trifluorides are similar and, in this respect, the data suggest that the
trifluorides are different from the other trihalides.

The quadrupole splittings recorded from the trihalides when X = Cl and Br are the
same, within experimental error, as those from the corresponding dihalides. The data are
consistent with the essentially similar arrangement of atoms about tellurium in these
halides in which the bonding is predominantly concerned with the involvement of
p orbitals. For the iodides the agreement is not as close, although the two measurements
on the triiodides are not in good agreement. For the fluorides the data are consistent
within themselves and show that the quadrupole splittings for the trifluorides are
significantly smaller than those for the difluorides. The data recorded from the trifluorides
are consistent with a more symmetrical environment about the tellurium and, given the
smaller chemical isomer shifts which are indicative of greater stereochemical activity in the
lone pairs, suggest that the coordination about the tellurium atom in the trifluorides must
be significantly different from that in the other trihalides.

3. Alkylaryltellurium(IV) halides

The ^{125}Te Mössbauer parameters recorded[26] from some alkylaryltellurium(IV) iodides
are collected in Table 5. The compound $PhMeTeI_2$ has essentially similar Mössbauer
parameters as $p\text{-}An_2TeI_2$, although a smaller quadrupole splitting than $\alpha\text{-}Me_2TeI_2$
(Table 3). Hence the presence of both alkyl and aryl substituents on the tellurium atom
fails to produce any exceptional changes in the Mössbauer parameters and the results
indicate that the alkyl and aryl ligands have very similar properties.

The compounds $PhMe_2TeI$ and Ph_2MeTeI probably contain the $PhMe_2Te^+$ and
Ph_2MeTe^+ cations, since X-ray crystallography has shown[49] that Ph_3SeCl contains the
Ph_3Se^+ cation and infrared spectroscopy has shown[50] Me_3SeCl to contain Me_3Se^+.
Further, conductance measurements on the compounds R_3TeX (R = Me, Ph; X = Cl,
Br, I) in a variety of solvents, including the compound Ph_2MeTeI, also support the
formulation of these compounds as $R_3Te^+X^-$ in solution[51–53].

TABLE 5. ^{125}Te Mössbauer parameters recorded[26] from some alkylaryl-tellurium(IV) iodides at 4.2 K

Compound	$\delta^a \pm 0.09$ (mm s^{-1})	$\Delta \pm 0.15$ (mm s^{-1})
Ph$_2$MeTeI	0.38	5.6
PhMe$_2$TeI	0.32	5.4
PhMeTeI$_2$	0.56	6.4

$^a \delta$ with respect to I/Cu.

The compounds PhMe$_2$TeI and Ph$_2$MeTeI have, as might be expected, identical Mössbauer parameters, within the limits of experimental accuracy. The small chemical isomer shifts recorded from these compounds are consistent with the presence of R$_3$Te$^+$ cations since the coordination of iodine to the tellurium atom would be expected to lead to a more positive value of δ than those recorded from the diorganotellurides, R$_2$Te, for which $\delta \approx 0.2$ mm s^{-1} (Table 1). It therefore seems that the covalent Te—C bond has significant s character but the removal of s and p electron density is such as to lead to a small net increase in $|\Psi_s(0)|^2$ through deshielding of the remaining 5s electrons at the nucleus. The small quadrupole splittings of these compounds are also consistent with s character in the Te—C bonds since the data imply some p character in the lone pair of electrons on tellurium. Although other possible contributions to the electric field gradient at the tellurium nucleus could arise from inequalities in the Te—C bonds in the Ph$_2$MeTe$^+$ and PhMe$_2$Te$^+$ cations or from the lattice terms, the main contributor to the electric field gradient is probably the lone pair of electrons on the tellurium atom.

It is interesting that the quadrupole splittings of *ca.* 5 mm s^{-1} for Ph$_2$MeTeI and PhMe$_2$TeI correspond to a coupling constant of 350 MHz, assuming $\eta = 0$, whilst the coupling constant for Ph$_3$Sb is 530 MHz[54]. Taking the ratio of the principal components of the field gradient tensor per 5p electron for antimony and tellurium to be[55] 0.87, the ratio of the coupling constants corresponds to a ratio of Q_{gnd} (^{121}Sb)/Q_{ex} (^{125}Te) of 1.7, which is not inconsistent with previous estimates of the magnitude of the quadrupole moments of these two states.[54,56]. Thus the magnitudes of the quadrupole splittings for Ph$_2$MeTeI and PhMe$_2$TeI are consistent with the compounds containing pyramidal Ph$_2$MeTe$^+$ and PhMe$_2$Te$^+$ cations which are isoelectronic and isostructural with Ph$_3$Sb.

4. Bis(organyltelluro)methane halides

The ^{125}Te Mössbauer chemical isomer shifts recorded[36] from the halide derivatives of the bis(organyltelluro)methanes have been found to be more positive than those in the parent telluromethanes (Section III.A.2) corresponding to an increase in the s electron density at the tellurium nucleus, $|\Psi_s(0)|^2$, and consistent with the tellurium—halogen bonds being predominantly p in character such that the removal of 5p electron density from tellurium leads to a deshielding of the 5s electrons from the nucleus and an increase in $|\Psi_s(0)|^2$.

The quadrupole splittings for the halide derivatives reflect the p orbital imbalance resulting from the tellurium—carbon bonds on the one hand and the tellurium—halogen bonds on the other. As the electronegativity of the halogen decreases the covalency of the tellurium—halogen bond increases and the quadrupole splitting decreases. The quadrupole splittings for the CH$_2$[Te(X)$_2$Me]$_2$ compounds[36] are very similar to those of the

corresponding R_2TeX_2 halides[23-26]. However, the quadrupole splittings for the phenyl compounds, $CH_2[Te(X)_2Ph]_2$, are[36] smaller, at least for the chloride and bromide. The origin of this difference may lie in the stereochemical requirements of accommodating the bulky phenyl group and the halogen ligands about the two tellurium atoms in these molecules.

For $CH_2(TeCl_3)_2$ the problem of packing in the solid state may be even more marked. The organotellurium(IV) trichlorides[23,25,26] generally have chemical isomer shifts of ca. 0.9 mm s^{-1} and quadrupole splittings of ca. 9.0 mm s^{-1}. However, $CH_2(TeCl_3)_2$ has[36] Mössbauer parameters δ 0.9 mm s^{-1}, Δ 7.6 mm s^{-1}. It would seem that the polymeric nature of the $RTeCl_3$ compounds involving bridging Cl—Te bonds and tellurium bonded to four chlorines roughly in planar coordination and the Te—R bond directed out of the plane may be difficult to achieve in $CH_2(TeCl_3)_2$ where the two tellurium atoms are separated only by a methylene group.

5. Bis(trifluoromethyl)- and bis(pentafluorophenyl)-tellurium(IV) dihalides

The ^{125}Te Mössbauer parameters recorded from[35] the bis(trifluoromethyl)- and bis(pentafluorophenyl)-tellurium(IV) dihalides are collected in Table 6. The dihalides of $(CF_3)_2Te$ and $(C_6F_5)_2Te$ exhibit quadrupole splittings which are systematically smaller than those generally observed for dialkyl- and diaryl-tellurium dihalides. For example, $(C_6F_5)_2TeF_2$ has a quadrupole splitting of 8.8 mm s^{-1} in comparison with 10.4 mm s^{-1} recorded for Ph_2TeF_2. Similarly, the quadrupole splittings of $(C_6F_5)_2TeCl_2$ and $(CF_3)_2TeCl_2$, Δ 6.9 mm s^{-1}, are significantly smaller than the corresponding parameter for Ph_2TeCl_2 and Me_2TeCl_2, Δ 9.25 mm s^{-1}. Within each series of dihalides the quadrupole splittings follow a simple trend F > Cl > Br. These compounds, like the diaryltellurium(IV) dihalides previously discussed, can readily be interpreted in terms of the Ψ-trigonal bipyramidal structures where the quadrupole splittings reflect the p orbital imbalance between the X—Te—X axial linkage and the Te—C bonds, and the lone pair in the equatorial plane. As the electronegativity of the organic ligand increases this p orbital imbalance undergoes a consequent decrease consistent with the smaller quadrupole splitting in $(C_6F_5)_2TeF_2$ as compared with that recorded from $(C_6H_5)_2TeF_2$ and consistent with a greater removal of electron density from the tellurium in the equatorial plane by the C_6F_5 ligand.

TABLE 6. ^{125}Te Mössbauer parameters recorded[35] from bis(trifluoromethyl)- and bis(pentafluorophenyl)-tellurium(IV) dihalides at 4.2 K

Compound	$\delta^a \pm 0.08$ (mm s^{-1})	$\Delta \pm 0.08$ (mm s^{-1})
$(CF_3)_2Te$	-0.14	14.02
$(CF_3)_2TeF_2$	$+0.59$	7.36
$(CF_3)_2TeCl_2$	$+0.58$	6.89
$(CF_3)_2TeBr_2$	$+0.64$	5.60
$(C_6F_5)_2Te$	$+0.14$	13.40
$(C_6F_5)_2TeFe_2$	$+0.45$	8.78
$(C_6F_5)_2TeCl_2$	$+0.59$	6.91
$(C_6F_5)_2TeBr_2$	$+0.59$	5.38

^{a} δ relative to I/Cu.

The chemical isomer shifts recorded from the $(CF_3)_2TeX_2$ and $(C_6F_5)_2TeX_2$ compounds are all similar and more positive than those of the parent tellurides and, as observed in the other diaryltellurium(IV)dihalides, are consistent with the removal of predominantly p electron density from tellurium in the X—Te—X linkage leading to a deshielding of the 5s electrons from the nucleus.

6. Tetrahaloaryltellurates

The tetrahaloaryltellurate anions and a number of mixed tetrahaloaryltellurate anions have recently been examined[57]. The parent tetrahalotellurate anions, $RTeX_4^-$ ($R = p$-$C_2H_5OC_6H_4^-$; X = Cl, Br or I), all give quadrupole split Mössbauer spectra. The electric field gradient in these ions, which are square pyramidal with the organic ligand occupying the axial position[58] with bonding to the halogen ligands being viewed as three-centre, four-electron bonds involving only tellurium 5p orbitals, may be considered as deriving from p orbital imbalance between the z-axis, as defined by the Te—C bond, and the x—y plane in which the four halogen ligands lie. This p orbital imbalance arises because of the difference in the ionicity of the Te—C and Te—halogen bonds and also because of the significant tellurium s character associated with the Te—C bond, which confers significant p character on the lone pair. The stereochemically active lone pair is then viewed as occupying the sixth coordinate position *trans* to the aryl group. The interpretation is supported by the observation that the quadrupole splittings decrease in the order $RTeCl_4^- > RTeBr_4^- > RTeI_4^-$. As the electronegativity of the halogen ligands decreases, the removal of p electron density from the tellurium in the x–y plane decreases and the quadrupole splittings likewise decrease. The isomer shift of $RTeCl_4^-$ is significantly
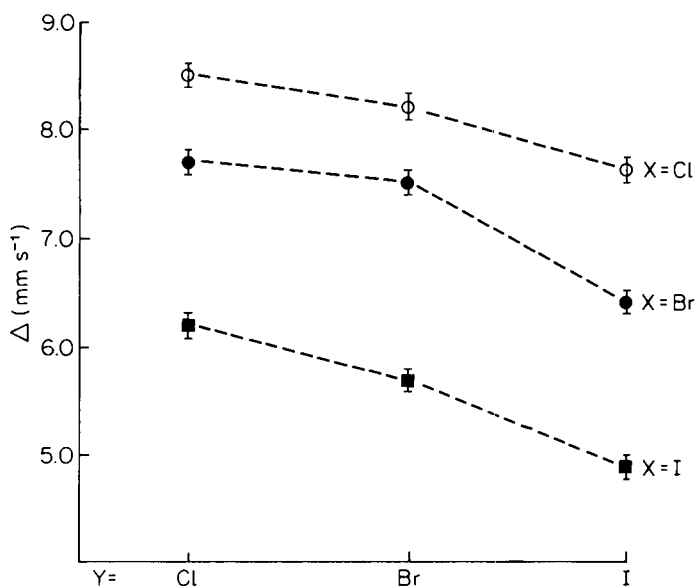
FIGURE 16. Quadrupole splittings recorded from ⌀ $RTeCl_3Y$, ⬥ $RTeBr_3Y$ and ⬢ $RTeI_3Y$ where Y = Cl, Br or I. Reproduced with permission from *Can. J. Chem.*, **59**, 913 (1981)

smaller than that of $TeCl_6{}^{2-}$ or $TeCl_5{}^-$, and this reflects the marked decrease in nuclear s electron density as a result of removal of tellurium 5s electrons into the Te—C bond.

In the mixed tetrahaloaryltellurates $RTeX_3Y$, where X = Cl and Y = Cl, Br or I, Δ decreases in the series Y = Cl > Br > I. For the bromide series, i.e. X = Br, Y = Cl, Br or I, the Δ values again decrease in the series Y = Cl > Br > I and a similar trend is again observed for the iodides, i.e. $RTeI_3Cl^- > RTeI_3Br^- > RTeI_4^-$ (Figure 16). These trends again reflect a decrease in the removal of p orbital electron density from the tellurium in the $x-y$ plane as the electronegativity of the halogen ligand, Y, decreases. It would appear that in these compounds Δ is a simple additive property of the ligands attached to tellurium. To a first approximation, and ignoring any asymmetry in the $RTeX_3Y$ anions, the difference in quadrupole splitting between $RTeCl_4^-$ and $RTeBr_4^-$ should be twice that between $RTeCl_3Br^-$ and $RTeClBr_3^-$. This relationship has been confirmed[57].

The findings are consistent with the application of an additivity model to rationalise the values of the quadrupole splittings in the organotellurides and organotellurium dihalides and trihalides, as will be discussed later (Section 8).

7. Diaryltellurium(IV) dicarboxylates

The ^{125}Te Mössbauer parameters recorded[26] from some diaryltellurium(IV) diacetates and dibenzoates are collected in Table 7 and a representative spectrum is illustrated in Figure 17.

The infrared spectra recorded[59] from the diaryltellurium(IV) dicarboxylates have been interpreted in terms of Ψ-trigonal bipyramidal structures in which the carboxylate ligands occupy the *trans* axial positions. The ^{125}Te Mössbauer parameters recorded from these compounds are generally consistent with such a description with the chemical isomer shifts and quadrupole splittings being essentially similar to the Mössbauer parameters recorded from the diaryltellurium(IV) dichlorides. However, the phenyl derivatives exhibit much smaller quadrupole splittings than the other compounds and in this respect it is interesting that the infrared spectrum of $(p\text{-}EtOC_6H_4)_2Te(OCOMe)_2$ has been found to be more complex than that of $Ph_2Te(OCOMe)_2$, suggesting the possible presence of both uni- and bi-dentate carboxylate ligands in the former case and only unidentate ligands in the latter. The different quadrupole splittings of $p\text{-}An_2Te(OCOMe)_2$ and $Ph_2Te(OCOMe)_2$ are certainly consistent with a different environment about the tellurium atom in these two compounds.

The compound $Ph_2Te(OCOPh)_2$ was found to give a complex infrared spectrum similar

TABLE 7. ^{125}Te Mössbauer parameters recorded[26] from some diaryltellurium(IV) dicarboxylates at 4.2 K

Compound	$\delta^a \pm 0.07$ (mm s^{-1})	$\Delta \pm 0.1$ (mm s^{-1})
$Ph_2Te(OCOMe)_2$	0.59	8.0
$p\text{-}An_2Te(OCOMe)_2$	0.50	9.3
$p\text{-}Tol_2Te(OCOMe)_2$	0.60	9.5
$Ph_2Te(OCOPh)_2$	0.76	8.2
$p\text{-}An_2Te(OCOPh)_2$	0.52	9.5
$(p\text{-}EtOC_6H_4)_2Te(OCOPh)_2$	0.56	9.4

^{a} δ with respect to I/Cu.
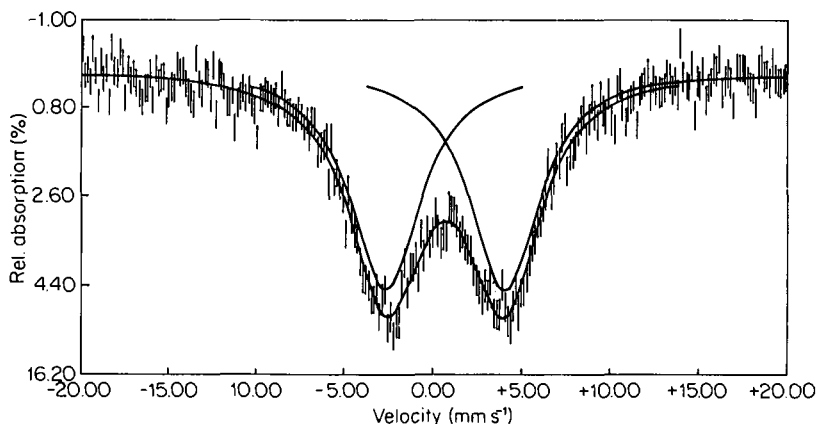
FIGURE 17. ^{125}Te Mössbauer spectrum recorded from $Ph_2Te(OCOMe)_2$. Reproduced with permission from *Can. J. Chem.*, **54**, 3737 (1976)

to that of $(p\text{-}EtOC_6H_4)_2Te(OCOMe)_2$ rather than that of the diphenyltellurium diacetate. However, the Mössbauer data suggest that the tellurium environments in the diphenyltellurium diacetate and dibenzoate are very similar. Thus the infrared and Mössbauer data are not wholly consistent but both suggest that the structures of the diacetates and dibenzoates may show subtle differences with changes in the nature of the aryl ligands. A fuller interpretation of the Mössbauer data from these compounds must await structural studies on the carboxylates.

8. Additivity model for the quadrupole splittings

The ^{125}Te Mössbauer quadrupole splittings recorded from the diorganotellurium(IV) dihalides and organotellurium(IV) trihalides have been found[25] to be amenable to consideration within the theory of Townes and Dailey. By considering the dihalides to be trigonal bipyramidal structures with nominally sp^2 hybrids in the equatorial plane and axial pd hybrids defining the z-axis,

$$\frac{e^2qQ}{e^2q_0Q}\left(1-\frac{\eta}{3}\right) = U_x - U_C$$

and

$$\frac{e^2qQ}{e^2q_0Q}\eta = \tfrac{3}{2}(U_C - U_2)(1-\cot^2{}_y)$$

where U_x, U_C and U_2 are the Te—X, Te—C and non-bonding orbital populations, respectively, η is the asymmetry parameter and 2_y is the C—Te—C bond angle. This equation is applicable only if $(1-\cot^2{}_y)$ is small, i.e. if the lone pair is predominantly 5s in character, which appears to be valid[25] for example in Me_2TeCl_2 ($2_y = 98°$), Ph_2TeBr_2 ($2_y = 94°$) and $\alpha\text{-}Me_2TeI_2$ ($2_y = 91 - 97°$). For large values of 2_y, approaching 120°, and for the U_x and U_C values observed in these compounds, V_{zz} would lie through the lone pair. By assuming[25] that the bonding occurs only through tellurium 5p orbitals ($2_y = 90°$), then

$\eta = 0$ and

$$\frac{e^2 qQ}{e^2 q_0 Q} = -U_p = U_{X-Te-X} - U_c$$

i.e.

$$U_p = U_C - U_{X-Te-X}$$

The X—Te—X linkage would be viewed as a three-centre, four-electron bond.
If $2_y = 120°$ and V_{zz} lies through the lone pair, it may be shown[25] that

$$U_p = -\frac{4}{3} + \frac{U_C}{6} + \frac{U_{X-Te-X}}{2}$$

$$\eta = \frac{3}{2} \frac{(U_X - U_C)}{U_p}$$

In the trihalides, assuming the structure in Figure 15 and the presence of $sp^3 d^2$ hybrids, the application[25] of the Townes and Dailey theory predicts

$$\frac{e^2 qQ}{e^2 q_0 Q} = -U_X + \left(1 + \frac{U_C}{2}\right)$$

$$\eta = 0$$

If the bonding is assumed to be pure p in character with the $5s^2$ electrons constituting the lone pair,

$$U_p = U_{X-Te-X} - U_C$$

Thus, if the Te—C and X—Te—X bonds each have predominantly p character and constant covalent character in the dihalides and the trihalides, then Δ should have the same magnitude but opposite signs in the two cases. Since it would be expected that $U_C > U_{X-Te-X}$, then Δ should be negative in the dihalides and positive in the trihalides. The experimental results (Tables 3 and 4) show that for the chlorides, bromides and iodides the quadrupole splittings for the dihalides are of similar magnitude to those of the trihalides but the results give no indication of the sign of Δ.

The application of the additivity model as described[25] suggests that, where the model is applicable, the X—Te—X bond has the same covalent character whether X is terminal or bridging. The analysis also suggests that, in those instances where the dihalides and trihalides have the same magnitude for Δ, intermolecular bonding in the dihalides is not a major factor in determining Δ. The observation[25] that $(p\text{-EtOC}_6\text{H}_4)\text{TeCl}_3$ and $(\text{pyH})^+$ $(p\text{-EtOC}_6\text{H}_4)\text{TeCl}_4^-$ have the same Δ, within the errors, supports the assumption that the field gradient derives from the valence shell orbital populations and that the lattice terms are not important. Thus, for the compounds $R_2\text{Te}$, $R_2\text{TeX}_2$ and $R\text{TeX}_3$ the quadrupole splittings appear to be an additive property of the ligands.

The ^{125}Te Mössbauer parameters recorded[25] from the adducts of p-AnTeCl$_3$ with pyridine and tetramethylthiourea (tmtu), together with those from tellurium tetrachloride with pyridine, provide a further test of the additivity model for the ^{125}Te Mössbauer quadrupole splittings. The starting point in such an analysis is the Te—C bond orbital population obtained from the tellurides. From the quadrupole splittings recorded from the dichlorides it is then possible to estimate $U_{Cl-Te-Cl}$ and, from Δ recorded from TeCl$_4$(py), U_{py}. These data, together with the orbital population[34] of the Te—S bond, $U_S = 0.73$, give orbital populations as summarized in Table 8 and leads to the conclusion that $U_C = 1.11$, $U_{Cl-Te-Cl} = 0.35$ and $U_{py} = 0.73$.

TABLE 8. Orbital populations derived[25,34] using the Townes and Dailey theory

Compound	Δ^a (mm s^{-1})	Orbital populations			
		$U_p{}^b$	$U_x{}^c$	$U_y{}^c$	$U_z{}^c$
Ar$_2$Te	(+)10.6	− 0.89	1.11	1.11	[2.0]
p-An$_2$TeCl$_2$	(−) 9.1	+ 0.76	[1.11]	[1.11]	0.35
p-AnTeCl$_3$	(+) 9.2	− 0.76	0.35	0.35	[1.11]
TeCl$_4$.py	(+) 4.5	− 0.38	[0.35]	[0.35]	0.73
Te(thiourea)$_2^{2+}$	(+)15.6	− 1.30	0.70	0.70	[2.0]

^{a}The signs of Δ assumed are shown in parentheses.
$^b U_p = -e^2Q/e^2q_0Q$ and $e^2qQ = +24$ mm s^{-1}.
^{c}The values shown in brackets were assumed in any one case.

TABLE 9. Predicted and observed quadrupole splittings[25]

Compound	Δ(mm s^{-1})	
	Observed	Calculated
p-AnTeCl$_3$.py	7.6	(+)7.3
p-AnTeCl$_3$.tmtu	7.9	(+)7.3

TABLE 10 Bound orbital populations, U_L, for different ligands[25,26]

Estimator	Parameter	U_L
Ph$_2$TeCl$_2$	$U_{Cl-Te-Cl}$	0.4
Ph$_2$TeBr$_2$	$U_{Br-Te-Br}$	0.5
p-Tol$_2$TeI$_2$	U_{I-Te-I}	0.6
Ph$_2$Te(OCOMe)$_2$	$U_{O\ Te\ O}$	0.4
p-An$_2$Te(OCOMe)$_2$	U_{O-Te-O}	0.3
Ph$_2$Te(OCOPh)$_2$	U_{O-Te-O}	0.4
p-An$_2$Te(OCOPh)$_2$	U_{O-Te-O}	0.3
TeCl$_4$(py)	U_{py}	0.7
Te(thiourea)$_2^{2+}$	U_S	0.7
(C$_6$F$_5$)$_2$TeBr$_2$	$U_{C_6F_5}$	0.8
Tellurides	U_C	1.1

The values of U were used[25] to estimate values of Δ for p-AnTeCl$_3$(py) and p-AnTeCl$_3$(tmtu) and the results found to compare well with the experimentally determined values of Δ as summarized in Table 9.

The orbital populations for a number of ligands derived by these methods are summarized in Table 10. Given the many assumptions implicit in the analysis of the Δ values and the fact that e^2q_0Q is not accurately known, the U values have relative rather than absolute significance.

9. Colour in organotellurium(IV) halides

Many organotellurium compounds are highly coloured and, on the basis of structural data, the occurrence of colour has been associated with the overlap of orbitals of intermolecularly associated heavy atoms[60]. Using these concepts the [125]Te Mössbauer parameters recorded from a variety of organotellurium compounds have been used[27] to examine the occurrence of colour in terms of the population of low energy conductance bands by non-bonding electrons.

C. Heterocyclic Tellurium Compounds

Two [125]Te Mössbauer studies of organotellurium heterocycles have appeared in recent years[61,62]. In these compounds the bond lengths and bond angles are largely determined by the constraint of accommodating the tellurium atom in the ring.

1. Cyclic tellurides

The structural formulae of the cyclic tellurides (a) dibenzotellurophene ($C_{12}H_8Te$), (b) phenoxtellurine ($C_{12}H_8OTe$), (c) tellurium acetylacetonate ($C_5H_6O_2Te$) and (d) some substituted tellurium(II) acetylacetonates are illustrated in Figure 18. The [125]Te Mössbauer parameters are recorded in Table 11 and some crystal structure data, which are compared with that of $(p\text{-Tol})_2Te$, are collected in Table 12. In the relatively simple molecules (a)–(c) the C—Te—C bond angles vary slightly and some variation is observed in the bond lengths. The [125]Te Mössbauer quadrupole splitting data, and possibly the chemical isomer shift data, show small differences from one compound to another but, given the variation in the C—Te bond lengths and hence the tellurium bond orbital populations, a simple dependence of Δ on the C—Te—C bond angle θ is not to be expected. It is interesting, however, that both $C_{12}H_8OTe$ and $C_5H_6O_2Te$, for which $\theta \approx 90°$, exhibit larger values of δ and Δ than the simple diorganotellurides (Table 1). The results are consistent with a greater p character in the Te—C bonds and a greater lone pair character for the tellurium 5s electrons. The inductive effect of the oxygen atom in $C_{12}H_8OTe$ and of the carbonyl group in $C_5H_6O_2Te$ may be important and influential factors in influencing Δ for these compounds.

(1) $R^1 = R^2 = H, R^3 = R^4 = CH_3$
(2) $R^1 = R^2 = CH_3, R^3 = R^4 = H$
(3) $R^1 = R^2 = R^3 = R^4 = H$
(4) $R^1 = R^2 = R^3 = CH_3, R^4 = H$
(5) $R^1 = R^3 = CH_3, R^2 = R^4 = H$

(a)   (b)   (c)   (d)
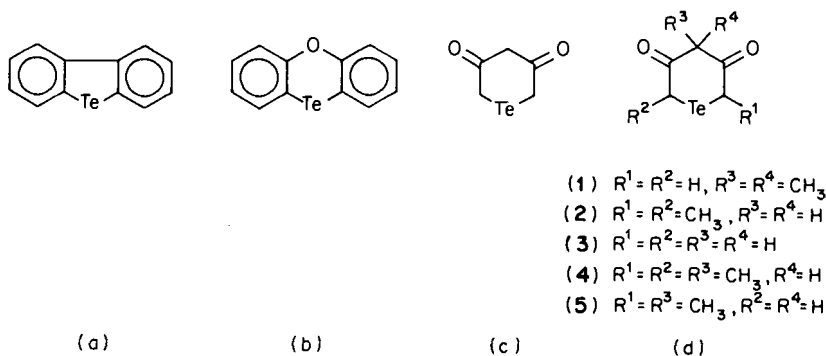
FIGURE 18. Structural formulae of the cyclic tellurides (a) dibenzotellurophene ($C_{12}H_8Te$), (b) phenoxtellurine ($C_{12}H_8OTe$) (c) tellurium acetylacetonate ($C_5H_6O_2Te$) and (d) substituted tellurium(II) acetylacetonates

TABLE 11. ^{125}Te Mössbauer parameters recorded from some cyclic tellurides at 4.2 K

Compound (see Figure 18)		$\delta^a \pm 0.08$ (mm s^{-1})	$\Delta \pm 0.2$ (mm s^{-1})	Ref.
(a)	$C_{12}H_8Te$	0.14	9.3	61
(b)	$C_{12}H_8OTe$	0.24	11.2	61
(c)	$C_5H_6O_2Te$	0.39	11.7	61
(d) (1)	$C_7H_{10}O_2Te$	0.70	12.77	62
(2)	$C_7H_{10}O_2Te$	0.39	10.99	62
(3)	$C_5H_6O_2Te$	0.42	9.81	62
(4)	$C_8H_{12}O_2Te$	0.47	10.58	62
(5)	$C_7H_{10}O_2Te$	0.41	11.25	62

$^a \delta$ with respect to I/Cu.

TABLE 12. Crystallographic data for some tellurides

Compound	C—Te—C bond angle (°)	C—Te bond length (Å)	Ref.
$(p\text{-Tol})_2Te$	101	2.05 (5)	31
(a)^a $C_{12}H_8Te$	81.7(2)	2.087(5)	63
(b)^a $C_{12}H_8OTe$	89.4(3)	2.10(9)	64
(c)^a $C_5H_6O_2Te$	89.5(4)	2.17(1)	65

^{a} See Figure 18.

The C—Te—C bond angle of 81.7° in $C_{12}H_8Te$ implies that a simple combination of s and p orbitals cannot be used to rationalize the bonding about tellurium. The quadrupole splitting for $C_{12}H_8Te$ is smaller than that of other cyclic tellurides and may indicate significant π delocalization around the essentially planar five-membered ring.

The ^{125}Te Mössbauer parameters recorded for all the tellurium(II) acetylacetonates except 1 (Figure 18) fall within a narrow range and reflect the similar structures[65-69] of compounds 2–5 where the C—Te—C bond angles of ca. 90° suggest that the bonding occurs primarily through the p orbitals. The main structural difference between these compounds is the smaller[70] C—Te—C bond angle of 86.4° in 1 which cannot be simply rationalised in terms of the tellurium s and p orbitals. On first inspection, the small bond angle may reasonably be associated with enhanced repulsion by the lone pair of electrons on the tellurium atom. Both Mössbauer parameters for this compound are larger than those recorded from compounds 2–5 and are indicative of a relatively higher s electron density at the tellurium nucleus and a larger p orbital imbalance around the tellurium atom. Clearly it is difficult to correlate the crystallographically determined small bond angle and the proposed high stereochemical activity of the tellurium lone pair with the Mössbauer parameters which imply that the lone pair is 5s in character and contributes significantly to a high electron density at the tellurium nucleus. Indeed, it would be reasonable to expect that any significant stereochemical activity of the 5s lone pair would be reflected in a smaller chemical isomer shift in 1 compared with 2–5. However, it is interesting that the intermolecular packing of the tellurium(II) acetylacetonates[66-69] involves the yellow materials 2–5 having intermolecular Te···Te associations of ca. 4 Å

which give rise to polymeric chains of tellurium atoms. The methyl groups in these compounds are equatorial to the heterocyclic ring. The colour of 1 is less intense and, although the molecular structure is essentially the same, there is no evidence[70] of short intermolecular Te $\cdots$ Te associations as in 2–5. It would appear that one of the two methyl groups which occupy the positions designated by R[3] and R[4] in 1 is axial to the heterocyclic ring and sterically prevents the formation of short intermolecular Te $\cdots$ Te associations.

The significance of such close intermolecular distances in coloured tellurium compounds has been noted during structural investigations in the past[60] and it has also been suggested[71–76] that colour in other p block elements, particularly those of tin and antimony, which also give lower than expected Mössbauer chemical isomer shifts, may be explained by the direct population of low-energy conduction bands by non-bonding valence electrons. It therefore seems that the low ^{125}Te Mössbauer chemical isomer shifts in the yellow associated tellurium(II) acetylacetonates 2–5 may be indicative of the population by $5s^2$ non-bonding tellurium electrons of conductance bands formed by overlap of orbitals on intermolecularly associated tellurium atoms. The donation and movement of these non-bonding valence electrons in the conductance bands may give rise to the colour, and the consequent reduction of the 5s electron density at the tellurium nucleus is reflected in the chemical isomer shift which is smaller than expected. The smaller quadrupole splittings in the tellurium(II) acetylacetonate compounds 2–5, compared with unassociated compound 1, presumably reflects the higher degree of coordination and symmetry of the tellurium atom in the associated species.

Hence the delocalization of electrons into a π-bonded aromatic ring or into a low-energy conductance band formed by overlap of orbitals on intermolecularly associated heavy atoms may be as important in explaining the ^{125}Te Mössbauer parameters of heterocyclic tellurium compounds as is a consideration of the bond angle alone.

2. Heterocyclic tellurium dichlorides

The heterocyclic tellurium dichlorides, with structural formulae as illustrated in Figure 19, (a) $C_{12}H_8TeCl_2$, (b) $C_{12}H_8OTeCl_2$ and (c) $C_5H_6O_2TeCl_2$, give the ^{125}Te Mössbauer parameters summarized in Table 13. The crystal structure[65] of $C_5H_6O_2TeCl_2$ shows the tellurium to be in a Ψ-trigonal bipyramidal geometry with the halogen ligands in *trans* axial positions. The dihalides exhibit more positive chemical isomer shifts than the parent tellurides, the halogen ligands removing predominantly p electron density from the tellurium, and the values of δ are comparable to those recorded from the diaryltellurium(IV) dichlorides (Table 3). However, the quadrupole splittings recorded from the cyclic dichlorides are all significantly smaller which, although partly arising from differences in the asymmetry parameter, η, may be better understood in terms of the additivity model. According to these principles, and the appropriate discussion in Sections
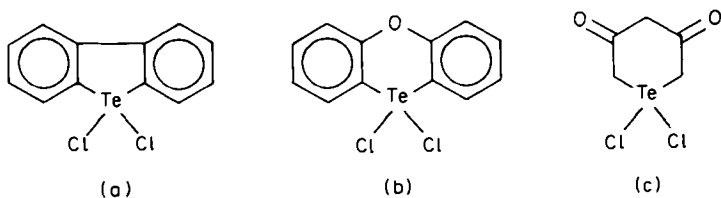
FIGURE 19. Structural formulae of (a) $C_{12}H_8TeCl_2$, (b) $C_{12}H_8OTeCl_2$ and (c) $C_5H_6O_2TeCl_2$

TABLE 13. ^{125}Te Mössbauer parameters re-
corded[61] from some heterocyclic tellurium
dichlorides at 4.2 K

Compound (see Figure 19)		$\delta^a \pm 0.08$ (mm s^{-1})	$\Delta \pm 0.2$ (mm s^{-1})
(a)	$C_{12}H_8TeCl_2$	0.75	8.1
(b)	$C_{12}H_8OTeCl_2$	0.70	8.0
(c)	$C_5H_6O_2TeCl_2$	0.71	8.2

^{a} δ relative to I/Cu.

III.A and III.B, it is reasonable to expect the cyclic dihalides to have quadrupole splittings which are smaller than those recorded from the parent tellurides.

It is also interesting that the cyclic dinitrate related to Figure 19b of composition $C_{12}H_8OTe(NO_3)_2$ gave[61] ^{125}Te Mössbauer parameters of $\delta\,0.56$ mm s^{-1} and $\Delta\,9.3$ mm s^{-1}, in which the large quadrupole splitting is comparable to that recorded from the dichloride and is consistent with the Ψ-trigonal bipyramidal array about tellurium in which the nitrate groups adopt the *trans* axial positions[64].

D. Organotellurium Ligands

The use of Mössbauer spectroscopy to examine the ligand properties of various species including tellurium has recently been reviewed[77]. A survey of the chemical isomer shift and quadrupole splitting data recorded from several metal complexes of $(p\text{-EtOC}_6H_4)_2Te$ showed that the $R_2Te \rightarrow M$ donation involves primarily the tellurium 5p orbital and that changes in chemical isomer shift are due to deshielding.

It is also interesting that whereas carbonyl groups on a metal are generally able to enhance the Lewis acidity of the metal centre allowing a greater degree of ligand-to-metal donation, the trend does not appear to hold for R_2Te ligands from which carbonyl systems apparently remove ca. 0.33 electrons whilst non-carbonyl acceptors take ca. 0.4–0.6 electrons. It is possible that the presence of two lone pairs on tellurium, only one of which is involved in coordination, is significant such that R_2Te can be regarded as a potential π-donor ligand.

It is relevant to record the examination by ^{125}Te Mössbauer spectroscopy of complexes of di-(ethoxyphenyl) telluride, $(p\text{-EtOC}_6H_4)_2Te$, with various metal halides[78]. By assuming that the quadrupole interaction is dominated by an imbalance in the tellurium p-orbital population the quadrupole splitting data were interpreted in terms of the donor–acceptor interaction of the telluride with the metal halides and used to show that the order of Lewis acidity towards $(p\text{-EtOC}_6H_4)_2Te$ is $Hg(II) > Pt(II) > Pd(II) > Cu(I)$. In a subsequent report[79] some diorganotelluride–mercury(II) complexes of the type $R_2Te.HgX_2$ ($R = Ph$, $EtOC_6H_4$, $X = Cl$, Br, I) were examined by ^{125}Te Mössbauer, infrared and Raman spectroscopy. The results indicated that the tellurium atom in these complexes adopts a similar environment to that of tellurium in a triorganotellurium salt and the complexes were described by the formulation $[R_2Te^+ \text{—HgX}]X^-$. The structure of $(Ph_2Te).HgI_2$ was subsequently investigated[80] by X-ray crystallography and found to exhibit a novel tetrameric structure involving two different types of iodine bridges.

In another report[81], a new series of copper(I) derivatives of organotellurols of composition RTeCu, where R is an alkyl or aryl group, were described and the ^{125}Te Mössbauer parameters interpreted in terms of only limited electron transfer from tellurium to copper. A series of diorganoditelluride complexes of copper(I) halides of

composition $R_2Te_2.CuX$, where R = alkyl or aryl and X = Cl, Br or I, gave[81] Mössbauer data which indicated the tellurium atoms to be only weakly coordinated to copper with the halide ligands involved in intermolecular bridging. The complexes of some diorganoditel-lurides with mercury(II) halides have also been investigated[79] and the compounds were found to correspond to two distinct classes of complex. The majority, of stoichiometry $RTeHgX_2$ or $R_2Te_2HgX_2$, gave ^{125}Te Mössbauer parameters which indicated the presence of a single trigonally coordinated tellurium site. The second group gave Mössbauer parameters indicative of two-coordinate tellurium in complexes of the type $R_2Te_2.HgX_2$ where both the Te—Te and the Hg—X bonds remain essentially similar to those present in the reactants.

Some other organotellurium–mercury(II) complexes of the type α-$Me_2TeI_2.HgBr_2$, $Ph_2Hg.(Me_2TeI_2)_2$, $(p$-$EtOC_6H_4Te)_2.Hg$ and p-$EtOC_6H_4Te.HgCl$ have also been examined[79] and the Mössbauer data interpreted in terms of the possible structures of the complexes.

E. Compounds with Tellurium to Metal Bonds

Several Mössbauer studies of compounds containing tellurium–tin bonds have appeared and are particularly important because they allow the examination of the compounds by both ^{125}Te and ^{119}Sn Mössbauer spectroscopy.

Some triphenylstannyl(aryl) tellurides prepared by the reaction of triphenyltin hydride with various diaryl ditellurides were amongst the first compounds to be studied by both ^{125}Te and ^{119}Sn Mössbauer spectroscopy[82]. The ^{119}Sn chemical isomer shifts for Ph_3SnXPh, X = O, S, Se or Te, were found to follow the order $Ph_4Sn < Ph_3SnOPh < Ph_3SnSPh \approx Ph_3SnSePh \approx Ph_3SnTePh$, thereby demonstrating a greater p character in the Sn—XPh bonds than in the Sn—Ph bonds. However, the Sn—XPh bonds must retain significant s character and the relative chemical isomer shifts of Ph_3Sn—OPh and Ph_3Sn—TePh suggested the presence of greater s electron density and enhanced covalency of the S—Te bond relative to the Sn—O bond. The ^{125}Te Mössbauer chemical isomer shifts recorded from the compounds Ph_3SnTeR, R = Ph, p-An, p-$EtOC_6H_4$, were less positive than those of the diaryl ditellurides, R_2Te_2, suggesting a greater occupancy of the tellurium 5p orbital in the Sn—Te bond than in the Te—Te bond. The smaller ^{125}Te quadrupole splittings for the triphenylstannyl compounds were consistent with this model. Hence both the ^{119}Sn and ^{125}Te Mössbauer data are consistent with the donation of electron density from the tin to the tellurium and give no evidence for any significant $5p\pi$ Te $\rightarrow 5d\pi$ Sn overlap such that only an s–p bonding model gives a self-consistent explanation of the combined ^{119}Sn and ^{125}Te Mössbauer data.

A ^{119}Sn and ^{125}Te Mössbauer and NMR study of some Group IV organotellurides is another example of the successful combined use of two Mössbauer isotopes in chemical investigations[83]. In these compounds of composition$(R_3X)_2Te$, R = Me, X = C, Si, Ge and Sn; R = Ph, X = Ge and Sn; R_3MTePh, R = Me, X = Si, Ge and Sn; R = Ph, X = Ge, Sn, Pb; $R_2Sn(TePh)_2$, R = Me and t-Bu; and the cyclic compounds $(Me_2SnTe)_3$ $(Me_2Sn)_3Te_2$ and $(t$-$Bu_2SnTe)_2$, the ^{119}Sn and ^{125}Te Mössbauer and NMR data have provided evidence that there is little transmission of bonding effects through the tin—tellurium bond as the chemical environments about the tin or the tellurium atoms are changed.

In a recent study[84] of some tellurium- and transition metal-containing compounds the ^{125}Te Mössbauer spectra were recorded from $(\mu$-$Te)[V(CO)_3$diphos$]_2$, where diphos is ethylenebis(diphenylphosphane), $(\mu_3$-$Te)[Mn(CO)_2(\eta^5$-$C_5H_5)]_3$, $(\mu$-$Te)[Mn(CO)_2(\eta^5$-$C_5Me_5]_2$, $(\mu,\eta^2$-$TeCH_2)[Mn(CO)_2(\eta^5$-$C_5Me_5)]_2$ and $(\mu$-$Te)[Cr(CO)_3(\eta^5$-$C_5H_5)]_2$. The chemical isomer shifts, δ, were found to be essentially similar and independent of whether the tellurium is considered as acting as a six-, four- or two-electron donor. The first three

compounds gave very small quadrupole splittings, which were interpreted in terms of multiple bond character in the tellurium—metal bonds.

F. Tellurium-containing Charge-transfer Complexes

In a study[85] of the reaction of NaTeR, R = p-EtOC$_6$H$_4$ or Ph, with organic dihalides, $(CH_2)_nX_2$, $n = 1$–4, which gives tellurium salts when $n = 3$ or 4 and X = Cl or Br, some charge-transfer complexes of stoichiometry $(RTe)_2CH_2.CH_2X_2$ were formed when $n = 1$ and X = Br or I. The Mössbauer spectrum recorded from the complex [(p-EtOC$_6$H$_4$)Te]$_2$CH$_2$.CH$_2$Br$_2$ was dissimilar to those recorded from the telluronium salts. The more positive chemical isomer shift was associated with a greater s electron density at tellurium as a result of the withdrawal of 5p electron density. The quadrupole splitting was smaller than that recorded from simple tellurides (Table 1), but larger than that recorded from telluronium salts. The description of the material, which also gave a broad ESR signal centred on $g = 2.18$, as a charge-transfer complex is consistent with the Mössbauer data since the transfer of electron density from the spare-pair p orbital on tellurium would decrease the p orbital occupation imbalance and give rise to a smaller quadrupole splitting and more positive chemical isomer shift.

Similar effects were subsequently observed[86] in the Mössbauer spectra recorded from organotellurium complexes with 7, 7, 8, 8-tetracyanoquinodimethane (tcnq). In these investigations a range of organotellurium(II) compounds were used as donors to form donor–acceptor complexes with tcnq. Although most reactions gave 1:1 complexes, the ditelluride gave complexes of the type R$_2$Te$_2$.2tcnq, where R is Ph or (p-EtOC$_6$H$_4$). Although the complexes were insulators the conductivities did vary over several orders of magnitude and the two ditelluride complexes showed evidence of semiconducting properties. Infrared and ESR data indicated the degree of charge transfer to be small in most cases. However, the tcnq complexes of 1, 3-dihydro-2-telluraindene and diphenyl ditelluride gave ^{125}Te Mössbauer spectra which were interpreted in terms of significant charge transfer and the results have led to the development of a method whereby the Mössbauer parameters can be used to assess the degree of charge transfer for donor–acceptor complexes containing organotellurium compounds. Given the likely growth in this area of chemistry, it is important that the potential use of ^{125}Te Mössbauer spectroscopy as an investigative technique for these types of compounds be explored more fully. Some evidence for this development is reflected in a more recent study[13] of some 2-phenylazophenyl-C, N'-tellurium(II) dithiocarbamates of composition (C$_{12}$H$_9$N$_2$)Te(II)(dtc) and the corresponding tellurium(IV) tris compounds (C$_{12}$H$_9$N$_2$)Te(dtc)$_3$, where dtc is dimethyl, diethyl or dibenzyl dithiocarbamate. The ^{125}Te Mössbauer parameters recorded from these complexes were used to formulate the tris compounds as loose charge-transfer complexes of the type (C$_{12}$H$_9$N$_2$)Te(II)(dtc).[R$_2$NC(S)SS(S)CNR$_2$].

G. Iodine-125 Emission Mössbauer Studies

In Mössbauer emission spectroscopy the sample to be studied is prepared with a radioactive isotope and is used as a source. The radiation emitted from the sample is absorbed by a standard absorber that contains the corresponding Mössbauer isotope. Since an iodine-125 nucleus undergoes radioactive decay to populate the 35.48 keV excited state of tellurium-125, compounds labelled with iodine-125 can be used as sources in Mössbauer emission spectroscopy. It must be appreciated, however, that the decay processes may create unstable but long-living changes in the surroundings of the Mössbauer nucleus and that such source experiments are often complicated and the
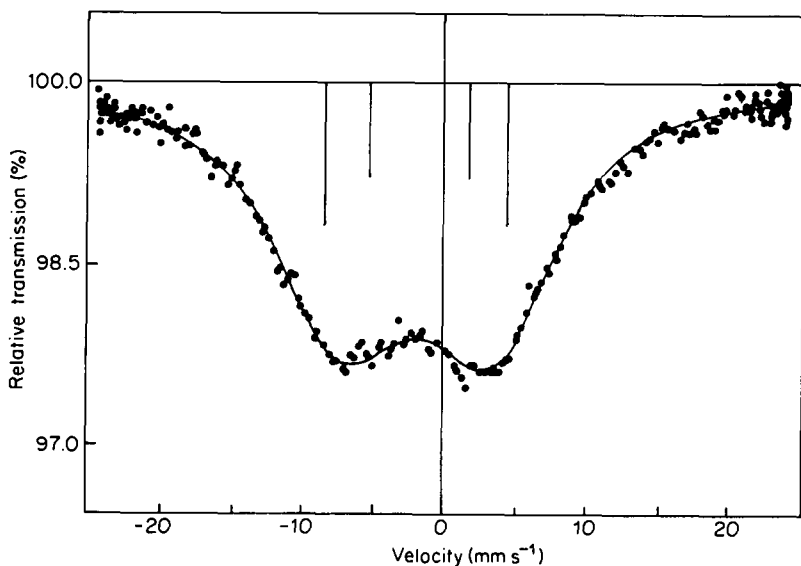
FIGURE 20. Mössbauer emission spectrum recorded from [^{125}I]iodobenzene in hexane
at 4.2 K. Reproduced with permission from *Chem. Phys. Lett.*, **94**, 227 (1983)

consequences of nuclear transformations which involve both oxidation and reduction are
not fully understood.

A Mössbauer emission spectroscopy study of ^{125}I-labelled iodobenzene, PhI, benzyl
iodide, PhCH$_2$I, and iodine in benzene reported[87] similar spectra from all samples
showing quadrupole split absorptions, $\Delta \approx 11.3$ mm s^{-1}, which were associated with the
formation of Te—C bonds. In a subsequent study[88] by ^{125}I Mössbauer emission
techniques and ^{127}NQR spectroscopy a series of *o*-, *m*- and *p*-substituted iodobenzenes
were found to undergo at least partial decomposition to diorganotellurides. The most
recent Mössbauer emission investigation of ^{125}I-labelled iodobenzene, methyl iodide and
their dilute solutions in benzene and hexane[89] gave spectra (Figure 20) which, by careful
computer analysis, were interpreted in terms of the presence of two species. One of the
species was tentatively described as a diaryl, arylalkyl or dialkyl telluride whilst the other
was described as a tellurium atom attached to a single aryl or alkyl moiety with a positive
charge, e.g. [PhTe]$^+$, [IC$_6$H$_4$Te]$^+$ or [C$_6$H$_{13}$Te]$^+$. The observations were rationalized in
terms of the ^{125}I in MeI or PhI undergoing decay by electron capture with the rupture of
the Te—C bond and the excited and highly reactive tellurium ion undergoing reaction
with neighbouring molecules of iodobenzene or methyl iodide.

H. Tellurium Complexes with Thiourea and Related Compounds

It is relevant to mention here several significant studies of thiourea and related
compounds. ^{125}Te Mössbauer data recorded from TeTu$_4$X$_2$, where Tu is thiourea and X is
halide, were used in the initial derivations of relationships between the ^{125}Te Mössbauer
chemical isomer shifts and holes in the tellurium 5p shell in tellurium compounds which
are p bonded[90]. In a subsequent study[91], asymmetry in the Mössbauer spectra of
tellurium(II) thiourea complexes was shown to arise predominantly from single crystal

orientation effects and the asymmetry in the spectrum recorded from $TeTu_4Cl_2.2H_2O$ was shown to be consistent with a negative sign for the nuclear quadrupole moment of the 3/2 excited state in ^{125}Te. In other studies[34,56,92] of tellurium(II) and tellurium(IV) complexes with sulphur-containing ligands the Mössbauer parameters have been interpreted in terms of bonding and the structural properties of the complexes. Finally, it is pertinent to record that the ^{125}Te Mössbauer emission spectra recorded from a number of tellurium(II) thiourea complexes have given evidence[93] of extensive molecular fragmentation during the isomeric transition which precedes the Mössbauer transition.

IV. CONCLUSION

Tellurium-125 Mössbauer spectroscopy is a technique which is well suited for the investigation of organotellurium compounds. The different types of compounds which have been examined to date illustrate the variety of materials which are amenable to study by the technique. The results which have been interpreted in terms of the bonding and structural properties of the compounds exemplify the power of the technique to give unique information and also demonstrate the capacity of Mössbauer spectroscopy to complement other methods of investigation. The currently developing interst in tellurium-containing compounds with potentially technologically important properties will undoubtedly lead to a further growth in the application of Mössbauer spectroscopy, in both conventional and unconventional modes of operation, to the study of organotellurium compounds.

V. REFERENCES

1. R. L. Mössbauer, *Z. Phys.*, **151**, 124 (1958).
2. G. K. Wertheim, *Mössbauer Effect: Principles and Applications*, Academic Press, New York, 1964.
3. N. N. Greenwood and T. C. Gibb, *Mössbauer Spectroscopy*, Chapman and Hall, London, 1971.
4. L. May (Ed.), *An Introduction to Mössbauer Spectroscopy*, Plenum Press, New York, 1971.
5. G. M. Bancroft, *Mössbauer Spectroscopy, An Introduction for Inorganic Chemists and Geochemists*, McGraw-Hill, Maidenhead, 1973.
6. U. Gonser (Ed.), *Topics in Applied Physics, Vol. V: Mössbauer Spectroscopy*, Springer-Verlag, Berlin, 1975.
7. T. C. Gibb, *Principles of Mössbauer Spectroscopy*, Chapman and Hall, London, 1976.
8. F. J. Berry and D. P. E. Dickson (Eds.), *Mössbauer Spectroscopy*, Cambridge University Press, Cambridge, 1986.
9. F. J. Berry, in *Physical Methods of Chemistry* (Eds. B. W. Rossiter and J. F. Hamilton), 5th ed., Wiley, New York, in press.
10. Pham Zuy Hein, V. G. Shapiro and V. S. Shpinel, *Sov. Phys. JETP*, **15**, 489 (1962).
11. N. Shikazono, T. Shorji, H. Takekoshi and P. Tseng, *J. Phys. Soc. Jpn.*, **17**, 1205 (1962).
12. G. M. Bancroft, *Mössbauer Spectroscopy, An Introduction for Inorganic Chemists and Geochemists*, McGraw-Hill, Maidenhead, 1973, p. 27.
13. M. A. K. Ahmed, A. E. McCarthy, W. R. McWhinnie and F. J. Berry, *J. Chem. Soc., Dalton Trans.*, 771 (1986).
14. E. P. Stepanov, K. P. Aleshine, R. A. Manapov, B. N. Samoilau, V. V. Sklyarevskii and V. G. Stankevich, *Phys. Lett.*, **6**, 155 (1963).
15. M. Pasternak and A. L. Spijkervat, *Phys. Rev.*, **181**, 574 (1969).
16. N. E. Erickson and A. G. Maddock, *J. Chem. Soc. A*, 1665·(1970).
17. R. N. Kuzmin, A. A. Opalenko, V. S. Shpinel and I. A. Avenarius, *Sov. Phys. JETP*, **29**, 94 (1969).
18. V. A. Lebedev, R. A. Lebedev, A. M. Babeshkim and A. N. Nesmeyanov, *Vestn. Mosk. Univ. Khim.*, **24**, 128 (1969).
19. C. E. Violet, R. Booth and F. Wooten, *Phys. Lett.*, **5**, 230 (1963).
20. H. Voorthius, W. Beens and H. Verheul, *Physica*, **33**, 695 (1967).

21. B. Martin and R. Schule, *Phys. Lett. B*, **46**, 367 (1973).
22. B. P. Dailey and C. H. Townes, *J. Chem. Phys.*, **23**, 118 (1955).
23. F. J. Berry, E. H. Kustan and B. C. Smith, *J. Chem. Soc., Dalton Trans.*, 1323 (1975).
24. K. V. Smith, J. S. Thayer and B. J. Zambransky, *Inorg. Nucl. Chem. Lett.*, **11**, 441 (1975).
25. C. H. W. Jones, R. Schultz, W. R. McWhinnie and N. S. Dance, *Can. J. Chem.*, **54**, 3234 (1976).
26. F. J. Berry and C. H. W. Jones, *Can. J. Chem.*, **54**, 3737 (1976).
27. F. J. Berry and J. Silver, *J. Organomet. Chem.*, **129**, 437 (1977).
28. F. J. Berry, C. H. W. Jones and W. R. McWhinnie, in *Mössbauer Effect Methodology* (Eds. I. J. Gruverman and C. W. Seidel), Vol. 10, Plenum Press, New York, 1976, p. 227.
29. F. J. Berry, C. H. W. Jones and W. R. McWhinnie, in *Proceedings of the Fourth International Conference on the Organic Chemistry of Selenium and Tellurium* (eds. F. J. Berry and W. R. McWhinnie), University of Aston Press, Birmingham, 1983, p. 492.
30. C. H. W. Jones and R. D. Sharma, *J. Organomet. Chem.*, **255**, 61 (1983).
31. W. R. Blackmore and S. C. Abrahams, *Acta Crystallogr.*, **8**, 317 (1955).
32. F. H. Kruse, R. E. Marsh and J. D. McCullough, *Acta Crystallogr.*, **10**, 201 (1957).
33. G. Llabres, O. Dideberg and L. Dupont, *Acta Crystallogr., Sect. B*, **28**, 2438 (1972).
34. R. M. Cheyne, C. H. W. Jones and S. Husebye, *Can. J. Chem.*, **53**, 1855 (1975).
35. C. H. W. Jones, R. D. Sharma and D. Naumann, *Can. J. Chem.*, **64**, 987 (1986).
36. C. H. W. Jones and R. D. Sharma, *Organometallics*, **5**, 805 (1986).
37. G. T. Morgan and H. D. K. Drew, *J. Chem. Soc.*, 531 (1925).
38. F. J. Berry, B. C. Smith and C. H. W. Jones, *J. Organomet. Chem.*, **110**, 201 (1976).
39. G. D. Christofferson and J. D. McCullough, *Acta Crystallogr.*, **11**, 249 (1958).
40. G. D. Christofferson, R. A. Sparks and J. D. McCullough, *Acta Crystallorg.*, **11**, 782 (1958).
41. G. Y. Chao and J. D. McCullough, *Acta Crystallogr.*, **15**, 887 (1962).
42. L. Y. Y. Chan and F. W. B. Einstein, *J. Chem. Soc., Dalton Trans.*, 316 (1972).
43. F. J. Berry and A. J. Edwards, *J. Chem. Soc., Dalton Trans.*, 2306 (1980).
44. W. R. McWhinnie and M. G. Patel, *J. Chem. Soc., Dalton Trans.*, 199 (1972).
45. J. J. Johnstone, C. H. W. Jones and P. Vasudev, *Can J. Chem.*, **50**, 3037 (1972).
46. L. H. Bowen, J. G. Stevens and G. G. Long, *J. Chem. Phys.*, **51**, 2010 (1969).
47. H. Pritzkow, *Inorg. Chem.*, **18**, 311 (1979).
48. W. R. McWhinnie and P. Thavornyutikarn, *J. Chem. Soc., Dalton Trans.*, 551 (1972).
49. J. D. McCullough and P. F. Marsh, *J. Am. Chem. Soc.*, **72**, 4556 (1950).
50. K. J. Wynne and J. W. George, *J. Am. Chem. Soc.*, **91**, 1649 (1969).
51. D. A. Couch, P. S. Elmes, J. E. Ferguson, M. C. Greenfield and C. J. Wilkens, *J. Chem. Soc. A*, 1813 (1967).
52. M. T. Chen and J. W. George, *J. Am. Chem. Soc.*, **90**, 4580 (1968).
53. K. J. Wynne and P. S. Pearson, *Inorg. Chem.*, **9**, 106 (1970).
54. L. H. Bowen, in *Mössbauer Effect Data Index for 1972* (Eds. J. G. Stevens and V. E. Stevens), Plenum Press, New York, 1973, p. 71.
55. R. G. Barnes and W. V. Smith, *Phys. Rev.*, **93**, 9 (1954).
56. R. M. Cheyne, C. H. W. Jones and P. Vasudev, *Can. J. Chem.*, **50**, 3677 (1972).
57. N. S. Dance, P. Dobud and C. H. W. Jones, *Can. J. Chem.*, **59**, 913 (1981).
58. N. S. Dance and C. H. W. Jones, *Can. J. Chem.*, **56**, 1745 (1978).
59. B. C. Pant, W. R. McWhinnie and N. S. Dance, *J. Organomet. Chem.*, **63**, 305 (1973).
60. J. D. McCullough, *Inorg. Chem.*, **12**, 2669 (1973).
61. N. S. Dance and C. H. W. Jones, *Can. J. Chem.*, **56**, 1747 (1978).
62. F. J. Berry and J. Silver, *J. Organomet. Chem.*, **188**, 255 (1980).
63. J. D. McCullough, *Inorg. Chem.*, **14**, 2639 (1975).
64. M. R. Smith, M. M. Mangion, R. A. Zingaro and E. A. Mengers, *J. Heterocycl. Chem.*, **10**, 527 (1973).
65. C. L. Raston, R. J. Secomb and A. H. White, *J. Chem. Soc., Dalton Trans.*, 2307 (1976).
66. J. C. Dewan and J. Silver, *J. Organomet. Chem.*, **125**, 125 (1977).
67. J. C. Dewan and J. Silver, *Aust. J. Chem.*, **30**, 487 (1977).
68. J. C. Dewan and J. Silver, *Acta Crystollogr., Sect. B*, **33**, 1469 (1977).
69. J. C. Dewan and J. Silver, *Acta Crystallogr., Sect. B*, **33**, 261 (1977).
70. J. C. Dewan and J. Silver, *J. Chem. Soc., Dalton Trans.*, 644 (1977).
71. J. Barrett, S. R. A. Bird, J. D. Donaldson and J. Silver, *J. Chem. Soc. A*, 3105 (1971).
72. J. D. Donaldson, D. Laughlin, S. D. Ross and J. Silver, *J. Chem. Soc., Dalton Trans.*, 1985 (1971).

73. J. D. Donaldson and J. Silver, *Inorg. Nucl. Chem. Lett.*, **10**, 537 (1974).
74. J. D. Donaldson, J. Silver, S. Hadjiminolis and S. D. Ross, *J. Chem. Soc., Dalton Trans.*, 1500 (1975).
75. J. D. Donaldson and J. Silver, *J. Solid State Chem.*, **18**, 117 (1976).
76. J. D. Donaldson, D. R. Laughlin and M. J. K. Thomas, *Radiochem. Radioanal. Lett.*, **28** 91 (1977).
77. R. V. Parish, *Coord. Chem. Rev.*, **42**, 1 (1982).
78. I. Davies, W. R. McWhinnie, N. S. Dance and C. H. W. Jones, *Inorg. Chim. Acta Lett.*, **29**, L203 (1978).
79. N. S. Dance and C. H. W. Jones, *J. Organomet. Chem.*, **152**, 175 (1975).
80. F. W. B. Einstein, C. H. W. Jones, T. Jones and R. D. Sharma, *Inorg. Chem.*, **22**, 3924 (1983).
81. I. Davies, W. R. McWhinnie, N. S. Dance and C. H. W. Jones, *Inorg. Chim. Acta Lett.*, **29**, L217 (1978).
82. N. S. Dance, W. R. McWhinnie and C. H. W. Jones, *J. Organomet. Chem.*, **125**, 291 (1977).
83. C. H. W. Jones, R. D. Sharma and S. P. Taneja, *Can. J. Chem.*, **64**, 980 (1986).
84. C. H. W. Jones and R. D. Sharma, *Organometallics*, **5**, 1194 (1986).
85. K. G. K. De Silva, Z. Monsef–Mirzai and W. R. McWhinnie, *J. Chem. Soc., Dalton Trans.*, 2143 (1983).
86. H. B. Singh, W. R. McWhinnie, R. F. Ziolo and C. H. W. Jones, *J. Chem. Soc., Dalton Trans.*, 1267 (1984).
87. C. H. W. Jones and A. F. Skinner, in *Proceedings of the International Conference on Mössbauer Spectroscopy* (Eds. D. Barb and D. Tarina), Vol. 1, Bucharest 1977, p. 283.
88. G. L. Shtyrkov, N. G. Iroshnikova, V. V. Khrapov, T. A. Babushikina and V. I. Stanko, *Zh. Fiz. Khim.*, 5322 (1979).
89. Ch. Sauer, M. Rieche, A. Halpern and A. Nath, *Chem. Phys. Lett.*, **94**, 227 (1983).
90. R. M. Cheyne, J. J. Johnstone and C. H. W. Jones, *Chem. Phys. Lett.*, **14**, 545 (1972).
91. R. M. Cheyne and C. H. W. Jones, *Can. J. Chem.*, **52**, 564 (1974).
92. P. W. C. Barnarc, J. D. Donaldson, R. M. A. Grimsey, G. Dennes, U. Russo and S. Calogero, *Inorg. Chim. Acta*, **51**, 217 (1981).
93. C. H. W. Jones and M. Dombsky, *J. Phys. (Paris), Colloq. C2*, **40**, 417 (1979).

CHAPTER **3**

Preparative uses of organoselenium and organotellurium compounds

THOMAS G. BACK

Department of Chemistry, University of Calgary, Calgary, Alberta, Canada, T2N 1N4

I. INTRODUCTION

Although organoselenium chemistry had been widely studied and exhaustively reviewed[1,2] by the early 1970s, only a few selenium-based synthetic methods existed in the literature of that time. The discovery and subsequent recognition of the selenoxide *syn*-elimination as an exceptionally efficient olefin-forming reaction did much to enhance the appreciation of selenium compounds by synthetic organic chemists. Increasing interest in the field soon led to other discoveries of widespread synthetic utility based on the unique properties of this element. The resulting proliferation of the literature on organoselenium chemistry prompted several excellent reviews in the late 1970s[3-8] as well as a number of later ones[9-11]. Very recently, two new books (in addition to Volume 1 of the present series) have appeared on the subject which are based on reaction types[12] and applications in the synthesis of natural products[13]. A number of more specialized reviews have been written recently and these will be cited at appropriate points in this chapter to direct the reader to additional information.

The history of organotellurium chemistry is also lengthy, but again contributions of broad synthetic potential have only begun to appear in the past few years. The general

subject has been reviewed periodically[8,14-22] and appears to be generating increasing interest. However, broad acceptance of tellurium-based synthetic methodology lags behind that of selenium at present.

The aim of this chapter is to provide coverage of recent preparative uses of selenium and tellurium compounds. In keeping with the general theme of this series, and in order to provide a complementary treatment to existing reviews, this chapter will be organized principally according to the types of functional group and skeletal transformations which can be achieved. Considerations of mechanisms and of the strategic role played by selenium and tellurium reagents in specific syntheses of natural products will be kept to a minimum. No attempt is made to provide exhaustive coverage of all known examples of the more widely employed procedures, although illustrative examples will be shown as required to demonstrate their scope and limitations. Coverage of the literature up to early 1985 is provided.

II. OLEFIN PREPARATIONS BY ELIMINATION

A. Selenoxide *syn*-Elimination

1. General comments

The selenoxide *syn*-elimination (equation 1) constitutes one of the most expedient methods for introducing a carbon—carbon double bond into a saturated substrate. It is formally akin to older methods such as ester pyrolyses and the Chugaev, Cope and sulfoxide eliminations, but has the advantage of proceeding under far milder conditions, often at or even below room temperature. Further, the required selenide starting materials are readily available from a variety of sources (see the chapter by McWhinnie) and are efficiently oxidized to their selenoxides by many common reagents. Over-oxidation to selenones is seldom a complication, in contrast to sulfur analogues where competing sulfone formation is more difficult to avoid.
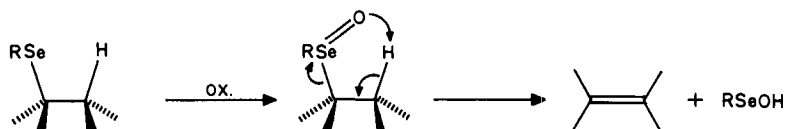
$$\tag{1}$$

Despite several earlier reports of successful but isolated selenoxide eliminations[23-25], the synthetic potential of the method remained largely unrecognized until 1973. In that year Sharpless and coworkers[26-28], Reich and coworkers[29] and Clive[30] independently demonstrated its merits. Subsequent applications have been rapid and now number many hundreds. The subject has been reviewed recently[31].

2. Stereochemistry

The selenoxide *syn*-elimination requires the coplanarity of all five participating centers and so is highly stereospecific. This is illustrated by the examples in equations 2 and 3. Thus, in the first example, the *erythro*- and *threo*-selenides 1 and 2 produced the corresponding (*E*)- and (*Z*)-olefins, respectively, on oxidation[28]. In the second example, the *cis*-selenide 3, where the PhSe group is *cis* to the ring-fusion hydrogen, eliminated to afford mainly the more stable *endo* olefin, while the *trans*-selenide 4 produced only the *exo*

isomer[32]. The latter result is attributed to the inability of the system to achieve the required planar conformation for *endo* elimination.

(2)
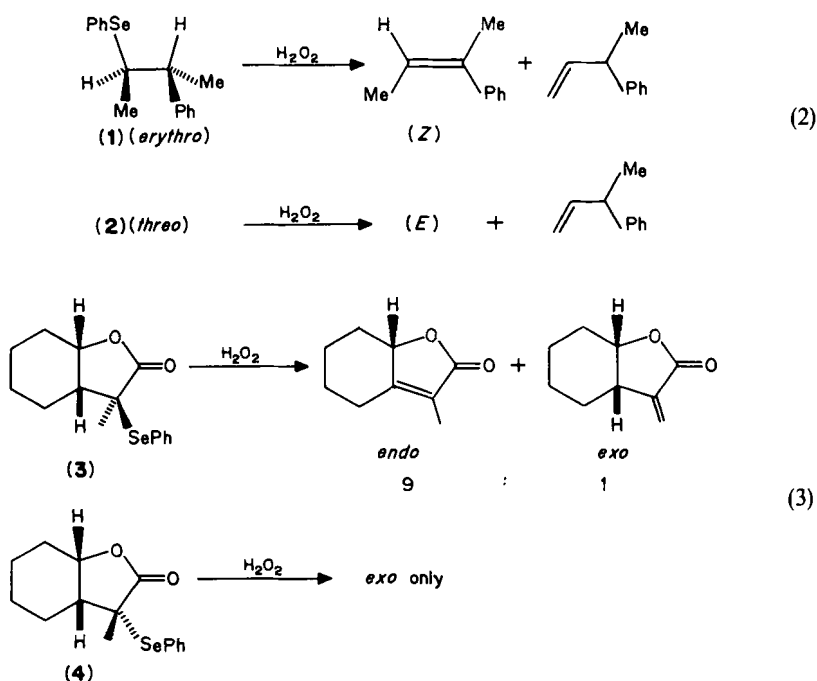
When the product of elimination is a 1,2-disubstituted olefin, it is generally formed preferentially with the *E* configuration[26-28,33-35]. The stereoselectivity is usually high unless the substituents are small, in which case *E, Z* mixtures result[34].

The oxidation of a selenide containing a chiral substituent can generate a pair of diasteromeric selenoxides, since the selenium atom itself becomes a chiral center. Such diastereomers may eliminate at substantially different rates[24,36], or follow different pathways altogether[37].

3. Regiochemistry

In the case of branched selenoxides, elimination towards the less substituted position is generally favoured[28,34] (e.g. equation 4[28]).

(4)

In selenoxides of general structure **5**, α-alkyl substituents tend to accelerate elimination whereas β-[38,39] and even γ-alkyl[39] groups retard it. Phenyl substituents in either the α- or β-position enhance the rate[38].

(5)

The regiochemistry of elimination can be strongly influenced by the presence of a heteroatom in the β-position of the selenoxide. Oxygen substituents in the form of hydroxyl, ether or acetoxy groups strongly direct elimination toward the allylic site and numerous examples demonstrating this effect are known (e.g. equation 5[40]). When an allylic hydrogen is unavailable elimination towards the vinylic position can occur, although more forcing conditions are often required. Enol ethers[36,41,42], enol acetates[43], ketones[43], ketene acetals[44-47] and an enol phosphate[48] have been prepared in this manner (equation 6). In a few exceptional cases secondary selenoxides have been observed to eliminate preferentially toward β-acetoxy[49,50] or acetal[51] functions to give the vinylic instead of allylic products. Presumably conformational or other factors suppress reaction at the allylic site.

$$R = H, Ac \text{ or alkyl} \qquad \geqslant 97 \qquad : \qquad \leqslant 3 \qquad (5)$$

$$R = alkyl, Ac, P(O)(OMe)_2 \qquad (6)$$

β-Nitrogen substituents also exert a directing effect, although its direction and magnitude depend on the nature of the functional group. β-Amido selenoxides produce allylic amides exclusively[52,53] whenever an allylic hydrogen atom is available. Otherwise, enamides[54,55] or dehydroamino acids[25] are formed. Allylic elimination is also preferred in the case of cyclic[56,57] and acyclic[58] amines, although the regiospecificity is lower than in the case of oxygen substituents. Azides[59] and isothiocyanates[60] favour allylic and vinylic elimination, respectively. Examples are shown in equations 7 and 8[58]. When intramolecular hydrogen bonding is possible between the selenoxide and a β-hydroxyl[61] or β-amido function[52,53] (e.g. 6), then the resulting stabilization necessitates the use of elevated temperatures to effect elimination.

Y = NHAc :	100	:	0	(Refs. 52,53)
Y = N$_3$:	60	:	40	(Ref. 59)
Y = NCS :	17	:	83	(Ref. 60)

$$(7)$$

$$R=H : \quad\quad 84\%\quad\quad\quad\quad\quad\quad < 2\%$$
$$R=Me: \quad\quad 54\%\quad\quad\quad\quad\quad\quad 20\%$$

(8)

(6)

The effect of halogens on the regiochemistry is less predictable. It has been reported that a chloro substituent in either the α- or β-position enhances elimination[38]. However, there are numerous examples where elimination occurs preferentially away from a chlorine or bromine atom to produce chiefly the allylic halide[62-66]. In many other instances mixtures containing significant amounts of both regioisomers were observed[40,63,65] (equation 9). Vinyl bromides are formed in high yield from primary β-bromo selenoxides[62] (equation 10).

$$X = Cl, Br$$

(9)

(10)
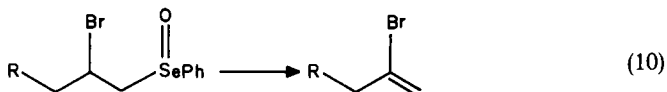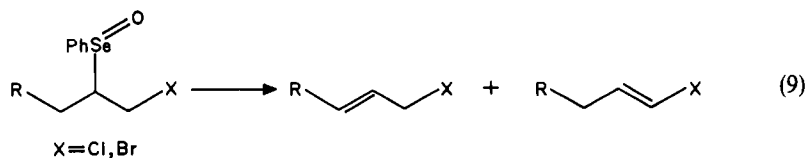
γ-Stannyl substituents are reported to have a mild directing effect towards the homoallylic rather than allylic site for selenoxide elimination[67].

Groups which have an acidifying effect on an adjacent hydrogen atom (e.g. carbonyl[28,68,69], sulfone[70-78], sulfoxide[77,78], nitro[79,80] and cyano[81] groups) strongly accelerate elimination towards that site, often to the complete exclusion of other regioisomers (equation 11).

$$Y = SO_2Ar, NO_2, CN, \overset{O}{\overset{\|}{C}}R$$

(11)
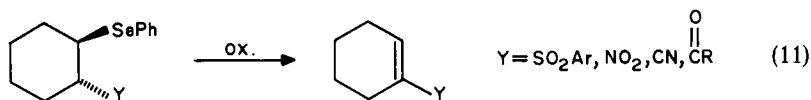
4. *Techniques and side reactions*

The oxidation of selenides to selenoxides can be achieved with diverse reagents. Those most commonly employed are hydrogen peroxide, ozone, sodium periodate and peracids,

especially *m*-chloroperbenzoic acid (MCPBA). Their relative merits have been considered in various reviews (see Section I). The use of *t*-butyl hydroperoxide has been especially recommended[82] as it suppresses side reactions such as epoxidation (see below) during the elimination step. The presence of alumina is beneficial with this reagent[83]. Other less frequently used oxidants include Chloramine-T[82], *N*-chlorosuccinimide (NCS)[84], *t*-butyl hypochlorite[84,85], thallium(III) nitrate[86], sodium perborate[87], oxaziridines[88,89], singlet oxygen[90] and Jones reagent[91,92].

Selenoxide eliminations are sometimes accompanied by undesirable side reactions. Detailed studies by Reich and coworkers[38] and Sharpless and coworkers[28,82] have resulted in effective countermeasures. The selenenic acid (RSeOH) or one of its disproportionation products which forms during the elimination (equation 1) can add to the double bond of the desired olefin[38,82,93], particularly under neutral or acidic conditions[38]. This can be suppressed by the presence of an amine which removes the selenenic acid as it forms[38,93]. Other scavengers which have been employed for this purpose are reactive olefins such as enol ethers[51,94,95], enol acetates[95] and norbornadiene[41].

Competing decomposition of the selenoxide via other routes can occur when the elimination is slow, and so conditions should be chosen to enhance the elimination rate to the fullest extent. Water deactivates selenoxides through hydrate formation and so anhydrous conditions are advantageous. The addition of anhydrous $MgSO_4$ has been recommended for this purpose[28].

Other protic solvents also suppress elimination and should be avoided in troublesome cases[38]. When hydrogen peroxide is employed in the oxidation step, its catalytic decomposition by the selenoxide may require a large excess of the oxidant[38]. Epoxidation of the olefin is sometimes observed, especially with highly substituted products[38,82], but can usually be avoided through the use of *t*-butyl hydroperoxide[82]. In particularly difficult cases, it is sometimes expedient to pre-form the selenoxide at low temperature with ozone or a peracid and then to pyrolyse it rapidly in a refluxing non-polar solvent such as hexane[38] or carbon tetrachloride[38,60,96].

In general, aryl selenoxides eliminate more efficiently than alkyl selenoxides[83] and electron-withdrawing substituents on the aryl group further enhance the process[38,39,97-99]. The 2-pyridylseleno group has also been reported to give particularly efficacious results[100-102].

Other side reactions include the reduction of the selenoxide back to the selenide[25,103] by divalent selenium byproducts, isomerization of a previously existing double bond (*cis* to *trans*) in the substrate[104] and the formation of alcohols or other oxygenated products[105-107], particularly when elimination is rendered difficult by strain or other factors such as the formation of stabilized carbonium ions[107] from C—Se cleavage (e.g. equation 12).

$n = 1: 36\%$
$n = 2: 41\%$

(12)
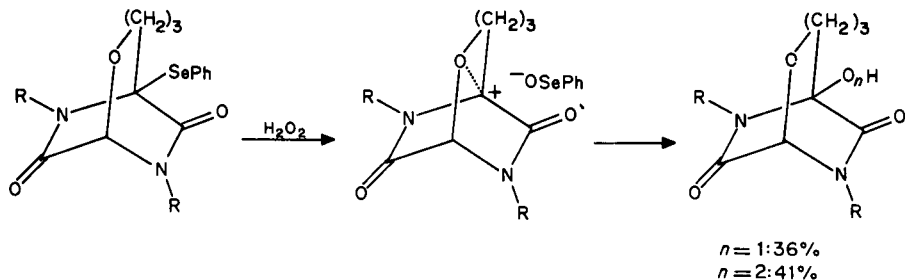
5. Acetylenes and allenes from vinyl selenoxides

The *syn*-eliminations of vinyl selenoxides were studied by Reich and Willis[108] and provide a route to acetylenes and allenes. The former compounds are produced preferentially, provided that a *cis*-hydrogen atom is available for elimination (equation 13). The selenoxides derived from β-(phenylseleno)vinyl sulfones can be employed in the preparation of acetylenic[109-111] or allenic[112] sulfones (see Sections VIII.C.2 and 3).

$$\text{(13)}$$
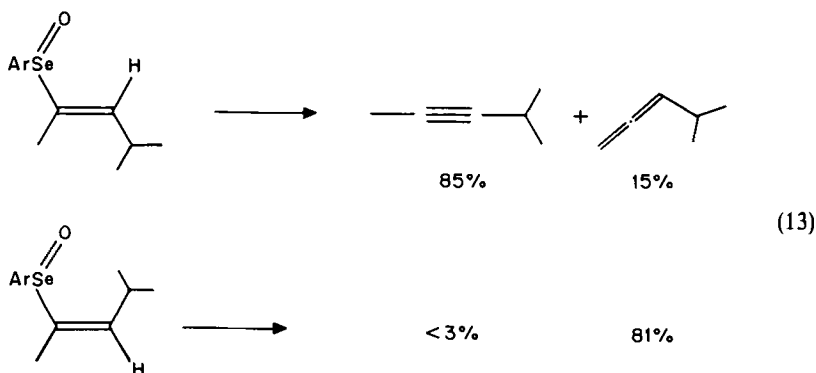
B. Telluroxide Elimination

Only a few examples of olefin preparations via telluroxide elimination have been reported[113-120]. Telluroxides form stable hydrates which may require pyrolysis at temperatures of ca. 200 °C[116,118]. They are also readily reduced by the byproduct tellurenic acid (RTeOH) back to the original tellurides[113], and overoxidized to tellurones[113], resulting in the formation of oxygenated byproducts[113,114,120]. The greater difficulty in controlling the desired oxidation state of telluroxides makes them less attractive than selenoxides for olefin preparations in most cases.

Telluroxides, like selenoxides, tend to eliminate towards the less substituted position[118,120] and to the allylic position with respect to an oxygen function[116-119]. A series of monosubstituted olefins were prepared in high yields from primary tellurides, using Chloramine-T as the oxidant[115] (equation 14).

$$\text{(14)}$$
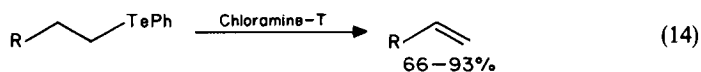
C. Elimination of Selenonium Salts

Krief and coworkers[91,121-124] reported that the base-catalysed elimination of selenonium salts provides a viable alternative to the selenoxide elimination as an olefin-forming procedure (e.g. equation 15[121]). A selenide starting material is first alkylated with reagents such as methyl iodide, methyl fluorosulfate or dimethyl sulfate, and elimination is then effected with potassium hydroxide, potassium *t*-butoxide or potassium hydride, usually in DMSO. Selenoacetals eliminate to produce vinyl selenides when treated with methyl iodide in DMF[125] (equation 16), or with PI_3 or P_2I_4[126] in a related process. The transformation of selenoorthoesters to ketene selenoacetals (i.e. equation 16, where $R^3 = SeR$) occurs under similar conditions[126] or with the reagents $SnCl_4-i-Pr_2NEt$[127].

$$R = Me, Ph$$
$$R^1 = C_{10}H_{21}$$

$$65 \quad : \quad 35$$
$$82-88\%$$

(15)

$$50-65\%$$

(16)
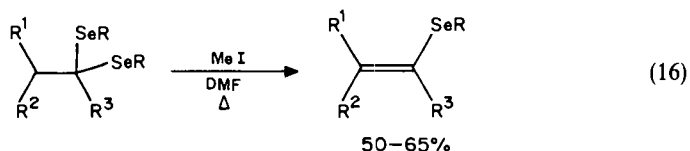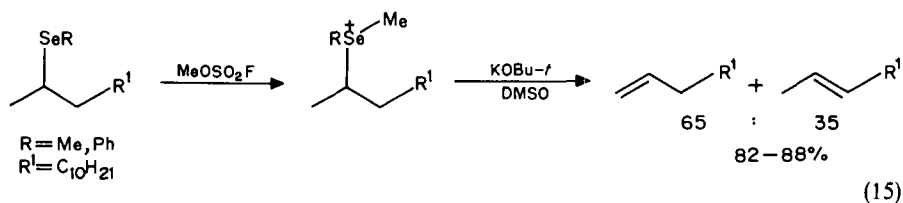
III. DEHYDROGENATION OF CARBONYL COMPOUNDS

A. Via α-Selenenylated Derivatives

1. Aldehydes and ketones

The dehydrogenation of aldehydes and ketones to their α,β-unsaturated derivatives can be effected by α-selenenylation followed by oxidation and selenoxide elimination. Several different protocols have been devised for the selenenylation step. Sharpless and coworkers[27] discovered that the treatment of aldehydes or ketones with benzeneselenenyl chloride (PhSeCl) in ethyl acetate provides the α-selenides in high yield (equation 17).

(17)
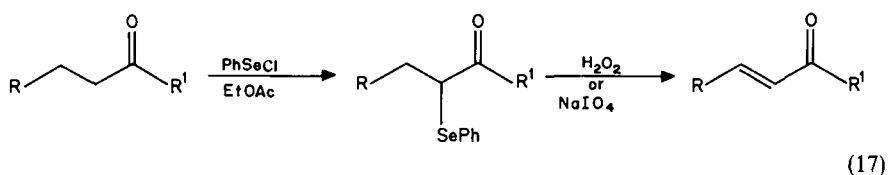
The reaction proceeds via the enol form of the carbonyl compound and is sometimes aided by catalysts such as HCl[27], $BF_3 \cdot OEt_2$[128,129] or Dowex 50-X8 (H^+)[130]. The direction of enolization dictates the regiochemistry of selenenylation in unsymmetrical ketones and the procedure is compatible with a large variety of functionalities including other carbonyl groups, olefins, hydroxyl and carboxyl groups, ethers and epoxides. Basic amino groups, however, can create complications, as demonstrated by equation 18, where the codeinone derivative **8** failed to undergo selenenylation whereas, the urethane analog **7** reacted smoothly[131,132].

$$85\% \qquad\qquad 68\%$$

(7) $R = CO_2Et$
(8) $R = Me$

(18)

An alternative procedure which employs basic conditions was developed by Reich and coworkers[29,133,134]. The ketone is first converted into its kinetic enolate, usually with LDA at $-78\,°C$, and then selenenylated with PhSeCl or PhSeBr. Oxidation in the usual manner affords the desired enone (equation 19).

$$(19)$$

Enones are themselves selenenylated at the α'-position[135-137] and produce cross-conjugated dienones[135] or phenols[136,137] on oxidation. γ-Selenenylation occurs[138,139] if the α'-position is fully substituted (e.g. equations 20[135] and 21[138]).

$$(20)$$

69%

$$(21)$$

50–60%

Both methods are relatively free from side reactions. Bisselenenylated ketones are sometimes formed from the further selenylation of the monosubstituted products[29,140,141] but seldom in significant amounts. The oxidation step may be accompanied by Pummerer reactions of the selenoxide intermediates[133,134], which can be suppressed by the addition of an amine. Baeyer–Villiger reactions of the product enones[114,142,143] or of remote ketone groups[102] sometimes occur under these conditions. In some cases these processes are promoted deliberately if the oxygenated byproducts are desired instead of the enone (see Sections V.F.2 and V.H.1).

Although the above procedures have proved the most versatile and widely employed, several other useful variations for the selenenylation of aldehydes and ketones have also been reported. Selenenamides 9 are sufficiently basic to deprotonate aldehydes[144], thus permitting their selenenylation according to equation 22[144-147]. The selenenylation of 4-substituted cyclohexanones with chiral selenenamides was accompanied by asymmetric induction, providing optically active enones with up to 26.2% enantiomeric excesses[148] after oxidation–elimination (equation 23).

$$(22)$$

$$(23)$$

α-(2-Pyridylseleno) ketones or aldehydes are easily prepared with the reagents **10**, **11** or **12** (equation 24) and permit particularly efficient elimination to enones[96,149], even in the case of cycloheptenones and cyclooctenones which are difficult to prepare from their 2-phenylseleno derivatives[134]. A polymer-supported areneselenenyl chloride was also reported to function as an effective selenenylating reagent[150]. A number of other selenenylation procedures employing elemental selenium[151], selenophosphoranes[152], PhSeSePh–selenium dioxide[153] and selenenic electrophiles generated from the anodic oxidation of PhSeSePh[154] are shown in equation 25.

$$(24)$$

$$(25)$$
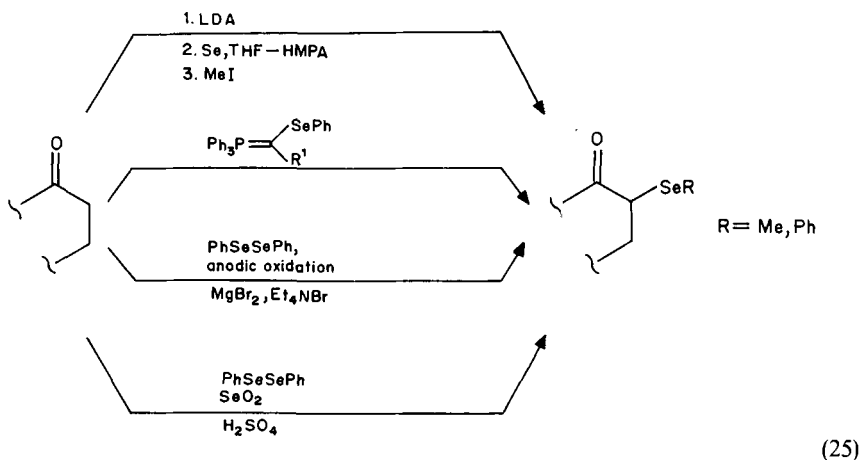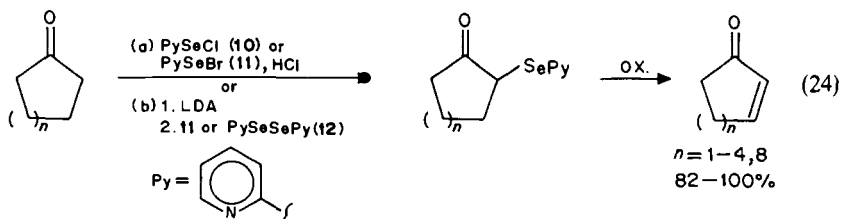
The further transformation of enones to other products with selenium- or tellurium-based methods is discussed separately in Section XVII.

2. Esters and lactones

In contrast to aldehydes and ketones, esters and lactones fail to undergo the direct selenenylation shown in equation 17, and prior generation of the enolate is required[27].

Typically LDA is employed for this purpose, although other bases such as potassium hydride[155-157], lithium cyclohexylisopropylamide[158-160], LiTMP[161] and lithium[162] or potassium[163] hexamethyldisilazide have been recommended in difficult situations. Selenenylating agents include PhSeCl and PhSeBr, and also the diselenide PhSeSePh, which is unsuitable for the reaction with ketone enolates[134]. The method tolerates acidic groups such as the hydroxyl[155-157,164,165], carboxyl[166] and sulfonamide[160] moieties provided that at least two equivalents of base are employed. The dehydrogenations of esters and lactones containing a variety of α-heteroatoms including oxygen[167], chlorine[167], nitrogen[168], sulfone sulfur[169] and phosphinate phosphorus[170,171] proceed normally (equation 26).

(Refs.170,171)

(26)
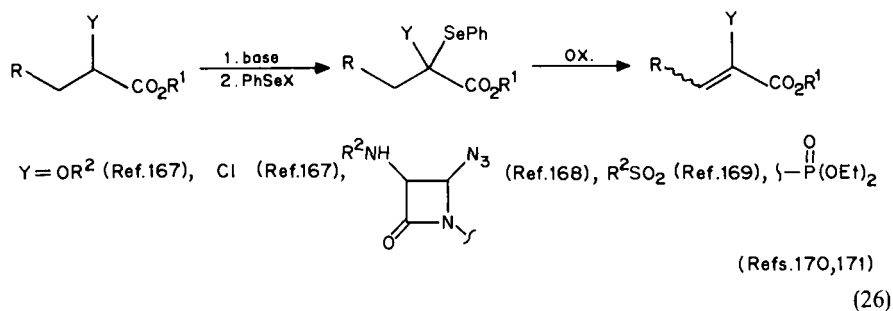
Grieco and coworkers[32,172,173] and Yamakawa and coworkers[174,175] reported the synthesis of α-methylene lactones from α-methyl lactones by selenenylation and selenoxide elimination, as in the example in equation 3. Unsaturated γ-lactones can be further transformed into furans by reduction with diisobutylaluminum hydride (DIBAL)[176,177] (equation 27[176]). Furans, pyrroles and thiophenes were prepared from the appropriate heterocyclic vinylidene esters (13) by selenenylation, oxidation and acid-catalysed double-bond isomerization[178] (equation 28).

(27)

(28)
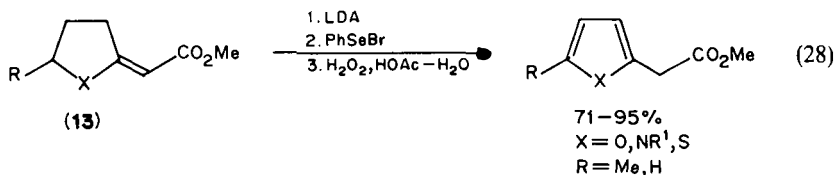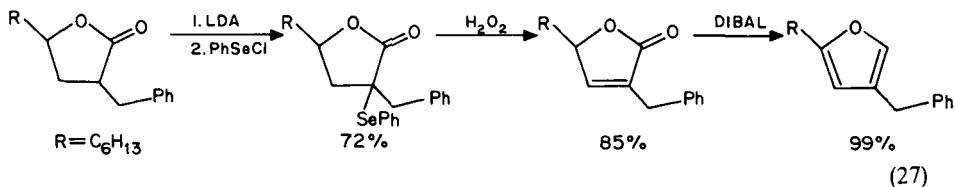
An interesting isomerization of the double bond of the enamine ester 14 was accomplished by selenenylation of the corresponding aluminum enolate generated with DIBAL, followed by selenoxide elimination[179] (equation 29). The simultaneous selenenylation and decarboxylation of ester 15 was performed without affecting the keto group[180] (equation 30).

(29)

65% overall

(30)

91%
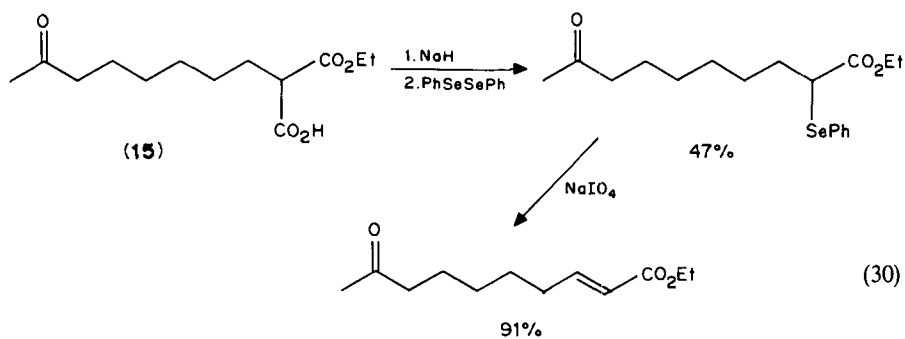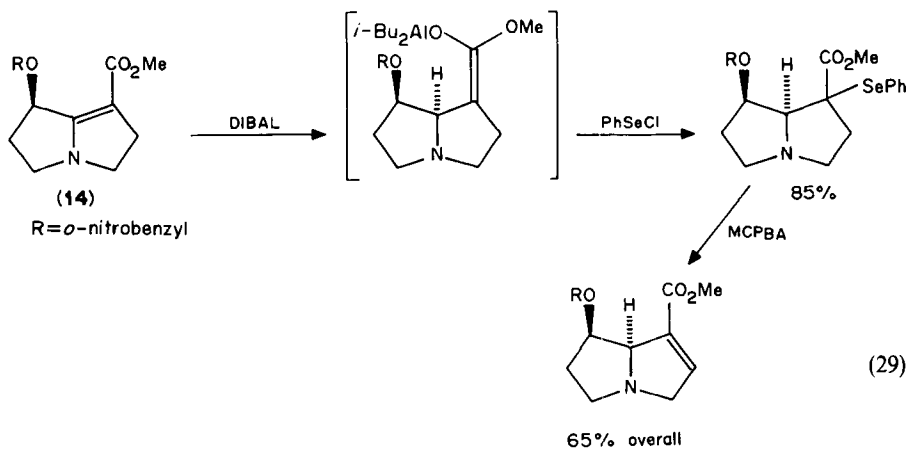
3. Amides and lactams

Relatively few examples of the dehydrogenation of amides and lactams are known. Zoretic and Soja[181,182] found that excess of base is required for the monoselenenylation of N-methylpyrrolidin-2-one. With only one equivalent of base, bisselenenylation dominates, as shown in equation 31. The dehydrogenations of several other γ-lactams[57,183,184],

(31)
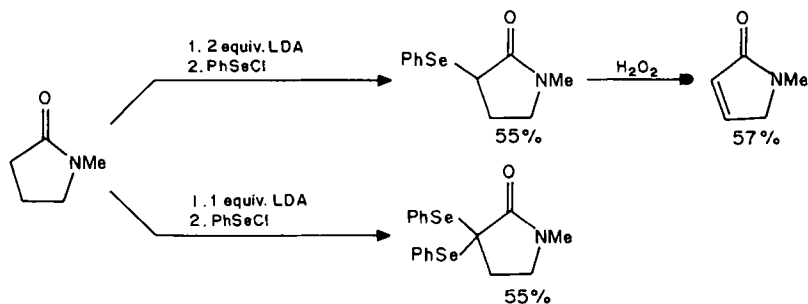
a δ-lactam[185] and a succinimide related to showdomycin[186] were reported. In addition, the α-selenenylations of N, N, N', N'-tetramethylsuccinamide[187] and an α, β-unsaturated amide[188,189] were accomplished in moderate yields, and the selenides shown in equation 12 were prepared from the parent bicyclic piperazinediones by treating their enolates with PhSeCl[107].

A different type of lactam selenenylation is displayed in equation 32, where **16** reacted directly with PhSeCl with concomitant cyclopropane ring opening, chlorination and elimination of a benzylthio moiety[190] (equation 32).

A reaction scheme showing compound (16) reacting with PhSeCl to give a 62% product, then with H$_2$O$_2$ to give a 100% product. (equation 32)
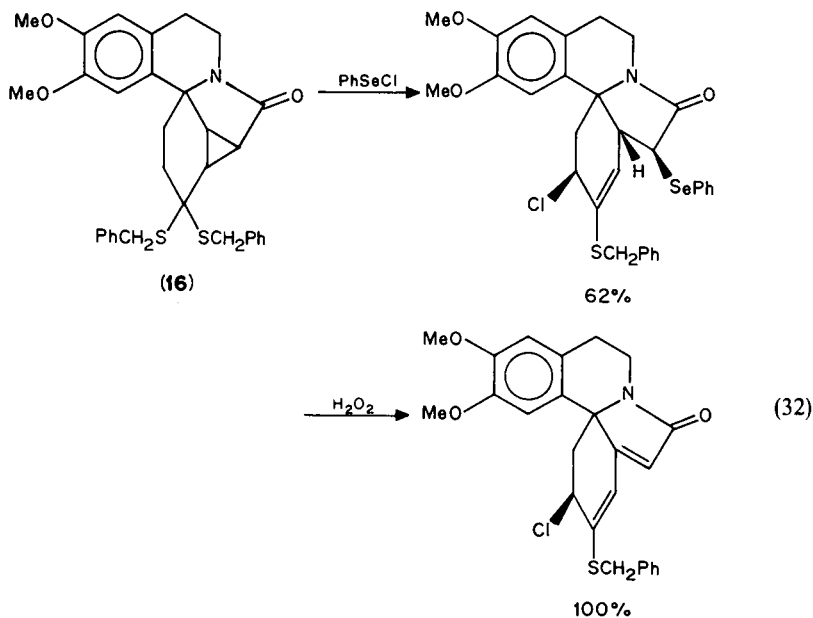
4. β-Dicarbonyl compounds

Numerous β-dicarbonyl compounds have been successfully dehydrogenated by α-selenenylation followed by selenoxide elimination. Examples include diketones[133,134,191,192], keto aldehydes[192–194], keto esters and lactones[133,134,165,191,192], keto lactams[195] and diesters[95,196]. As a result of the greater acidity of β-dicarbonyl compounds, milder bases such as pyridine[106,192,193], triethylamine[194] and KF–Celite[197] can be used in the selenenylation step, although sodium hydride[133,134,191,195], LDA[165,198] and even n-butyllithium[95,196] are also effective. The electrophilic reagent is typically PhSeCl or PhSeBr. In an illustrative example, Renga and Reich[191] prepared 2-acetylcyclohexen-2-one from the corresponding saturated diketone in excellent yield, as shown in equation 33.

$$\text{1. NaH} \quad \text{2. PhSeCl} \quad \text{3. H}_2\text{O}_2$$

79–85%   (33)
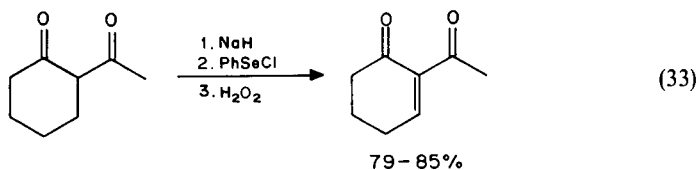
Other selenenylation procedures applicable to β-dicarbonyl compounds include the use of selenenamides[58], elemental selenium followed by methyl iodide[199] and PhSeSePh either electrolytically[154] or in the presence of selenium dioxide[153]. These processes are analogous to those depicted in equations 22 and 25.

The elimination step can be effected by the usual oxidative techniques via the selenoxide, or by a non-oxidative procedure in which the starting material is converted directly into the unsaturated product with excess PhSeCl in pyridine[192] (e.g. equation 34). One example of a similar non-oxidative elimination has also been reported in the case of an isolated aldehyde[200].

$$\text{(34)}$$
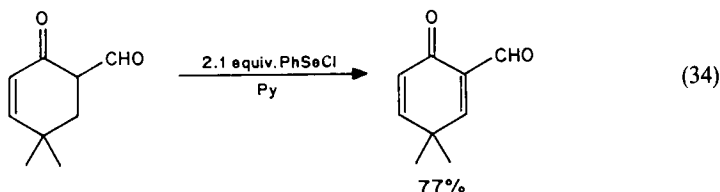
The dianion from the β-keto lactone **17** underwent chiefly γ-selenenylation, although significant reaction also occurred at the α-position[201,202] (equation 35).

An anomalous, although potentially useful, selenenylation was observed with the diketo lactone **18**, where accompanying fragmentation produced the α-phenylseleno enone **19**[203] (equation 36).

$$\text{(35)}$$

$$\text{(36)}$$
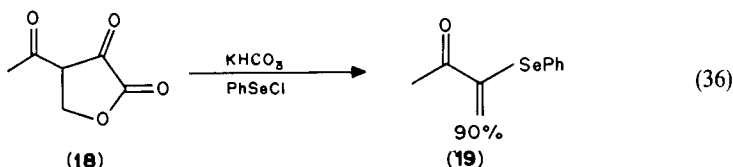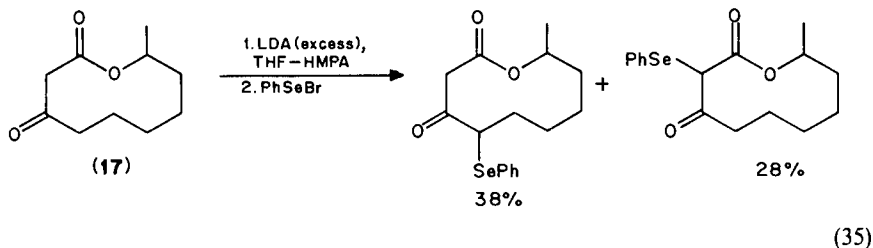
5. Enol acetates, enol silyl ethers, enamines and related compounds

As shown in equation 19, unsymmetrical ketones can be selenenylated on their less substituted flank via their kinetic enolates. On the other hand, enol acetates and enol silyl ethers can be prepared from ketones on the thermodynamically favored more substituted side. Their selenenylation with an appropriate electrophile therefore permits the synthesis of α-seleno ketones (and hence enones) which are regioisomers of those obtained via equation 19.

Enol acetates can be selenenylated in this manner by their sequential treatment with methyllithium and PhSeBr[133], by their direct reaction with benzeneselenenyl acetate

(PhSeOAc)[49] or trifluoroacetate (PhSeOCOCF$_3$)[30,133,134,204] and electrochemically with PhSeSePh[205,206] (equation 37). Methyl ketones afford α-selenomethyl derivatives via the reaction of their enol acetates with PhSeCl[207,208].

$$\tag{37}$$

The enol silyl ether derivatives of ketones[209-213] or aldehydes[209,214] are typically selenenylated with PhSeCl or PhSeBr, and also with PySeBr (11)[96]. An example of the preparation of the more substituted enone from an unsymmetrical ketone in this manner is given in equation 38[213].

80% overall

$$\tag{38}$$

Danishefsky and coworkers demonstrated that the selenenylated products of dienol silyl ethers are useful in Diels–Alder reactions[215-217]. The α-seleno ketone **20** in equation 39 was resilylated to give the highly functionalized diene **21**[216,217], whereas the similar ketone **22** constitutes a valuable dienophile in which the selenium moiety provides a latent double bond through subsequent selenoxide elimination[215] (equation 40). Compound **22** thus represents a divinyl ketone equivalent.

Cyclopropyl silyl ethers (**23**) undergo electrophilic ring opening with PhSeCl and TiCl$_4$ catalyst to afford β-seleno ketones, as shown in equation 41[218].

$$\tag{39}$$

82%   80%

(20)   **(21)**

(40)

(41)

R=H: 69%
R=Me:88%

(23)

Enamines[219-222], enamides[223], enol boranes[224], enol ethers[183,225,226] and ketals[225,227] all react with electrophiles such as PhSeCl to provide the corresponding selenenylated products. Several aldehydes were thus dehydrogenated by subsequent selenoxide elimination[183,219] and an example is given in equation 42[219]. The enol ether **24** was converted into the naphthol **26** via its α-seleno ketone **25** (equation 43)[226].

74–94%

44–80%

(42)

(24)

74%

(25)

62%

(26)

(43)
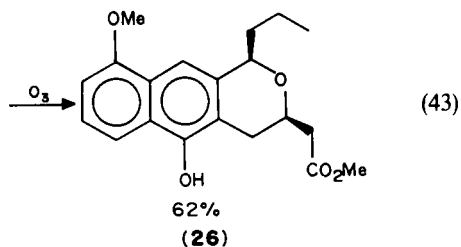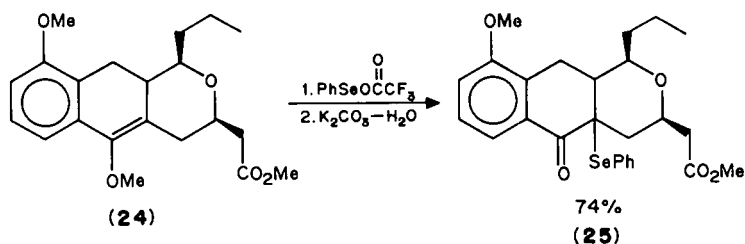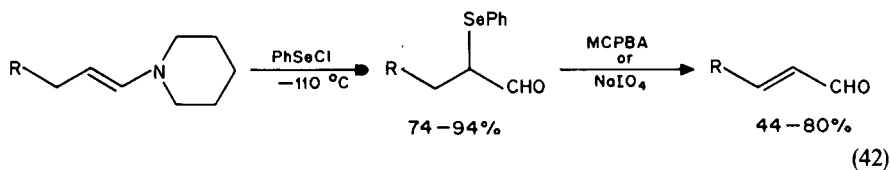
B. With Selenium Dioxide, Benzeneseleninic Anhydride and Benzeneseleninyl Chloride

1. Selenium dioxide

It may be argued that selenium dioxide was the first selenium-containing reagent to find widespread application in organic synthesis. Its usefulness as an oxidizing agent has long been appreciated and its properties have been thoroughly reviewed[228-233]. A discussion of its use as a dehydrogenating agent for carbonyl compounds, and other applications described in other sections, will therefore be brief and confined to recent illustrative examples.

Instances where carbonyl compounds are smoothly dehydrogenated with selenium dioxide are relatively rare and the presence of additional functional groups capable of conjugating with the newly formed double bond generally improves the yields (e.g. equations 44[234] and 45[235]). Attendant side reactions are common and may include more extensive dehydrogenation (e.g. equation 46[236]) or concomitant oxygenation (e.g. equation 47[237]). In some cases, of course, such further reactions may be desirable (see Sections V.B, C and F).

(44)

(45)

(46)

$$(47)$$

53%
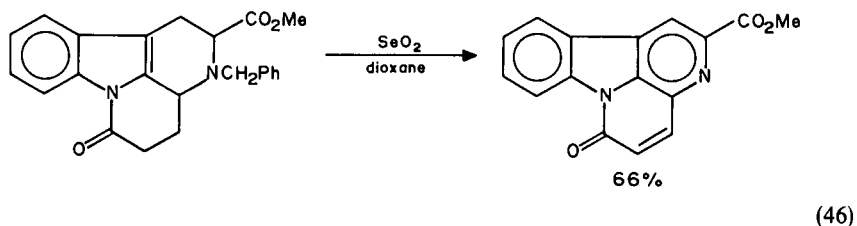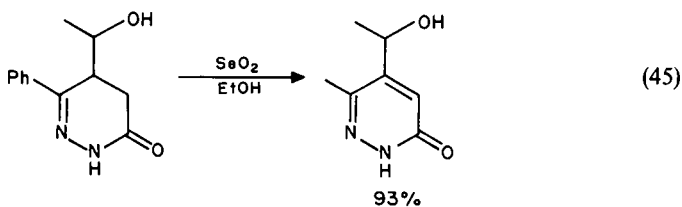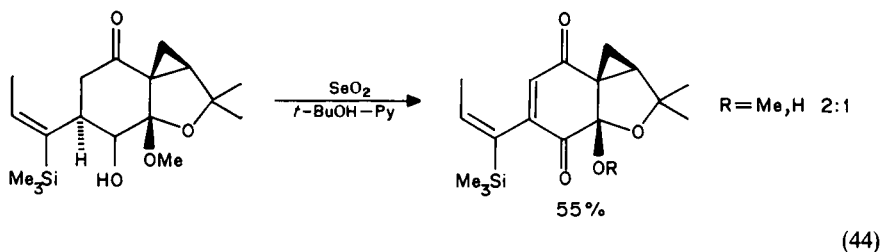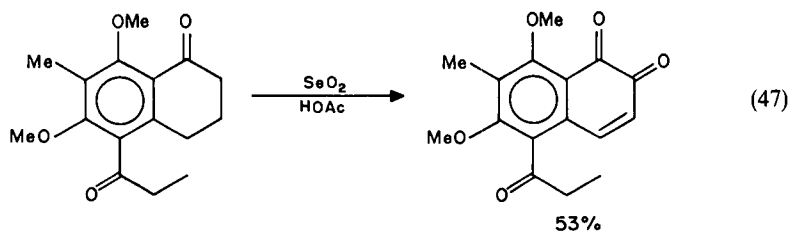
2. Benzeneseleninic anhydride

The use of benzeneseleninic anhydride (BSA) (27) as a reagent for the dehydrogenation of carbonyl compounds was first reported by Barton. For instance, 3-cholestanone and its Δ^1 and Δ^4 derivatives all produced the corresponding dienone 28 in high yield when heated with BSA in chlorobenzene[238,239] (equation 48). Since BSA also oxidizes alcohols to ketones (see Section X.A), it is possible to convert cholestan-3-ol and related alcohols directly into the dienones in one step[240]. In general, BSA is a cleaner reagent than selenium dioxide, although under forcing conditions the formation of side products can occur. For example, A-nordiketones were produced along with the expected enone product in the case of 4,4-dimethyl steroidal ketones such as α- or β-amyrone.

$$(48)$$
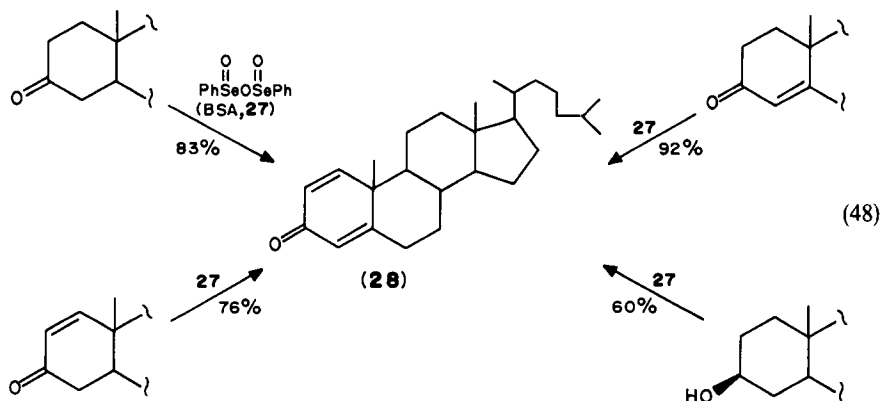
An attractive feature of this method is that BSA can be employed in catalytic amounts in the presence of a co-oxidant such as iodoxybenzene or m-iodoxybenzoic acid[241,242]. These reagents regenerate the anhydride from reduced selenium byproducts as they are formed, and PhSeSePh may also be used as the catalyst as it too is oxidized to BSA under these conditions.

Several other types of ketones[242-244], and also lactones[245-248] and lactams[249-250], were similarly dehydrogenated with BSA and representative examples are shown in equations 49[244], 50[248] and 51[250].

$$(49)$$

94%

$$(50)$$

$$(51)$$

R=C$_8$H$_{17}$: 88%

R=OAc : 64%
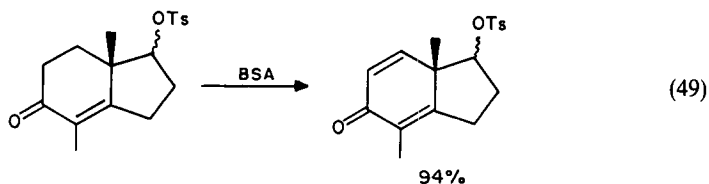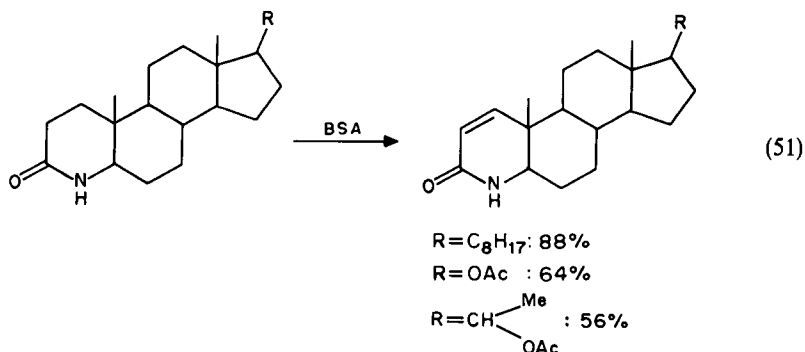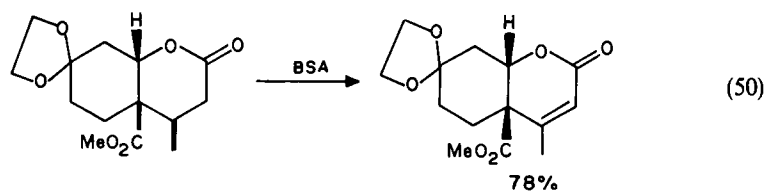
R=CH$\diagdown$$^{Me}_{OAc}$: 56%

Benzeneseleninic anhydride and the corresponding seleninic acid (PhSeO$_2$H) serve as useful reagents for the dehydrogenation and side-chain degradation of cholic acids via the 4,5-dihydrooxazole derivatives **29**[251] (e.g. equation 52).

$$(52)$$

3. Benzeneseleninyl chloride

Benzeneseleninyl chloride (**30**) was briefly investigated as a possible reagent for the dehydrogenation of ketones and esters[134] according to equation 53. However, difficulties in the preparation and handling of this compound have precluded its general acceptance in this regard.

$$(53)$$

IV. DEHYDROGENATION OF OTHER FUNCTIONAL GROUPS

A. Nitrogen Compounds

Apart from carbonyl groups, other functionalities which stabilize an adjacent carbanion can be selenenylated and dehydrogenated by means of selenoxide eliminations. Thus, aliphatic nitro compounds were converted into their α-seleno derivatives[252–255] and subsequently to nitroolefins by oxidation of the selenide moiety[253,254]. Aldol condensations of the selenides with aldehydes can be performed prior to oxidation[254], thereby providing hydroxylated nitroolefins as shown in equation 54.

Similarly, carbanions derived from N-nitroso compounds[256,257] and amidines[258] were selenenylated and dehydrogenated as indicated in equations 55[257] and 56[258].

$$ \text{(54)} $$

$$ \text{(55)} \qquad 64\% $$

$$ \text{(56)} $$

$$ n = 1-3 \qquad\qquad 60-99\% $$

B. Nitriles

Nitriles, like lactams (see Section III.A.3), require the presence of an excess of base[259,260]. Monoselenenylation followed by selenoxide elimination provides a convenient route to α,β-unsaturated nitriles[259–261]. The latter compounds can in turn be dehydrogenated to diene nitriles in high yield (equation 57[262]).

$$ \text{(57)} $$

R=H, R'=Ph: 63%
R=Ph, R'=H: 82.8%

C. Phosphorus Compounds

Phosphoranes[263-267], phosphonates[170,171,268] and phosphine oxides[265,269] have been selenenylated with selenenyl chlorides and bromides, and with elemental selenium and methyl iodide[268]. In several instances the corresponding unsaturated compounds were prepared by selenoxide elimination[170,171,265,266,268]. Examples are given in equations 58[266], 59[268] and 60[265].

(58)

(59)

(60)

D. Sulfur Compounds

Carbanions stabilized by sulfones[169,270,271], sulfoxides[134] and sulfides[268,272] were selenenylated in much the same way and dehydrogenated via the usual oxidative procedures[134,169,268]. Oxidation of the α-seleno-α-silyl sulfone 31 afforded the carboxylic acid 32 instead of the elimination product[270] (equation 61).

(61)

V. OXYGENATION REACTIONS

A. Oxyselenenylation and Oxytellurenylation

1. Olefins

Olefins react with various selenium electrophiles to produce 1,2-adducts via seleniranium ion intermediates (33) (equation 62). This may be exploited in the introduction of a new oxygen function into the olefin in either of two ways. First, if the electrophile is a selenenic* acid[38,82,273,274] or a derivative such as the selenenyl acetate PhSeOAc[40] or the trifluoroacetate PhSeOCOCF$_3$[275,276], then direct incorporation of the oxygen function occurs.

Alternatively, the olefin may be treated with other selenenic electrophiles in the presence of a nucleophilic oxygen-containing solvent such as water or an alcohol. The solvent then intercepts the bridged intermediate 33 and so affords the β-oxygenated selenide (equation 62). Similarly, electrophilic tellurium species produce β-oxygenated organotellurium products from olefins. The numerous types of electrophiles which have been used in this manner are listed in Table 1.

$$\tag{62}$$

In general, oxyselenenylation proceeds stereospecifically via *anti* addition. Markovnikov adducts usually predominate, but their regioisomers can form in substantial amounts. Since the adducts undergo selenoxide elimination away from the oxygen function (cf. equation 5), the method provides an excellent synthesis of allylic alcohols, ethers and acetates (equation 63).

$$R \diagup \diagdown \diagup R^1 \xrightarrow[\substack{\text{oxytellurenylation} \\ 2.\,\text{oxidation}- \\ \text{elimination}}]{\substack{1.\,\text{oxyselenenylation} \\ \text{or}}} R \diagup \diagdown \diagup R \qquad R^2 = H,\text{alkyl},Ac \tag{63}$$

Under some circumstances the oxygen function in the initial 1,2-adduct may be further oxidized to a carbonyl group. Kuwajima and coworkers found that the putative electrophile PhSeOSePh[306-309] [generated *in situ* from the oxidation of PhSeSePh with

---

*Selenenic acids RSeOH, and also the selenenyl acetate and trifluoroacetate, are unstable and must be generated *in situ*. The acids disproportionate readily according to the equation[38,82] $3RSeOH \rightleftharpoons RSeO_2 + RSeSeR + H_2O$ and dehydrate spontaneously to the anhydrides RSeOSeR[277,278]. The precise nature of the active electrophile in a given reaction is therefore equivocal and it may be present in only minute amounts[279]. However, such species are often designated as the parent selenenic acids for the sake of convenience.

TABLE 1. Reagents for oxyselenenylation and oxytellurenylation

Electrophilic reagent	Type of oxygen function	Ref.
PhSeCl	OH	208
	OR	40, 280–283
PhSeBr	OH	59
	OR	40, 284
MeSeBr	OH	59
PySeBr (11)	OR	101
PhSeN⟨⟩ (N-PSP) (34)	OH	285–288
	OR	286, 289
PhSeCN–CuCl$_2$	OH, OR, OAc	290, 291
RSeOH or RSeOSeR from:		
(a) RSeO$_2$H + H$_3$PO$_2$	OH	273, 274
(b) PhSeSePh + H$_2$O$_2$	OH	82
(c) PhSeSePh + PhSeO$_2$H	OH	38
PhSeSePh, anodic oxidation	OH, OR, OAc	205, 206, 292, 293
PhSeSePh + Cu(OAc)$_2$ or		
Pb(OAc)$_2$, HOAc	OAc	294
PhSeSePh, BrNHCOMe	OR	295
PhSeOAc from:		
(a) PhSeBr, KOAc, HOAc	OAc	40, 49, 50, 296
(b) PhSeCl, NaOAc, HOAc	OAc	297, 298
(c) PhSeCl, LiClO$_4$, HOAc	OAc	299
(d) PhSeNMe$_2$, Ac$_2$O	OAc	58
(e) PhSeO$_2$H, HOAc	OAc	40, 300
MeSeOAc from:		
(a) Me$_2$Se=O, HOAc	OAc	301, 302
(b) MeSeCH$_2$OAc, H$_2$O$_2$, HOAc	OAc	303
PhSeOCOCF$_3$ from		
PhSeCl or PhSeBr +		
AgOCOCF$_3$	OCOCF$_3$, OH^a	84, 275, 276, 296, 304
PhTeTePh–Br$_2$	OR	116, 118, 119
PhTeTePh–CuCl$_2$	OR	116
PhTeCN–CuCl$_2$	OR	116
PhTeBr$_3$^{b}	OR	116, 118, 119
TeCl$_4$	OR	305

^{a} After hydrolysis of the trifluoroacetate group.
^{b} The 1,2-adduct RO—C̶—C̶—TeBr$_2$Ph can be reduced to the telluride with N$_2$H$_4$, Na$_2$S$_2$O$_3$, Na$_2$S or NaHSO$_3$, or hydrolysed to the telluroxide with NaOH.

BSA (27) or t-butyl hydroperoxide] and PhSeOSnBu$_3$[308,310] [from PhSeSePh, Br$_2$ and (Bu$_3$Sn)$_2$O] afford α-seleno ketones and aldehydes from olefins (equation 64). The former products dominate in DMSO[306], whereas the latter are preferred in the presence of an already present allylic oxygen function[307,309].

(64)

The conversion of terminal olefins into 1-phenylselenoalkan-2-ones was also accomplished through the sodium periodate oxidation of their Markovnikov alkoxyselenenylation products[311] and by the DMSO-mediated oxidation of their PhSeBr adducts[312].

Oxyselenenylation of olefins may also be performed with nucleophilic selenenium species. Olefins react with copper(II) halides and potassium selenocyanate (KSeCN) in alcoholic media to produce β-alkoxy selenocyanates[313] (equation 65). The corresponding β-halo derivatives are formed in the absence of alcohols. A related procedure involves thallation of terminal olefins followed by treatment with KSeCN[314].

$$\text{(65)}$$

2. Enol ethers

The oxyselenenylation of enol ethers with alcohols followed by selenoxide elimination provides a convenient route to dihydropyran acetals[315-319] (e.g. equation 66[318]). The method constitutes an effective glycosylation procedure when the alcohol is an appropriate carbohydrate[51,320]. Ketene acetals are formed similarly. When they are derived from allylic alcohols and used in conjunction with a Claisen rearrangement[44-47], they provide access to γ,δ-unsaturated esters or acids (e.g equation 67[44]). Hydrolysis instead of

$$\text{(66)}$$

75%

$$\text{(67)}$$

99%

96%

oxidation–elimination of the acetal **35** affords synthetically useful phenylselenoacetaldeh-yde (**36**)[321] (see Section XVII.A) via equation 68.

(68)

3. Acetylenes

Acetylenes produce α-seleno ketones (and hence enones) when treated with PhSeOCOCF₃ followed by alkaline hydrolysis[134,276] (equation 69).

(69)

B. Allylic Oxidation

Selenium dioxide is a valuable reagent for the allylic oxidation of olefins, and numerous examples are known. The products are usually allylic alcohols, but enals[322,323], esters[324] or enones[325] can also be formed, depending on the nature of the olefin and the exact conditions. The rules formulated by Guillemonat[326] can be used to predict the site of oxidation in unsymmetrical olefins. More recent studies by Sharpless and coworkers[327-330] and others[331,332] indicate that the oxidation proceeds by an ene reaction followed by the [2, 3] sigmatropic rearrangement of an intermediate seleninic acid (**37**) (equation 70). Alternative pathways involving ionic or radical intermediates have been proposed in some cases[330,331].

(70)

An improved procedure employing *t*-butyl hydroperoxide and catalytic (or stoich-iometric) quantitites of selenium dioxide avoids the normal side reactions stemming from the formation of selenium-containing by products[333], and has found several recent applications[236,334-338] (e.g. equation 71[338]). The addition of silica gel to the reaction mixture has been recommended in some cases[339]. Selenium dioxide oxidations are often performed under acidic conditions, but pyridine is a suitable solvent if a basic medium is required[325,340]. Enones[341] and α, β-unsaturated esters[342] can be γ-hydroxylated as in the

example in equation 72^{342}. Dehydrogenation and aromatization (see Section III.B.1) sometimes occur simultaneously^{236,334,343} (equation 73^{236}) with allylic oxidation. Acetylenes furnish propargylic alcohols and ketones with selenium dioxide and t-butyl hydroperoxide^{344} (equation 74).

(71)

(72)

(73)

(74)

An alternative reagent to selenium dioxide was recently reported for the allylic oxidation of olefins. This consists of catalytic amounts of PySeSePy (12) in the presence of iodoxyarenes as indicated in the example in equation 75[345].

$$(75)$$

$$95\%$$

C. Benzylic Oxidation

Selenium dioxide oxidizes heterocyclic aryl methyl groups to aldehydes[346-349]. The presence of an electron-withdrawing group increases the reactivity of a methyl group in the *para*-position and so permits the selective oxidation of one of several methyl substituents (e.g. equation 76[348]).

$$(76)$$

$$80\%$$

Benzylic hydrocarbons are oxidized to aldehydes or ketones when heated with BSA (27)[245,350] (equation 77), and benzyl halides afford aldehydes when treated with dimethyl selenoxide (38) or $PhSeO_2H$[351] (equation 78).

$$ArCH_2R \xrightarrow[\Delta]{BSA} Ar\overset{O}{\overset{\|}{C}}R \qquad (77)$$

$$ArCH_2X \xrightarrow[\substack{\text{or } PhSeO_2K, \\ K_2HPO_4}]{\substack{MeSeMe\ (38), \\ K_2HPO_4}} ArCHO \qquad (78)$$
$$X = Cl, Br$$

D. Acetoxymethylation

The acetoxymethylation of toluene and other arenes with tellurium dioxide in acetic acid has been reported by Bergman and Engman[352,353] (equation 79). The reaction presumably proceeds by initial oxidation of the acetic acid prior to attack on the arene. It is interesting that related oxidants such as tellurium trioxide, the hydrate $Te(OH)_6$ and selenium dioxide all effect side-chain oxidation exclusively instead of acetoxymethylation under these conditions[353].

$$o:m:p = 50:12:38 \tag{79}$$

E. Oxidation of Phenols

Barton and coworkers reported that phenols are oxidized to orthoquinones[354,355] or hydroxydienones[356,357] with BSA (27) (e.g. equations 80[355] and 81[357]). In some instances, phenolic coupling products were also observed (see Section XI.E.3). Several polyaromatic hydrocarbon quinones were prepared from phenolic precursors[358,359] with this procedure, and the naphthol **39** yielded the corresponding hydroxyenone **40** with high regioselectivity[360] (equation 82). A polymer-supported seleninic acid was recently employed as an alternative to BSA for the similar oxidation of phenols[361].

$$62\% \tag{80}$$

$$75\% \tag{81}$$

$$\begin{array}{cc} \textbf{(39)} & \begin{array}{c} 85\% \\ \textbf{(40)} \end{array} \end{array} \tag{82}$$

F. Oxidation of Ketones

1. α-Oxygenation

The oxidation of ketones to α-diketones with selenium dioxide is well known and literature examples abound. Although several rationales for this useful reaction have been proposed, the most recent study provided evidence for the pathway in equation 83[362]. In addition, several methyl ketones were converted into the corresponding keto aldehydes[363]

in this fashion and equation 47 provides an example where α-diketone formation was accompanied by dehydrogenation.

$$(83)$$

Yamakawa and coworkers[243,364,365] employed BSA for the angular α-hydroxylation of ketones as in equation 84[364], while others have noted γ-hydroxylation during the reactions of BSA with an enone[247], and an α,β-unsaturated lactone which was itself formed by the dehydrogenation of the parent compound[246].

$$(84)$$

70%

Carbonyl compounds are α-acetoxylated with tellurium dioxide or trioxide in acetic acid in the presence of LiBr[353] (e.g. equation 85).

$$(85)$$

38—47%

2. Baeyer–Villiger reactions

The Baeyer–Villiger oxidation of cyclic ketones was mentioned as a side reaction during their dehydrogenation (Section III.A.1) via selenenylation and oxidation–elimination. In some cases lactone formation occurs at a rate which is competitive with that of selenoxide elimination and so the method has preparative value in providing direct access to unsaturated lactones from cyclic ketones[69,94,114,142,143]. Under these conditions, the selenenic acid byproduct of the elimination is oxidized to the corresponding perseleninic acid (41), which acts as the actual Baeyer–Villiger reagent. Lactone formation is especially prevalent when hydrogen peroxide is present and may be suppressed with other oxidants, as in the examples given in equation 86[69]. The perseleninic acid can also be generated from $PhSeO_2H$ and hydrogen peroxide and used *in situ* for the efficient transformation of cyclic ketones to lactones without accompanying dehydrogenation[366] (equation 87).

$$\begin{array}{c} O \\ \parallel \\ PhSeOOH \end{array}$$

(41)

$$(86)$$

$$(87)$$

Other effective Baeyer–Villiger reagents are a polymer-bound perseleninic acid[361] and selenium dioxide–hydrogen peroxide mixtures[367-371] in which the perseleninic acid **45** is a probable intermediate (e.g. equation 88[371]). The use of the latter reagent often results in relatively complex product mixtures.

$$\underset{(45)}{HOSeOOH}$$

$$(88)$$

G. Epoxidation, Hydroxylation and Acetoxylation of Olefins

1. Epoxidation

Perseleninic acids smoothly epoxidize olefins[38,82,372-375] (equation 89) even in catalytic amounts. They can be generated *in situ* for this purpose in the same way as when they are required for Baeyer–Villiger reactions. As with other peracid-mediated epoxidations, more highly substituted olefins react more efficiently than less substituted ones[372].

$$(89)$$

2. Hydroxylation

Olefins are oxidized to vicinal *cis*-diols with diphenyl or methyl phenyl selenoxide in the presence of osmium tetroxide catalyst[376]. The selenoxide too can function catalytically when singlet oxygen is passed through the reaction mixture (equation 90).

$$
\begin{array}{c}
\text{PhSeMe(cat),}\\
\xrightarrow{\text{Os}_4\text{(cat.),}}\\
{}^1\text{O}_2
\end{array}
\tag{90}
$$

Polymer-bound selenoxides[150] or seleninic acids[361] catalyse the conversion of olefins to diols when hydrogen peroxide is used as the co-oxidant. In the latter case the products were *trans*-diols, suggesting an epoxide intermediate.

3. Acetoxylation

Vicinal diacetoxylation of olefins takes place with tellurium dioxide and LiBr in acetic acid[305]. The *syn*-stereospecificity of the reaction was demonstrated by the fact that *cis*- and *trans*-but-2-ene produced predominantly *mesó*- and *d,l*-diacetates, respectively. 1,3-Dienes afforded mixtures of 1,2- and 1,4-diacetoxy products[377] (equation 91), with ratios of up to 9:1 in favor of the 1,4-isomer realized with a 5:1 excess of LiBr over TeO$_2$.

$$
\xrightarrow[\text{HOAc, Ac}_2\text{O}]{\text{TeO}_2, \text{LiBr}}
\tag{91}
$$

H. Oxidation of Selenides

Although the oxidation of selenides usually leads to selenoxide elimination, under some circumstances oxygenated products result instead. Several synthetically useful adaptations of the latter type of process are described below. The preparation of allylic alcohols from the oxidation and [2, 3] sigmatropic rearrangement of allylic selenides is discussed in Section XVI.A.

1. Pummerer reactions

As mentioned in Section III.A.1, unwelcome Pummerer reactions during the dehydrogenation of ketones can be suppressed by the use of basic conditions. In situations where they are desired, they occasionally take place spontaneously in preference to selenoxide eliminations[378], but more often must be promoted by electrophiles such as acetic anhydride[167,379-381] or BSA[223,382]. Pummerer reactions have proved useful for introducing new keto[223,381,382] or acetoxy groups[167,379,380] into the substrate, as shown in equation 92. A specific example of the preparation of an α-diketone from an α-seleno ketone by this method is presented in equation 93[381].

$$
\tag{92}
$$

$$(93)$$

58%

α-Silyl selenoxides undergo Pummerer rearrangements and provide access to silyl ketones[383], ketones[384] and aldehydes[385,386] (equation 94).

$$(94)$$

$R^1 = SiMe_3$, alkyl, H

2. Via selenones and tellurones

Selenones and tellurones react readily with nucleophiles in substitution reactions because the anions $RSeO_2^-$ and $RTeO_2^-$ are excellent leaving groups. These compounds are accessible from the oxidation of selenides and tellurides with excess of strong oxidants such as MCPBA. When primary or secondary alkyl phenyl selenides[283,387] or tellurides[117,283] are thus oxidized in methanol solvent, solvolysis occurs *in situ* to afford methyl ethers in high yields (equation 95). Rearranged products result when β-substituents with high migratory aptitudes (e.g. phenyl) are present, and cyclic compounds undergo ring contractions (see Section XVI.C.2).

$$\begin{array}{c} RSePh \\ or \\ RTePh \end{array} \xrightarrow[\text{MeOH}]{\text{excess MCPBA}} ROMe \qquad (95)$$

3. In 1,2-carbonyl transpositions

α-Seleno ketones produce α-ketals when oxidized with MCPBA[129] or when treated with mercury(II) perchlorate[128] in methanol. This α-oxygenation procedure can be used in conjunction will deoxygenation of the original carbonyl group to effect an overall 1, 2-carbonyl transposition[129] (equation 96).

75% overall

$$(96)$$

1. Hydrolysis of Vinyl Selenides

Vinyl selenides are easily obtained from many different types of precursors[388] and their hydrolysis provides an alternative method for introducing an oxygen function in the form of a ketone or aldehyde. The hydrolysis requires the presence of a catalyst such as $HgCl_2$[269], CF_3CO_2H[269], HCl[389], $HBr-DMSO$[390] or $HClO_4$[111]. Other reagents for this purpose include Br_2-EtOH[391] and BSA[392], which produces α-seleno ketones. Examples are shown in equations 97[389] and 98[392].

(97)

(98)

VI. AMINATION AND AMIDATION REACTIONS

A. Of Olefins

1. 1,2-Additions of selenenic electrophiles

In a manner reminiscent of oxyselenenylation, the reaction of olefins with selenium electrophiles in the presence of nitrogen nucleophiles results in the incorporation of both species into the olefin. Uemura and coworkers[53,393] treated a series of alkenes and cycloalkenes with PhSeCl in the presence of nitriles to generate the presumed intermediate **46**, followed by hydrolysis to afford β-amido selenides (**47**) (equation 99). The latter products were further transformed into allylic or saturated amides by oxidation[52,53] or reduction[53], respectively. The selenium-induced amidation of dienes is accompanied by cyclization (see Section IX.G). An electrochemical variation of this method has been reported[394] and consists in the anodic oxidation of PhSeSePh is acetonitrile in the presence of the olefin. Products **47** (R = Me) were obtained in generally high yields.

(99)

The sequential reaction of cyclohexene with RSeBr, sodium azide and lithium aluminum hydride provides an example of a potentially useful amination method[59] (equation 100). Oxidation instead of reduction of the β-seleno azide **48** also provides access to unsaturated azides (see equation 7). A different approach, shown in equation 101, affords tosylamides from olefins with PhSeSePh and Chloramine-T[395].

(100)

R=Ph: 80%
R=Me: 93%

(101)

2. Allylic amidation

Sharpless and coworkers[160,396] reported that the selenium diimide reagent **49** (and also its sulfur analog) smoothly effects the allylic amidation of olefins and acetylenes. The diimide resembles selenium dioxide in its mode of action, which involves an ene reaction followed by a [2, 3] sigmatropic rearrangement (cf. equation 70). A typical example is provided in equation 102[396]. The reaction of 1, 3-dienes with **49** furnished 1, 2-diamidation products in modest yields[397].

82%

(102)

Rearranged allylic tosylamides[398] or carbamates[399-402] were obtained by Hopkins and coworkers from allylic selenides via their reaction with Chloramine-T or N-chlorocarbamates. The [2,3] shift of a selenium imide (**50**) was implicated in this process[399] (equation 103) and applications include the preparation of β, γ-unsaturated amino acids[401] and optically active amino acids from chiral allylic selenides[402].

(103)

B. Of Phenols and Catechols

When the Barton procedure for the oxidation of phenols with BSA is carried out in the presence of hexamethyldisilazane, selenoimides such as **51** are produced[403,404]. These can be reduced to the corresponding anilines or anilides as indicated in equation 104. Catechols undergo amination when oxidized with diphenyl selenoxide (**52**) in the presence of aniline[405] (equation 105).

(104)

(105)

C. Of Michael Acceptors

Selenenamides are sufficiently nucleophilic to attack Michael acceptors such as enones[58], enals[406] or dimethyl acetylenedicarboxylate[407]. After intramolecular selenenylation of the α-position, 1,2-adducts are obtained. These can be further converted into α-seleno enones by deamination (equation 106[58]), or into unsaturated amines by selenoxide elimination (see equation 8).

(106)

88%

VII. HALOGENATION

A. By Electrophilic Addition of Selenium or Tellurium Halides to Olefins and Acetylenes

1. Olefins

In the absence of other nucleophiles, selenenyl halides add to olefins to furnish β-halo selenides (equation 107). The direct halogenation of the olefin is thus achieved and the adjacent selenium residue provides the means for further transformations. The mechanism, stereochemistry and regiochemistry of these processes have been extensively studied[62,63,408,409] and reviewed[410]. In general they are highly *anti*-stereospecific, but their regiochemistry depends on the nature of the olefin and the conditions employed. Complementary regioisomers are sometimes available in a high state of purity by choosing conditions which favor either the product of kinetic or that of theromodynamic control. Stereospecific reactions are also observed with aryl- or alkyl-selenium trichlorides[411], whereas tellurium electrophiles (e.g., $TeCl_4$, $RTeCl_3$) display more complex behavior[22,412], often producing both *syn*- and *anti*-adducts.

$$(107)$$

Numerous examples have been reported with selenenyl chlorides and bromides, and recently the first instance of an olefin fluorination was described with N-PSP **(34)** and pyridinium fluoride[286] (equation 108). The 1,2-addition of a selenenyl iodide to an olefin remains undocumented, although the electrophile PhSeI adds to hex-1-yne (see equation 113) and has found use in the cyclization of dienes (see equation 161).

80%

$$(108)$$

When the β-chloro- or bromo-selenides thus obtained are subjected to selenoxide elimination, vinyl or allyl halides are formed[62-66] (see Section II.A.3). Since the regiochemistry of the addition can sometimes be precisely controlled (see above), a choice of products is possible (e.g. equation 109[62]).

Enones undergo α-halogenation when treated with excess of PhSeCl or PhSeBr in pyridine[413] (equation 110). Isoprene gives mixtures of 1,2- and 1,4-addition products with PhSeCl, and their ratio is temperature dependent[414].

Engman has developed several synthetically useful procedures based on the reactions of tellurium tetrachloride with olefins. This reagent was used to prepare stereospecifically

(109)

X = Cl, Br   (110)

chlorohydrin esters and epoxides from allylic esters via the rearrangement depicted in equation 111[415]. The *syn*-addition of tellurium tetrachloride to *trans*-olefins followed by reduction with Na_2S and loss of tellurium from the resulting epitelluride intermediate provides a method for the *trans*-to-*cis* isomerization of the double bond[416] (equation 12). On the other hand, the equilibration of *cis–trans* mixtures of stilbenes with tellurium tetrachloride affords the pure *trans* isomers[417].

81%   (111)

(112)

2. Acetylenes

The additions of selenenyl halides to acetylenes produce β-halovinyl selenides[418] which can then be further transformed into other useful products. Most such additions have been restricted to chlorides and bromides, but one example involving a selenenyl iodide is given in equation 113[147].

$$\text{(113)}$$

98%

1,4-Dichlorobut-2-yne afforded highly functionalized 1,3-dienes when treated with PhSeCl or PhSeBr[419-421] (equation 114). The products proved of value in Diels–Alder reactions[420,421]. Similarly, the additions of PhSeCl to alkynols[422,423] and to the stannylynamine 53[424] furnished adducts of potential synthetic utility. In the latter example, elimination of the stannyl moiety occurred together with addition (equation 115). β-Halovinyl selenides were also prepared from the reaction of acetylenes with phenyl selenocyanate (PhSeCN) in the presence of $CuCl_2$ or $CuBr_2$ and triethylamine[425].

X=Cl: 75%
X=Br: 76%

X=Cl: 46%
X=Br: 68%

$$\text{(114)}$$

$$\text{(115)}$$

(53)

B. Allylic Halogenation

Hori and Sharpless reported that olefins are converted into rearranged allylic halides by their reaction with N-chlorosuccinimide (NCS) and catalytic amounts of PhSeCl or PhSeSePh[426] (e.g. equation 116). Allylic selenides are intermediates in this process and so they too produce allylic chlorides when treated with NCS[427].

$$
\text{(116)}
$$

The structures show a trisubstituted alkene reacting with NCS / PhSeSePh (cat.) / Py—CH$_2$Cl$_2$ to give two chlorinated products in a 96 : 4 ratio, 87%.

C. Halogenolysis of Selenides and Tellurides

The brominolysis of alkyl selenides with bromine[428–430] or NBS[428] was reported by Krief and coworkers. Secondary or tertiary alkyl selenides gave the best results[428] and the corresponding alkyl bromides were formed with inversion of configuration[430] (equation 117).

$$
\text{(117)}
$$

An alternative procedure consists of the alkylation of the selenide with methyl iodide, followed by displacement of the resulting selenonium salt with iodide ion[102,428,431] to provide primary alkyl iodides in high yield (equation 118[431]).

$$
\text{RSePh} \xrightarrow{\text{MeI}} \text{RSe}^{+} \overset{\text{Ph}}{\underset{\text{Me}}{}} \ \ \text{I}^{-} \xrightarrow{\text{NaI}} \text{RI} + \text{PhSeMe} \qquad \text{(118)}
$$

Vinyl selenides afford vinyl bromides on brominolysis[391] and alkyl phenyl or alkyl methyl selenoxides furnish alkyl chlorides and bromides when reacted with HCl or HBr, respectively[432]. A method for the vicinal cis-dichlorination of olefins[433], and procedures for the one-[428] and two-carbon[434] homologation of alkyl halides, are based on the halogenolysis of appropriate selenides. These are displayed in equations 119–121, respectively. It is interesting that the analogous dibromination in equation 119 gave trans- instead of cis-dibromides[433].

$$
\text{(119)}
$$

$$
\text{(120)}
$$

$$
\text{RX} \longrightarrow \text{RLi} \xrightarrow{\text{SePh}} \text{R} \diagup\diagdown \text{SePh} \xrightarrow{\text{Br}_2} \text{R} \diagup\diagdown \text{Br} \qquad \text{(121)}
$$

Alkyl halides are accessible from alkyl phenyl tellurides by halogenolysis with sulfuryl chloride, bromine and iodine, or via their telluronium salts, in a manner akin to equation 118[435]. Studies by Uemura and coworkers indicate that aryl-, vinyl- and alkyl-tellurium trihalides produce the corresponding organohalides with retention of configuration when they are photolysed in benzene[436,437] or when oxidized with *t*-butyl hydroperoxide[437,438]. The required vinyl- and alkyl-tellurium trihalide precursors were in turn obtained by the addition of $TeCl_4$ to acetylenes and olefins, respectively. Aryl-[439] and vinyl-tellurium[440] trichlorides were also converted into aryl and vinyl iodides and bromides by halogenolysis with iodine, bromine or NBS. In some cases, diaryltellurium dihalides can be used in place of the monoaryl trihalides[436,437,439].

Several illustrative examples are given in equations 122–124.

$$ArTeX_3 \xrightarrow[\substack{or \\ h\nu, C_6H_6}]{t\text{-BuOOH}} ArX \tag{122}$$

$$X = Cl, Br, I$$

$$ (123) $$

$$ (124) $$

D. Other Halogenation Methods

Selenium and tellurium halides are capable of halogenating arenes and certain other hydrocarbons. Electron-rich arenes are preferentially chlorinated at the *para*-position by PhSeCl[441] (equation 125) while anthracene and other aromatics produce mixtures of mono- and di-halo products with tellurium(IV) halides[442]. Also, substituted cyclo-heptatrienes furnish the corresponding benzyl chlorides with $TeCl_4$[443].

$$Y = Me, OH, OMe,$$
$$NHCOMe \tag{125}$$

An interesting fluorination technique employing SeF_4 or its pyridine complex was reported by Olah and coworkers[444]. This reagent converts ketones into *gem*-difluoroalkanes, carboxylic acids or anhydrides into acyl fluorides and alcohols into fluoroalkanes (equation 126).

Several heteroaromatic hydrazines have been oxidized with selenium dioxide in the presence of HCl and Cu_2Cl_2 to produce poor to moderate yields of aryl chlorides[445] (equation 127).

$$ \left. \begin{array}{c} R-\!\!\!\overset{\overset{\textstyle O}{\|}}{C}-\!\!\!R \\[2mm] RCO_2H \\[3mm] ROH \end{array} \right\} \xrightarrow[\text{Py.SeF}_4]{\overset{\text{SeF}_4}{\text{or}}} \left\{ \begin{array}{c} \overset{\textstyle F \quad F}{R-\!\!\overset{|}{C}\!\!-\!\!R} \\[2mm] \overset{\textstyle RCF}{\underset{\textstyle O}{\|}} \\[2mm] RF \end{array} \right. \tag{126} $$

$$ ArNHNH_2 \xrightarrow[\substack{HCl \\ Cu_2Cl_2}]{SeO_2} ArCl \tag{127} $$

Finally, a halogenolysis of a different type was reported by Detty[446] and Detty and Seidler[447], who noted that phenyl trimethylsilyl selenide (54) reacts with iodine (and other halogens) to generate trimethylsilyl iodide according to equation 128. The latter reagent can then be employed *in situ* for such purposes as the silylation of alcohols or the elimination of epoxides.

$$ 2 \ PhSeSiMe_3 + I_2 \longrightarrow 2 \ Me_3SiI + PhSeSePh \tag{128} $$
$$ \text{(54)} $$

VIII. INTRODUCTION OF OTHER FUNCTIONAL GROUPS INTO OLEFINS AND ACETYLENES

Methods were described in the preceding sections for the introduction of oxygen, nitrogen and halogen moieties into unsaturated (and other) substrates. Various other functional groups can be similarly incorporated into olefins and acetylenes through the use of organo-selenium and -tellurium reagents. These methods are discussed below.

A. Vinyl Selenides

Vinyl selenides are key intermediates in the preparations of many types of compounds[388]. They are in turn available from selenium-free olefins and acetylenes. When the addition of a selenenyl halide to an olefin is followed by dehydrohalogenation, the corresponding vinyl selenide is obtained[408,448-450]. It has already been stated that the initial addition can be performed with either Markovnikov or anti-Markovnikov orientation in many cases (Section VII.A.1), and so it follows that regiosomeric vinyl selenides are available by this route. Studies by Raucher and coworkers[408,448] have indicated optimum conditions for the preparation of either product (equation 129).

$$ \tag{129} $$

Fluorinated olefins furnish vinyl selenides in a similar manner[451,452], and in the case of 3,3,3-trifluoropropene[452] give the product **55**, which has interesting properties as a Michael acceptor (equation 130). Deactivated olefins such as enones[453,454] and also α, β-unsaturated esters[455], sulfones[454], nitriles[453] and nitro compounds[454] undergo additions with selenenyl halides, although in some cases very slowly and in poor yield[455]. Dehydrohalogenation of the adducts provides α-seleno enones[453,454] (e.g. equation 131) or other captodative olefins of current interest. An alternative route to α-seleno enones involves the electrochemical selenenylation and rearrangement of propargyl alcohols[456] (equation 132). These products served as useful dienophiles in cycloadditions. Alkynyl borates (**56**) react with PhSeCl, accompanied by the boron to carbon alkyl migration[457,458] shown in equation 133. The adducts **57** furnish α-seleno ketones (and therefore indirectly enones via selenoxide elimination) when oxidized with trimethylamine oxide[458]. This procedure thereby provides a useful synthesis of enones from acetylenes. The reactions of silylallenes such as **58** with PhSeCl afforded the silyl ketones **59** and the functionalized butadiene **60** as indicated in equation 134[459,460].

(130)

(131)

(132)

(133)

$$(134)$$

B. Electrophilic Additions of Selenenyl Pseudohalides

Many divalent selenium compounds of general structure RSeX, where X is a non-halide leaving group, add to olefins or acetylenes electrophilically, as in the case of the selenenyl halides themselves. This provides a convenient method for introducing the functionality X, along with the accompanying selenium residue, into the unsaturated substrate.

Benzeneselenenyl thiocyanate (PhSeSCN), phenyl selenocyanate (PhSeCN) and selenosulfonates (ArSO$_2$SePh) all form 1,2-adducts with olefins. The thiocyanate reacts rapidly, but its synthetic utility is limited by its unpredictable regio- and stereo-chemistry, and by its propensity to form mixtures of thiocyanate and isothiocyanate products[461,462]. Some degree of control of chemoselectivity was recently made possible by the observation that isothiocyanate adducts are formed in high yield with the reagent PhSeCl–Hg(SCN)$_2$ and long reaction times, while the thiocyanates are favoured with PhSeCl–NaSCN and brief reaction times[60]. The method of preparation of this reagent was also observed to affect its chemoselectivity in other contexts[463].

Phenyl selenocyanate adds to the activated double bonds of enamines[464] and ketene acetals[465], but requires catalysis with a Lewis acid in the case of unactivated olefins[81]. Selenosulfonates similarly require the presence of boron trifluoride etherate[70,71]. Both reagents add stereospecifically anti, but with limited regioselectivity which favours

$$(135)$$

Markovnikov orientation. The free-radical additions of $ArSO_2SePh$ to olefins produce regioisomeric anti-Markovnikov adducts exclusively (see equation 136 and Section VIII.C).

Although the species $PhSeNO_2$ has not been isolated, its formal addition to olefins can be achieved with PhSeBr or PhSeCl and $AgNO_2$[79,80,466]. Further, the presence of $HgCl_2$ suppresses the competing formation of oxyselenenylated products[80,466]. *Anti* addition and Markovnikov orientation again prevail, and in all four types of additions subsequent selenoxide eliminations yield the corresponding vinyl isothiocyanates, nitriles, sulfones and nitro compounds, respectively (see equations 7 and 11). The results of the additions of all four selenenyl pseudohalides to cyclohexene are shown in equation 135.

C. Free-radical Selenosulfonation

1. Olefins

Gancarz and Kice[72,73] and Back and Collins[70,71] independently reported that selenosulfonates ($ArSO_2SePh$) add to olefins by a free-radical chain mechanism. The process may be initiated photochemically[72,73], or by pyrolysis in refluxing benzene or chloroform[70,71], in which case the addition of a radical initiator such as AIBN is beneficial[71]. Monosubstituted olefins react efficiently whereas more highly substituted olefins give lower yields of addition products. As expected in a free-radical process, the addition is non-stereospecific but highly regioselective in the antiMarkovnikov sense. The product β-phenylseleno sulfones are readily converted into vinyl sulfones in virtually quantitative yield by selenoxide elimination[70–73] (equation 136). The latter products are complementary regioisomers of those produced by electrophilic selenosulfonation and elimination (see preceding section). Several vinyl sulfones prepared from olefins by free-radical selenosulfonation have found applications as dienophiles in Diels–Alder reactions[74–76].

(136)

In some instances, dienes afford cyclized products (see Section IX.H)[73,467], whereas strained substrates such as β-pinene ring-open during selenosulfonation[467].

A related free-radical addition of selenothiocarboxylates (61) to olefins was recently reported[468]. The process serves to introduce vicinal phenylseleno and thiobenzoate groups into the double bond (equation 137).

(137)

2. Allenes

Allenes undergo addition to the less substituted double bond, with attack by the sulfonyl radical occurring at the central sp-hybridized carbon atom[469,470]. The corresponding selenoxides react via a $[2,3]$ sigmatropic shift which provides high yields of β-sulfonyl allylic alcohols (equation 138).

$$(138)$$

3. Acetylenes

The thermal selenosulfonation of terminal or disubstituted acetylenes[109-112] proceeds efficiently and affords 1,2-adducts both regio- and, surprisingly, stereo-specifically, as shown in equation 139. The addition products can be converted into a variety of useful compounds which include acetylenic sulfones[109-111], allenic sulfones[112], β-keto sulfones or their ketal derivatives[111] and enamine sulfones[222] as depicted in equation 140. The adducts also undergo substitution of the PhSe group by organocuprates, as described in Section XI.B.1.

$$(139)$$

$$(140)$$

IX. CYCLIZATION

As seen in previous sections, the reactions of olefins with selenium electrophiles in the presence of external nucleophiles result in the addition of both the selenium residue and the nucleophile. However, when the nucleophile is part of the unsaturated substrate, the process becomes intramolecular and results in cyclization (equation 141). In most cases the cyclization step is followed by selenoxide elimination or reductive deselenization to afford unsaturated or saturated products, respectively. The term 'cyclofunctionalization' was introduced by Clive and coworkers[471,472] to describe such processes in general. The subject has recently been reviewed[473].

$$(141)$$

Certain selenium-induced cyclizations can be reversed with sodium in liquid ammonia[78,474] or with $Me_3SiCl–NaI$[475]. Cyclization can thus provide a method for the protection of the original olefin.

Although most cyclization procedures are mediated by electrophilic selenium species, several free-radical procedures have also appeared in recent years, as described in Section IX.H.

A. Unsaturated Alcohols

The cyclization of unsaturated alcohols was first reported independently by Corey and coworkers[476], Clive and coworkers[477] and Nicolaou and coworkers[478,479], and consists of an intramolecular version of oxyselenenylation. The method affords tetrahydrofurans, tetrahydropyrans and other cyclic ethers efficiently. Numerous examples are known, mostly employing PhSeCl as the electrophilic species[477–481]. Other effective reagents include PhSeBr[476,482], N-PSP (34)[286], $TeO_2–LiCl$ in acetic acid[483], electrochemically generated selenium electrophiles from diselenides[484] and SeO_2 in an oxidative cyclization procedure[485]. A typical example is shown in equation 142[478].

$$(142)$$

Propargyl alcohols and other alkynols fail to cyclize, giving only the products of 1,2-addition with PhSeCl[422,423]. On the other hand, α-allenic alcohols afford 2,5-dihydrofurans[406,486] (equation 143). Conjugated dienols can cyclize via a conjugate

addition mechanism[177] (equation 144), and *o*-alkenylphenols produce benzofurans or benzopyrans when treated with PhSeCl[471] (equation 145).

$$\text{(143)}$$

$$\text{(144)}$$

31%

$$\text{(145)}$$

81%   54%

When the cyclization is followed by cleavage of the original C—O bond, the net effect is the transposition of an oxygen function to the initial olefinic site[487] (equation 146). The method thus provides an alternative to oxyselenenylation of the double bond.

$$\text{(146)}$$

68%   71%

Hydroxyalkyl enol ethers[378,488] and hydroxyalkyl enamides[379] cyclize to ketals and amino ethers respectively (e.g. equation 147[378]). Similarly, unsaturated hemiacetals or hemiketals produce cyclized acetals[489] or spiroketals[490,491] (e.g. equation 148[491]). The required precursors can in turn be generated *in situ* from the inter- or intra-molecular addition of an alcohol to a carbonyl group.

$$\text{(147)}$$

86%

$$n = 1,2$$
$$m = 1,2$$

(148)

B. Unsaturated Carboxylic Acids

The selenium-induced cyclization of unsaturated carboxylic acids to lactones was first reported by de Moura Campos and Petragnani[492]. As in the preparation of cyclic ethers, PhSeCl again serves as the most popular electrophile[479,493–497], although N-PSP (34) is also convenient[285,286,496,498]. Aryltellurium trichlorides[492,499] and electrochemically generated selenium electrophiles[206] were employed in several examples. Extensive work by Clive and coworkers[472] and Nicolaou and coworkers[474] has demonstrated that γ-lactones are formed preferentially to δ-lactones, and that the latter are preferred to larger ring sizes. An illustrative example is provided in equation 149[472]. Larger rings are accessible, however, and several examples of macrolide ring closures with N-PSP or its succinimide analog were reported[285].

(149)

94%

Both allenic[500] and acetylenic[498] carboxylic acids afford γ-lactones (equations 150 and 151), the latter in contrast to the corresponding alcohols, which failed to cyclize. Silyl esters can be used instead of free carboxylic acids in cyclizations promoted by PhSeCl[501]. An oxygen transposition procedure related to equation 146 is based on lactonization followed by lactone hydrolysis[104]. Anomalous reactions were observed with β,γ-unsaturated carboxylic acids containing β- but not γ-substituents. These compounds undergo decarboxylation instead of lactonization[495] when treated with PhSeCl (equation 152).

(150)

34%

(151)

R = Me: 89%
R = Et : 76%

$$\text{(152)}$$

R = Me: 88%

R = Et: 89%

C. Unsaturated Nitrogen Compounds

Several unsaturated urethanes[502-504] and amides[505] were cyclized with PhSeCl[502,503,505] or N-PSP (34)[504] (e.g. equation 153[503]). Difficulties have been encountered with free amines[503], although isolated examples of the cyclization of a secondary amine[506] and an aniline[56] are known.

$$\text{(153)}$$

82%

A different type of cyclization occurred when the enamido thiol 62 was treated with PhSeBr in pyridine[507]. The selenosulfide 63 is an intermediate in this reaction (equation 154).

$$\text{(154)}$$

(62)   O
        ‖
R = PhCH$_2$CNH

(63)

D. Unsaturated Thiols

Several unsaturated thiols or their corresponding thioacetates were cyclized[77,78,508] as in equation 155[508].

$$\text{(155)}$$

R = H: 80%

R = Ac: 85%

E. Allenic Phosphonates

Allenic phosphonates afford cyclic phosphonates according to equation 156[509,510].

$$(156)$$

F. Unsaturated β-Dicarbonyl Compounds

Carbocyclic ring closures of unsaturated β-keto esters[511-516] with N-PSP (34) and catalysts such as $SnCl_4$[512-516], p-toluenesulfonic acid[511,512], iodine[511] and ZnI_2[511] were developed by Ley and coworkers for a number of synthetic applications. Cyclization occurs either through the ketone oxygen or the enolic carbon. The former products are favoured under the conditions of kinetic control, but are converted into the corresponding carbocycles on further equilibration. An example is provided in equation 157[515]. Benzeneselenenyl chloride (PhSeCl) with $AlCl_3$ catalyst also serve as an effective reagent combination for this type of transformation[517].

$$(157)$$

Unsaturated β-diketones can be similarly cyclized to either the corresponding cyclic enol ethers or carbocycles with N-PSP[511] or benzeneselenenyl hexafluorophosphate ($PhSe^+PF_6^-$)[518]. Equilibration was promoted with $SnCl_4$[518].

The acid-catalysed addition of the β-keto ester moiety in 64 to the vinyl selenide provides the basis for a different cyclization as shown in equation 158[519].

$$(158)$$

G. Dienes

Dienes can be converted into cyclic ethers with PhSeCN or KSeCN in the presence of $CuCl_2$ in aqueous or alcoholic media[520-522]. The example of cycloocta-1,4-diene is shown in equation 159, which also indicates that the ratio of the two products 65 and 66 is highly dependent on the reaction medium. Other reagents which have been used in the similar cyclization of this and other dienes are PhSeCl in aqueous acetonitrile[523], $PhSeOCOCF_3$[84], $PhSeOH$[524] (from the oxidation of PhSeSePh with hydrogen peroxide) and N-PSP (34) or its succinimide analog[285,286].

(159)

(65)   **(66)**

95   :   5 (in MeOH)

0   :   100 (in THF – H₂O)

Carbocyclic products containing acetoxy and acetamido substituents were prepared from dienes using PhSeCl in acetic acid[299,525], and PhSeCl[526] or PhSeI[527] in acetonitrile, respectively (e.g. equations 160[525] and 161[527]).

(160)

68%

(161)

cis:trans = 17:83
75%

The lactone or cyclic ether products obtained from the selenium-induced cyclization of diene carboxylic acids[528,529] or dienols[530] can be further transformed into bicyclic products with strong acids (e.g. equation 162[529]). A related technique employs unsaturated β-hydroxy selenides which cyclized via the attack of a neighbouring π-bond on a seleniranium ion intermediate generated from the acid-catalysed dehydration of the alcohol moiety[281,297,298,531-534] (e.g. equation 163[532]).

70%

(162)

80%

$$
(163)
$$

H. Free-radical Cyclizations

Carbon-centered radicals formed by the free-radical deselenization of alkyl phenyl selenides with tin hydrides (see Section XIV) undergo inter-[535] or intra-molecular capture by olefins[196,536-538], allenes[539] and acetylenes[536,540,541]. Some recent examples are illustrated in equations 164[536], 165[539] and 166[540].

$$
n=0-3
$$

$$
59-86\%
$$

$$
(164)
$$

$$
(165)
$$

$$
X=CO_2Me: 35\%
$$
$$
X=CN: \quad 30\%
$$

$$
(166)
$$

The free-radical selenosulfonation of dienes affords carbocycles[73,467] together with mono- and di-1, 2-addition products. Cyclization is enhanced by increasing the dilution (equation 167[467]).

$$
+ 1,2\text{-adducts} \quad (167)
$$

I. Hydroxyl-substituted Vinyl Selenones

Selenones are capable of both stabilizing an adjacent anionic center and of acting as a leaving group (cf. equation 95). Hence γ- or δ-hydroxyl-substituted vinyl selenones undergo facile base-catalysed Michael addition in methanol solution, followed by intramolecular displacement of the selenonyl group as shown in equation 168[542,543]. A useful route to oxetanes and tetrahydrofurans is the result.

$$(168)$$

It is appropriate to mention that the above properties of selenones also permit the fragmentation of cyclic γ-hydroxyl vinyl selenones according to equation 169[543,544].

$$(169)$$

X. OXIDATIONS OF FUNCTIONAL GROUPS

A. Alcohols, Hydroquinones and Catechols

Primary, secondary and allylic alcohols are smoothly oxidized to aldehydes or ketones with dimesityl diselenide (67) and t-butyl hydroperoxide[545-547] (equation 170). Presumably, these reactions proceed via intermediate selenenic or seleninic esters of the starting alcohols. The diselenide can be employed in catalytic quantities and the method is sufficiently mild to tolerate the presence of olefins and even neighbouring sulfide and selenide groups.

$$(170)$$

Benzylic alcohols[240] are readily oxidized to aldehydes or ketones with BSA (27), whereas the oxidation of aliphatic alcohols[240-242,250] is sometimes, but not always, accompanied by dehydrogenation (see equation 48). Examples are shown in equations 171[240] and 172[250].

$$PhCH_2OH \xrightarrow{\text{BSA}} PhCHO \tag{171}$$
$$99.5\%$$

$$(172)$$

$$86\%$$

Other reagents which are reported to oxidize alcohols to carbonyl compounds are dimethyl selenoxide (38)[351], di(p-methoxyphenyl) selenoxide (68) in the presence of selenium dioxide[548], di(p-methoxyphenyl) tellurone (69)[549], the species 71 which are generated *in situ* from selenides and NCS[550] and a polymer-bound seleninic acid[361].

Hydroquinones and catechols afford p- or o-quinones, respectively, without accompanying oxygenation (see Section V.E) on oxidation with the telluroxide 70[551] or with selenoxides 68[552] and 52[553]. The last reagent has also been employed in the conversion of adrenaline to adrenochrome[554] and ascorbic acid to its dehydro derivative[555].

$$\underset{p\text{-AnSeAn-}p}{\overset{O}{\underset{\|}{}}} \qquad \underset{p\text{-AnTeAn-}p}{\overset{O}{\underset{\|}{\underset{\underset{O}{\|}}{}}}} \qquad \underset{p\text{-AnTeAn-}p}{\overset{O}{\underset{\|}{}}}$$

$$(68) \qquad \qquad (70)$$

$$(69)$$

$$(71)$$

$$\underset{(72)}{Ph_2Se(OCCF_3)_2}$$

B. Nitrogen Compounds

1. Amines

Amines can be oxidized to imines with a variety of selenium oxidants. These include BSA (27)[556-558], diphenylselenium bistrifluoroacetate (72)[559] and benzeneseleninyl chloride (30)[560]. The imines so obtained can be used in the preparation of other compounds. Thus, hydrolysis affords ketones[556,560] (equation 173), further oxidation provides nitriles[556,560] (equation 174) and the addition of NaCN or Me₃SiCN furnishes α-cyanoamines[557] (equation 175).

$$(173)$$

$$PhCH_2NH_2 \xrightarrow[\textbf{27}]{\textbf{30} \text{ or}} PhCN \qquad (174)$$
$$85-96\%$$

$$(175)$$

Other studies indicate that anilines can be converted into azo compounds with Ph_2SeCl_2, or with diphenyl selenoxide (52) and $ZnCl_2$[561]. Tertiary amines afford N-oxides when treated with selenoxides[562]. In a different approach, the cephalosporin selenenamide 73 was used to prepare the methoxy derivative 74 by oxidation with MnO_2 and methanolysis[563] (equation 176).

$$(176)$$

2. Indolines and indoles

The oxidation of indolines to indoles with BSA (27) was studied by Barton and coworkers[558,564-566]. Selenenylation of the indoles with electrophilic selenium byproducts accompanied the oxidation unless scavengers such as indole or dihydropyran were added to the reaction mixture[565,566] (e.g. equation 177[565]). Alternatively, the selenenylated byproducts were reductively deselenized to free indoles with nickel boride[564,566]. Various indoles undergo further oxidation with reagents such as 72[559] or selenium dioxide[236,334,343], as in the example shown in equation 178[559].

$$(177)$$

$$(178)$$

3. Hydrazines

Hydrazines are oxidized to a wide array of products with selenium and tellurium oxidants, often in a preparatively useful manner. Hydrazine hydrate generates the hydrogenating agent diimide when treated with $PhSeO_2H^{249,567}$ or elemental selenium in the presence of oxygen[568]. Monoarylhydrazines produce mixtures of arenes and aryl phenyl selenides with BSA or $PhSeO_2H^{249,567,569,570}$ (equation 179). Arenes and tellurides are formed similarly when the telluroxide 70^{571} or the reagent TeO_2–LiCl–$HOAc^{572}$ is employed as the oxidant.

$$ArNHNH_2 \xrightarrow[\text{or } PhSeO_2H]{\text{BSA}} ArH + ArSePh \qquad (179)$$

Hydrazides are smoothly oxidized to 1,2-diacylhydrazines with diphenyl selenoxide $(52)^{573}$, the telluroxide 70^{571} or $PhSeO_2H^{567,574}$ if the seleninic acid is introduced by slow addition. On the other hand, if the hydrazide and triphenylphosphine are added slowly to the seleninic acid, then diacylhydrazine formation is suppressed and selenoesters are obtained in good yield[567,574] (equation 180). Similarly, sulfonhydrazides produced selenosulfonates in excellent yield without the need for triphenylphosphine[575] (equation 181). Hydrazides bearing γ- or δ-hydroxy substituents underwent nearly quantitative cyclization to lactones when oxidized with $PhSeO_2H^{472,567}$ (equation 182), and phthalhydrazide formed the dimer 75 when treated with the selenoxide 52 in acetic acid[576] (equation 183).

$$(180)$$

$$(181)$$

$$(182)$$

$$(183)$$

1,1-Disubstituted hydrazines dimerize to tetrazenes when treated with PhSeO$_2$H[577] or SeO$_2$[577] (equation 184). The products were obtained in generally high yield unless an N-aryl or N-sulfonyl substituent was present. 1,2-Disubstituted hydrazines and hydroxylamines produced azo compounds[249,567,569,570], including Cookson's reagent[578], and nitroso compounds[551,569,570,571], respectively, on oxidation with BSA, PhSeO$_2$H or the telluroxide **70** (equations 185, 186).

$$\underset{R'}{\overset{R}{\diagdown}}N-NH_2 \xrightarrow[\text{or SeO}_2]{\text{PhSeO}_2\text{H}} \underset{R}{\overset{R}{\diagdown}}NN=NN\underset{R}{\overset{R}{\diagup}} \qquad (184)$$

$$RNHNHR \xrightarrow[\text{or PhSeO}_2\text{H}]{\text{BSA}} RN=NR \qquad (185)$$

$$RNHOH \xrightarrow{\text{BSA}} RN=O \qquad (186)$$

4. Hydrazones, oximes and semicarbazones

Barton and coworkers reported that BSA (**27**) is an exceptionally effective reagent for the regeneration of ketones from their oximes, semicarbazones or aryl- or tosyl-hydrazones[570,579] (equation 187). Aldehydes can be similarly prepared from their oximes or tosylhydrazones, whereas the corresponding phenyl- or p-nitrophenyl-hydrazones afford keto azo compounds instead[569,570] (equation 188). In related work, hydrazones were converted into vinyl selenides with PhSeBr and t-butyltetramethylguanidine[580] (equation 189). Tellurium dioxide was investigated for the purpose of regenerating carbonyl compounds from their hydrazones, semicarbazones and azines, but generally provides lower yields than BSA[572].

$$\underset{R'}{\overset{R}{\diagdown}}=N\diagdown_X \xrightarrow{\text{BSA}} \underset{R'}{\overset{R}{\diagdown}}=O \qquad (187)$$

$$X = OH, NHAr, NHTs,$$
$$\overset{\overset{O}{\parallel}}{NHCNH_2}$$

$$\underset{H}{\overset{R}{\diagdown}}=N\diagdown_X \quad \xrightarrow[\text{X=OH,NHTs}]{\text{BSA}} RCHO$$
$$\xrightarrow[\text{X=NHAr}]{\text{BSA}} R\overset{\overset{O}{\parallel}}{C}N=NAr \qquad (188)$$

$$\underset{R'}{\overset{R}{\diagdown}}=N-NH_2 \xrightarrow[\text{t-BuN=C(NMe}_2)_2]{\text{PhSeBr}} \underset{R'}{\overset{R}{\diagdown}}=\diagup^{SePh} \qquad (189)$$

The oxidation of semicarbazones with selenium dioxide constitutes an important route to acetylenes via the photolytic or pyrolytic fragmentation of selenadiazole intermediates (equation 190). Lalezari and coworkers[581-589] and Meier and coworkers[590-599] have studied this process extensively. They and others[600,601] prepared diverse acetylenes including diynes[585], sulfonylacetylenes[587], acetylenic sulfides[588], selenides[589] and ethers[588], radioactively labelled acetylenes[601] and a large number of highly strained cyclic acetylenes[590,591,593,595-599].

$$(190)$$

The dehydration of aldoximes with selenium dioxide[602-604], Se_2Cl_2[605], $PhSeCl$[606] and the seleninyl chloride 30[606] provides a useful preparative route to nitriles (equation 191).

$$(191)$$

5. Nitro compounds

Primary aliphatic nitro compounds undergo oxidation at the α-carbon and simultaneous reduction of the nitro group when treated with selenium dioxide and triethylamine[607]. This reaction permits the isomerization of such nitro compounds to hydroxamic acids (equation 192).

$$RCH_2NO_2 \xrightarrow[Et_3N]{SeO_2} R\overset{\overset{O}{\|}}{C}NHOH \qquad (192)$$

6. Azasteroid lactams

Azasteroid lactams display several modes of reaction when oxidized with BSA (27). When conformational considerations permit selenoxide elimination to take place across the $C-N$ bond, N-acylimines are first formed and then oxidized further to imides[250] (e.g. equation 193). If imine formation is precluded by conformational effects, then dehydrogenation occurs at higher temperatures according to equation 51.

$$(193)$$

Azasteroid enamides react in a more complex fashion. Keto carbinolamides such as **77** and hydroxylated products **78**, were formed from azasteroids such as **76** (equation 194)[223,382]. The carbinolamides were obtained in improved yield by selenenylation of the 6-position, with PhSeCl, followed by oxidation with excess MCPBA[223].

(194)

C. Phosphorus and Sulfur Compounds

Mild and selective oxidants of sulfur compounds are of importance, as mixtures of products with different oxidation states are often formed indiscriminately. A number of selenium and tellurium reagents have proved valuable in such reactions.

1. Thiols

Thiols are cleanly oxidized to disulfides by the selenoxide **68**[552], telluroxide **70**[551,571] and tellurone **69**[549] (equation 195). Tellurium tetrachloride forms tetrathiotellurium species which decompose to disulfides according to equation 196[608], and which are effective in converting dithiols to bisdisulfides.

$$2\ RSH\ \xrightarrow{\textbf{66,69 or 70}}\ RSSR \tag{195}$$

$$4\ RSH\ +\ TeCl_4\ \longrightarrow\ (RS)_4Te\ \xrightarrow{\Delta}\ 2\ RSSR \tag{196}$$

2. Sulfides and thioketals

The selective oxidation of sulfides to sulfoxides was accomplished with the selenoxide **68**[552] and also with areneseleninic and areneselenonic acids[609]. On the other hand, oxidation to sulfones was reported with perseleninic acids generated *in situ* from diselenides[610-614] or seleninic acids[373] and hydrogen peroxide, or from the oxidation of selenenic byproducts produced during selenoxide eliminations[78,508]. In some cases it was possible to proceed only to the sulfoxide stage by appropriate choice of reaction conditions[373,508]. Although perseleninic acids are known to epoxidize olefins (see

Section V.G.1), the selective oxidation of sulfides in the presence of double bonds is possible, as demonstrated by the example in equation 197[614]. Sulfides can also be cleanly converted into either sulfoxides[615] or sulfones[616] with selenium dioxide and hydrogen peroxide.

$$\text{(197)}$$

80%

Free ketones and aldehydes are unmasked from their dithioketal or dithioacetal protecting groups with BSA (27)[617-620] (equation 198). The reaction is applicable to hindered substrates and also to diselenoketals[621,622].

$$\text{(198)}$$

3. Thiocarbonyl compounds

Many types of thiocarbonyl compounds cleanly afford their carbonyl analogues on oxidation with BSA (27)[623,624], the telluroxide 70[551,571] or various selenoxides[552,625,626] (equation 199). A particularly useful variation of this process involves the chlorination of a catalytic amount of a telluride with 1,2-dibromo-1,1,2,2-tetrachloroethane, followed by *in situ* hydrolysis of the resulting diaryltellurium dichloride to the corresponding telluroxide, which then functions as the actual oxidant of the thiocarbonyl compound[571,627]. The conversion of telluroesters to esters was similarly effected with BSA[628].

$$X,Y = C,O,S,N, \text{etc.} \qquad \text{(199)}$$

4. Sulfinic acids

The oxidation of sulfinic acids with $PhSeO_2H$ provides a useful preparation of selenosulfonates[73,629] (equation 200).

$$RSO_2H \xrightarrow{PhSeO_2H} RSO_2SePh \qquad \text{(200)}$$

5. Phosphorus compounds

Various trivalent phosphorus compounds, and also their sulfides and selenides, produce the corresponding oxides when treated with dimethyl selenoxide (38)[626] (equation 201). Interestingly, acyclic systems undergo inversion of configuration at phosphorus whereas cyclic systems react with retention.

$$\left.\begin{array}{l} R_3P \\ R_3P=S \\ R_3P=Se \end{array}\right\} \xrightarrow{\quad 38 \quad} \begin{array}{l} R_3P=O \\ R=Ph,OEt,NEt_2 \end{array} \qquad (201)$$

Other oxidations of phosphines to phosphine oxides were reported using seleninic and selenonic acids[609], the selenoxide 68[552], the telluroxide 70[571] and $TeCl_4$[442] as oxidants.

XI. CARBON—CARBON BOND-FORMING REACTIONS

A. Connective Reactions With Selenium- and Tellurium-stabilized Anions

The stabilization of carbanions by adjacent selenium residues facilitates their formation while permitting the retention of a high degree of nucleophilic character. The synthetic applications of these species have been extensively studied by Krief, Seebach, Reich and others, and are generally based on their reactions with electrophiles, followed by further transformations of the selenium functionality[630,631]. α-Telluro carbanions have also been investigated, but so far their applications remain more limited. These procedures provide a powerful connective approach to products with new carbon—carbon single and double bonds.

1. Anions from selenides, selenoacetals and their tellurium analogues

Selenium-stabilized alkyl carbanions can be conveniently generated by the deprotonation of alkyl selenides, diselenoacetals or triselenoorthoformates with hindered amide bases. A different approach to these anions is based on the facile C—Se cleavage reactions of diselenoketals and triselenoorthoesters with alkyllithiums. These processes are summarized in Scheme 1.

When the α-carbon atom is substituted with another heteroatom besides selenium, alkyllithium-induced C—Se cleavage occurs preferentially to C—Si or C—S scission in α-selenosilanes[384,386,647,650] or α-selenosulfides[662], respectively, whereas α-bromoselenides undergo C—Br cleavage[663]. Alkyl tellurides and ditelluroacetals can be similarly deprotonated or cleaved with alkyllithiums[115,664]. Scission of the C—Te bond in mixed selenium–tellurium acetals occurs preferentially[665].

The cleavage of the C—Se bond in allyl[659], benzyl[660] or vinylcyclopropyl[661] selenides provides a convenient method for the in situ generation of allyl-, benzyl- or vinylcyclopropyl-lithiums, which are difficult to make otherwise.

The anions thus generated react with a wide array of electrophiles. They can be alkylated with alkyl halides[35,115,121,122,124,385,386,435,621,633,637,645,656–658,661,663–665], epoxides[91,122,429,621,637,648] and oxetanes[429], acylated with DMF[644,652,666], carbon dioxide[34,644,661] or other acylating reagents[644], silylated with trimethylsilyl chloride[386,635,642,647,650,654] and sulfenylated with sulfenyl halides[639,653] or disulfides[642]. They condense readily with aldehydes and ketones to afford β-hydroxy selenides[34,122,384,386,536,621,632,633,635–641,643,648,649,651,653–656,661,663,664,666–671], even with hindered or easily enolized substrates. Enones react via either 1,2-or 1,4-addition and good regioselectivity for either mode can be achieved by the appropriate choice of conditions[634,646,672–677]. Intramolecular alkylation of γ-chloro or γ-tosyl diselenoacetal anions affords the corresponding cyclopropanes[648].

Further transformations provide access to many useful types of compounds. The alkylated diselenoketals can be converted into ketones either hydrolytically with $HgCl_2$[622] or $CuCl_2$–CuO[621,622,637,673,676] or oxidatively with BSA[621,622] or

SCHEME 1

a. LiN(i-Bu)$_2$[632,633]; LDA[386,621]
b. BuLi[386,621,633,634]
c. LiN(i-Bu)$_2$[632,633]; LDA[621,635,636]; LiTMP[621]; KDA[637]
d. BuLi[91,122,124,384,536,633,639-655]; t-BuLi[639]; MeMgBr[638]
e. LDA[35,385,656,657]; LiTMP[656,659]; LiN(SiMe$_3$)$_2$[658]; BuLi-TMEDA[633]; sec-BuLi-TMEDA[33]
f. BuLi[647,650,654,659-661]; t-BuLi[660]

H_2O_2[622]. Similarly, ketones were obtained from alkylated ditelluroacetals with I_2–NaI[435] and aldehydes from α-silyl selenides with $NaIO_4$[386] or H_2O_2[385,386]. Since the starting seleno- or telluro-acetals or themselves prepared from aldehydes, the overall procedure permits the alkylation of an acyl anion equivalent (equation 202).

$$(202)$$

Alkylated α-seleno or telluro carbanions undergo selenoxide or telluroxide eliminations to afford olefins[35,115,122,124,644,656,657] while their condensation products with carbonyl compounds similarly provide allylic alcohols[34,122,639,640,649,653] (equation 203).

In some cases, eliminations of the corresponding selenonium salts gave results which were as effective as or even superior to those obtained with selenoxide elimin-

(203)

ations[91,121,122]. For instance, pure homoallylic alcohols are accessible via equation 204, whereas selenoxide elimination produced mixtures of allylic and homoallylic alcohols[91].

The β-hydroxy selenide condensation products are of value in the preparation of epoxides via their reaction with chloroform and thallium(I) ethoxide[678] or by treating their selenonium salts with bases[122,639,641,643,646,651,653,662,671] (equation 205). Repetition of the process permits the homologation of epoxides to oxetanes and tetrahydrofurans[429] (equation 206).

(204)

(205)

(206)

Selenium-stabilized carbanions provide a connective route to olefins through several approaches. Their formylated products can be elaborated by Wittig reactions[652,666], followed by [2, 3] sigmatropic shifts of the corresponding selenoxides to furnish allylic alcohols[652] (equation 207). α-Silyl carbanions generated from α-silyl selenides afford olefins via Peterson reactions[384,386,635,647,650], as shown in equation 208. Numerous examples have been reported where β-hydroxy selenides were prepared as in equation 209 and converted into olefins by reductive elimination. This procedure constitutes an alternative to the Wittig reaction and is less susceptible to steric effects. Further, reductive

elimination often takes place *anti* stereospecifically. Effective reagents for this transformation are: methanesulfonyl chloride (MsCl)–Et$_3$N[34,636,655,656,679,680], TsOH[681,682] HClO$_4$[681], (CF$_3$CO)$_2$O–Et$_3$N[681], POCl$_3$–Et$_3$N[384,672,683], POCl$_3$–SnCl$_2$[34], SOCl$_2$– Et$_3$N[214,384,683–685], PI$_3$–Et$_3$N[122,650,651,666,668,685], P$_2$I$_4$–Et$_3$N[391,666,685,686], 1,2-phenylenephosphorochloridite[653,684], Me$_3$SiCl–NaI[475] and N,N'-carbonylbisimidazole[122,668]. Finally, symmetrical olefins are accessible through the direct coupling of selenium-stabilized carbanions with CuI·SMe$_2$[124] or CuI[687] (equation 210).

$$(207)$$

$$(208)$$

$$(209)$$

$$(210)$$

Metalated triselenoorthoformates function as carbene equivalents in the cyclopropanation of ketene dithioacetals according to equation 211[632,633].

$$(211)$$

Ring expansions of β-hydroxy selenides prepared via equations 203, 205 and 209 are discussed in Section XVI.C.1.

2. Anions from allylic and propargylic selenides

Allylic selenides are deprotonated with hindered amide bases such as LDA[336,680,682,688–692], LiNEt$_2$[680,691], LiTMP[659,690] and KDA[659]. The resulting

anions react chiefly at their α-position with electrophiles which include alkyl halides[336,680,691], epoxides[680,691], silyl chlorides[680,689,691] and boranes[688]. The alkylated products are useful in the preparation of rearranged allylic alcohols after oxidation and [2,3] sigmatropic shifts[691,692] (equation 212). Allylic selenides were employed in a variation of the Mannich reaction as shown in equation 213[692].

$$
(212)
$$

$$
(213)
$$

1,3-Bis(phenylseleno)propene (79) can be alkylated at both the 1- and 3-positions and affords α,β-unsaturated silyl ketones[680] according to equation 214 (or gives enals if the silylation step is omitted). Similarly, the dianion of the propargyl selenide 80 was dialkylated and converted into α-seleno enones as shown in equation 215[693-695].

$$
(214)
$$

$$
(80)
$$

$$
(215)
$$

The anion of 81 adds to ketones or aldehydes principally through its γ-position, although α-selective attack was observed in the presence of triethylaluminum[682]

(equation 216). The same anion reacted with cyclopentenone mainly via 1, 2-addition in THF at $-78\,°C$, but exclusively via 1,4-addition in the presence of HMPA[696]. In both cases, the α-position of the anion was the favoured site of attack. In contrast to equation 216, the anion of **82** reacted with acetone through its α-position and furnished the allylic alcohol **83** after [1, 5] migration of the selenide moiety[697] (equation 217).

$$
\begin{array}{c}
\text{PhSe} \diagdown \!\!\!\!\!\!\!\!\!\!\!\overset{\text{Li}}{\diagup}\!\!\!\!\!\!\diagup \\
\textbf{(81)}
\end{array}
\quad
\begin{array}{c}
\xrightarrow[\substack{\text{or} \\ R_2CO}]{RCHO} \quad \text{PhSe}\diagdown\!\!\!\diagup\!\!\!\diagdown\!\!\!\overset{\text{OH}}{\underset{R}{\diagup}} \\[2em]
\xrightarrow[\substack{2.\,RCHO \\ \text{or} \\ R_2CO}]{1.\,Et_3Al} \quad \text{PhSe}\diagdown\!\!\!\overset{}{\underset{R\diagdown\;\;\;\text{OH}}{\diagup}}\!\!\!\diagup
\end{array}
\tag{216}
$$

$$
\diagup\!\!\!\diagdown\!\!\!\diagup\!\!\!\diagdown\!\!\!\overset{\text{SePh}}{\underset{\text{Li}}{\diagup}}
\quad \xrightarrow{\overset{O}{\overset{\|}{MeCMe}}} \quad
\diagup\!\!\!\diagdown\!\!\!\diagup\!\!\!\diagdown\!\!\!\overset{\text{SePh}}{\underset{\diagup\diagdown\text{OH}}{\diagup}}
$$
$$
\textbf{(82)}
$$

$$
\xrightarrow[[1,5]]{\Delta} \quad \text{PhSe}\diagdown\!\!\!\diagup\!\!\!\diagdown\!\!\!\diagup\!\!\!\diagdown\!\!\!\overset{}{\underset{\text{OH}}{\diagup}}
\tag{217}
$$
$$
\textbf{(83)}
$$

3. Anions from vinyl selenides and tellurides

Vinyl selenides[431,636,637,690] and vinyl tellurides[698] are deprotonated with hindered amide bases, and KDA is recommended for reluctant cases[637]. The metalated species can then be treated with the usual array of electrophiles to provide α-substituted vinyl selenides (equation 218). Since the products afford ketones after hydrolysis, vinyl selenides represent acyl anion equivalents[637]. 2-Pyridyl vinyl selenides are reported to deprotonate more easily than others and the subsequent alkylation takes place stereospecifically with retention of configuration[101]. Ketene diselenoacetals provide another source of selenium-stabilized vinyl anions through cleavage of one C—Se bond with n-butyllithium[391,699] (equation 218).

$$
\begin{array}{c}
\overset{R}{\diagdown}\!\!\!=\!\!\!\overset{\text{SePh}}{\underset{H}{\diagup}} \\[1em]
\overset{R}{\diagdown}\!\!\!=\!\!\!\overset{\text{SePh}}{\underset{\text{SePh}}{\diagup}}
\end{array}
\quad
\begin{array}{c}
\xrightarrow[\substack{\text{or} \\ KNR_2'}]{LiNR_2'} \\[1em]
\xrightarrow{BuLi}
\end{array}
\quad
\overset{R}{\diagdown}\!\!\!=\!\!\!\overset{\text{SePh}}{\underset{\text{Li(K)}}{\diagup}}
\quad \xrightarrow{E^+} \quad
\overset{R}{\diagdown}\!\!\!=\!\!\!\overset{\text{SePh}}{\underset{E}{\diagup}}
$$
$$
\xrightarrow{hydrolysis} \quad R\diagdown\!\!\!\overset{O}{\overset{\|}{C}}\!\!\!\diagdown E
\tag{218}
$$

The Michael additions of alkyllithiums to phenyl vinyl selenide produce α-metalated selenides, which react with various electrophiles as shown in equation 219[431,700]. If the latter step is followed by selenoxide elimination to the corresponding olefin, the selenide becomes the equivalent of the synthon $^+CH{=}CH^-$.

$$(219)$$

4. Anions from selenoxides

Selenoxides can be metalated with LDA at low temperatures (to prevent premature selenoxide elimination), and the resulting anions react with various electro-philes[33,34,679,701] such as aldehydes and ketones. The resulting β-hydroxy selenoxides afford allylic alcohols by subsequent selenoxide elimination, or olefins by reduction to the selenide followed by reductive elimination[34,679] (equation 220).

$$(220)$$

5. Dianions from α-phenylselenocarboxylic acids

The dianion **84** of 2-phenylselenopropanoic acid was exploited by Petragnani and coworkers[702,703] in several approaches to α-methylene lactones. One example is shown in equation 221[702]. The condensation of the dianion of α-phenylselenoacetic acid with benzaldehyde was also reported[656].

$$(221)$$

6. Anions from α-seleno nitriles, esters and lactones

Selenides bearing additional stabilizing groups can also be alkylated via their anions. These include α-seleno nitriles[261,704], esters[497,683] and lactones[683,705]. These reactions are often used in conjunction with selenoxide or reductive eliminations to yield unsaturated products. Two interesting examples are shown in equations 222[261] and 223[705]. Anions derived from α-seleno ketones are considered in Section XVII.A.

$$(222)$$

$$(223)$$

7. Selenium and tellurium ylides

Although selenium and tellurium ylides have been little investigated with respect to synthetic utility, several recent examples suggest potential value. Thus, the tellurium ylides **85** and **86** reacted with carbonyl compounds to afford α,β-unsaturated esters[706] and epoxides[707], respectively. The selenium ylides **87** also gave epoxides with non-enolizable aldehydes and ketones[708], including chalcone and cinnamaldehyde, whereas the ylide **88** cyclopropanated chalcone instead[709] (equations 224–227).

$$(224)$$

$$(225)$$

$$(226)$$

$$(227)$$

B. Connective Reactions from Substitution of Selenium and Tellurium Groups

Another approach to carbon—carbon bond formation is based on the substitution of ArSe or ArTe groups with organometallic reagents, or on the direct displacement of nucleofugal selenonyl groups with various nucleophiles.

1. Vinyl and allyl selenides and tellurides

Vinyl phenyl selenides[710,711] and tellurides[712,713] undergo substitution of the PhSe or PhTe moiety with Grignard reagents in the presence of Ni^{II} or Co^{II} catalysts, in most cases with retention of configuration (equation 228). Allyl phenyl selenide[711] and diaryl tellurides[712,713] give mixtures of products resulting from the cleavage of both C—Se and both C—Te bonds, respectively. The allylic selenide **89** in equation 229 reacted with Me_2CuLi with rearrangement[691].

$$(228)$$

$$(229)$$

β-(Phenylseleno)vinyl sulfones, which are available from the selenosulfonation of acetylenes (equation 139), react with organocuprates to afford alkyl-substituted vinyl sulfones[714]. Retention of configuration is observed and the reaction is applicable to hindered systems. The reagents $RCu(SePh)Li$ are particularly efficacious for this purpose.

When this procedure is followed by reductive desulfonylation, it permits the overall 2-alkylation of acetylenes as shown in equation 230.

$$R-\!\!\equiv\!\!-H(R) \xrightarrow{\text{eqn. 139}} \quad \begin{array}{c} R \\ \diagdown \\ \text{PhSe} \end{array}\!\!=\!\!\begin{array}{c} SO_2Ar \\ \diagup \\ H(R) \end{array} \xrightarrow{R^1Cu(SePh)Li} \quad \begin{array}{c} R \\ \diagdown \\ R^1 \end{array}\!\!=\!\!\begin{array}{c} SO_2Ar \\ \diagup \\ H(R) \end{array}$$

$$\xrightarrow{Na(Hg)} \quad \begin{array}{c} R \\ \diagdown \\ R^1 \end{array}\!\!=\!\!\begin{array}{c} H \\ \diagup \\ H(R) \end{array} \tag{230}$$

2. Selenoesters

The preparation of unsymmetrical ketones from selenoesters was reported with organocuprates and other organometallic reagents[715,716] (equation 231). Even vinyl cuprates are effective, permitting the synthesis of enones with little further Michael addition to the products[716].

$$\begin{array}{c} O \\ \parallel \\ RCSeMe \end{array} \xrightarrow[\substack{\text{or} \\ R^1MgX, \\ CuBr-Me_2S}]{R^1_2CuLi} \begin{array}{c} O \\ \parallel \\ RCR^1 \end{array} \tag{231}$$

Selenoesters function as acylating agents when activated by 'selenophilic' metal catalysts such as Cu^I, Cu^{II} and Hg^{II} species. They perform Friedel–Crafts acylations of electron-rich aromatic compounds[717,718] and produce cycloadducts **90** with isonitriles[717,718] (equation 232). Under similar conditions, selenoesters also acylate alcohols and amines to afford esters and amides, respectively[718,719].

$$\begin{array}{c} O \\ \parallel \\ RCSeMe \end{array} + ZCH_2\overset{+}{N}\!\!\equiv\!\!\overset{-}{C} \xrightarrow[\substack{Et_3N \text{ or} \\ DBu}]{Cu_2O} \tag{232}$$

(Z = electron–withdrawing group)   (**90**)

3. Selenones

As mentioned earlier (Sections V.H.2 and IX.I), selenones have strong nucleofugal character, as well as the ability to stabilize an adjacent carbanionic center. This combination of properties was exploited by Kuwajima and coworkers[720–722] in a cyclopropane synthesis based on the Michael addition of enolates or active methylene compounds to vinyl selenones, followed by the nucleophilic displacement of the selenonyl leaving group (equation 233). Several examples of the related cyclopropanation of vinyl selenoxides were also reported[722,723]. Equation 234 depicts an epoxide-forming reaction based on the condensation of a selenone with benzaldehyde[724] in a manner reminiscent of the Darzen condensation. Selenones also undergo displacement with other nucleophiles such as halides[102,724], CN^{-724}, H_2O^{724}, $MeONa^{724}$ and $NaSPh^{724}$.

(233)

(234)

C. Tellurium-mediated Aryl and Allyl Coupling Reactions

Bergman and coworkers reported that arenes couple to biphenyls when treated with TeCl$_4$ followed by Raney nickel[725-727]. Aryl- and diaryl-tellurium chlorides are intermediates in this process (equation 235). Other workers[728] have found that the latter compounds are similarly converted into biphenyls in the presence of Pd^{II} catalysts. The intramolecular coupling of diaryl ethers with TeCl$_4$ affords dibenzofurans[729], as shown in equation 236. This reagent also catalysed the cationic polymerization of olefins such as stilbene[730]. Biphenyls were produced together with diaryl tellurides when tetraaryltellurides (91) were pyrolysed[731,732] (equation 237).

(235)

(236)

$$TeCl_4 + 4\,ArLi \longrightarrow Ar_4Te \xrightarrow{\Delta} ArAr + ArTeAr \qquad (237)$$

(91)

Allyl halides were dimerized to 1, 5-dienes by treatment with the telluride dianion (Te^{2-}), probably via radical intermediates[733] (e.g. equation 238). In the case of unsymmetrical starting materials, varying amounts of all three coupled products (head-to-head, head-to-tail and tail-to-tail) were sometimes observed. Several sulfone-stabilized anions were dimerized to olefins with elemental tellurium[417] (equation 239).

$$2 \quad \langle\rangle\!\!-\!\!Br \xrightarrow{\ Te^{2-}\ } \langle\rangle\!-\!\langle\rangle \tag{238}$$

86%

$$ArCH_2SO_2Ph \xrightarrow[\text{2. Te(cat.)}]{\text{1. BuLi}} ArCH=CHAr \tag{239}$$

D. Selenium and Tellurium Extrusion Reactions

1. C—C bond formation

The flash vacuum pyrolysis or photolysis of selenides, diselenides and tellurides results in extrusion of the selenium or tellurium atom and concomitant coupling of the two α-carbon atoms. Applications have been found in the synthesis of bibenzyls[734] (equation 240) and various strained hydrocarbons. These include benzo- and naphtho-cyclobutane[735], cyclophanes[736-739] such as 93, biplanene (95)[740], lepidopterene (96)[740], and norcaradiene[741,742], the last compound reversibly. Illustrative examples are given in equations 241[735], 242[738] and 243[740]. Compounds 95 and 96 were produced from the dimerization of anthrylmethyl radicals generated by the extrusion of selenium from 94 followed by photochemical [4 + 4] or thermal [4 + 2] cycloadditions, respectively[740].

$$ArCH_2SeCH_2Ar \xrightarrow[\text{(600 °C)}]{\Delta} ArCH_2CH_2Ar + Se \tag{240}$$

$$\xrightarrow[\text{(500 °C)}]{\Delta} \tag{241}$$

74%

(92)

$$\xrightarrow[\text{P(NMe}_2)_3]{h\nu} \tag{242}$$

93%

(93)

$AntCH_2Se_nCH_2Ant$

(94) $n=1,2$

$Ant=$

$$\begin{array}{ccccc} & & (95) & : & (96) \\ 94 & \xrightarrow[h\nu]{Ph_3P} & 1 & & 3 \\ & \xrightarrow[210\ ^\circ C]{\Delta} & AntCH_2CH_2Ant & + & 96 \\ & & 1 & : & 3 \end{array}$$

$$\tag{243}$$

A related approach to bibenzyls and hydrocarbons such as **92, 93, 95** and **96** employs the disproportionation of aryl benzyl selenides induced by flash vacuum pyrolysis or photolysis, as shown in general form in equation 244[743,744].

$$2\ ArCH_2SePh \xrightarrow[h\nu]{\Delta\ or} ArCH_2CH_2Ar\ +\ PhSeSePh \tag{244}$$

The preparation of β-diketones or β-keto esters from the base-catalysed extrusion of selenium from the selenoesters **97** was reported[745] (equation 245).

$$\tag{245}$$

2. C= C bond formation

A particularly efficacious variation of the Barton two-fold extrusion technique for the synthesis of hindered olefins is based on the cycloadditions of diazo compounds (or their

phosphoranylidenehydrazones) with selenoketones[746,747]. The resulting selenadiazolines (**98**) fragment readily by loss of nitrogen to furnish episelenide intermediates, which collapse to the desired olefins by the spontaneous extrusion of selenium (equation 246). Extensive further studies by Guziec and coworkers[748-752] have resulted in the preparation of a number of exceptionally hindered olefins such as **99** and **100**, but tetra *t*-butylethylene has to date eluded all preparative attempts by this or other methods. In some related work, hindered azines were obtained from the photolytic extrusion of selenium from cycloadducts **98**[751], and the reaction of phenyl azide with selenoketones afforded hindered imines[753] by a process analogous to equation 246.

The extrusion of selenium and nitrogen from selenadiazoles shown in equation 190 is similar to the process in equation 246 and provides a nonconnective synthesis of acetylenes.

$$
\begin{array}{c}
\underset{R}{\overset{R}{>}}C{=}Se \;+\; \bar{N}{=}\overset{+}{N}{\overset{R^1}{\underset{R^1}{<}}} \longrightarrow \underset{R}{\overset{R}{>}}\overset{Se}{\underset{N=N}{\diagup\diagdown}}\overset{R^1}{\underset{R^1}{<}} \xrightarrow[\substack{-N_2 \\ -Se}]{\Delta} \underset{R}{\overset{R}{>}}C{=}C{\overset{R^1}{\underset{R^1}{<}}}
\end{array}
$$

(98)

(246)

(99)   **(100)**

E. Other Connective Reactions

1. With selenoacetals activated by Lewis acids

Several connective methods employing the reactions of nucleophilic carbon centers with selenium-stabilized cationic species have been reported. The intermediates are normally formed *in situ* by the abstraction of a second selenium moiety or a halide from an appropriate precursor with a Lewis acid. Enol silyl ethers thus produce *C*-alkylated products with selenoacetals and $SnCl_4$[69], triselenoorthoformates and $TiCl_4$[754], and with α-halo selenides and $TiCl_4$[754] or β-halo selenides and $ZnBr_2$[755]. An example is provided in equation 247[69].

$$
\underset{R^1}{\overset{OSiMe_3}{\underset{R}{>}{=}}} \;+\; \underset{R^2}{\overset{R^2}{>}}{\overset{SeR^3}{\underset{SeR^3}{<}}} \xrightarrow{SnCl_4} \underset{R}{\overset{O}{\diagup\!\!\diagdown}}\underset{R^1}{\overset{R^2\;R^2}{\diagup\!\!\diagdown}}SeR^3
$$

(247)

Pyrrole, furan, thiophene and 1,3,5-trimethoxybenzene undergo Friedel–Crafts alkylations with 1-seleno-[756] or 2-seleno-substituted[757] allyl cations generated according to equation 248.

$$RSe\diagdown\diagup SeR$$
$$\xrightarrow{AgClO_4, CaCO_3}$$

[furan structure] $\diagup SeR$ $R = Me, Ph$

(248)

$$\xrightarrow[AgClO_4]{}$$

[structure with SePh, R, R, Br]

[furan structure] R $R = H, Me$

2. Free-radical allylation

The free-radical exchange of phenylseleno and allyl groups can be effected by treating alkyl phenyl selenides with allyltributyltin hydride in the presence of a radical initiator[504,758]. An example is shown in equation 249[758]. The reaction constitutes a convenient allylation procedure.

[lactone structure with SePh] $+ \diagup\diagdown SnBu_3$ $\xrightarrow[AIBN]{\Delta \text{ or } h\nu}$ [lactone product]

75-84%

(249)

3. Phenolic coupling

Phenolic coupling reactions are sometimes observed during the oxidations of phenols and catechols with BSA (27)[356] or diphenyl selenoxide (52)[553] (see Section V.E.). In some cases the yields of coupled products are high enough to be of preparative value (e.g. equation 250[356]).

[phenol structure] $\xrightarrow[2.BSA]{1.NaH}$ [bicyclic product structure]

55%

(250)

4. Arylation of olefins

Olefins produce mixtures of arylated products with Ph_2Te[759], Ph_2Se[759] or Ph_2TeCl_2[728] in the presence of Pd^{II} catalysts. Yields are variable and aryl coupling products are also formed (equation 251).

[olefin] R $+ Ph_2TeCl_2$ $\xrightarrow{Pd^{II}}$ $Ph\diagdown\diagup\diagdown R$

(251)

5. Wittig reactions of α-selenophosphoranes

Petragnani, Comasseto and coworkers reported a connective approach to vinyl selenides via the Wittig reaction of α-selenophosphoranes with aldehydes[152,263,760], or the Horner–Wittig reaction of α-selenophosphonates with aldehydes or ketones[269,760]. The further transformation of the products to ketones by hydrolysis was carried out in several cases[269] (equations 252 and 253).

$$(252)$$

$$(253)$$

XII. CLEAVAGE REACTIONS WITH SELENIUM AND TELLURIUM NUCLEOPHILES

Selenolates (RSe⁻) are weak bases but exceptionally powerful, soft nucleophiles. These properties make them valuable and sometimes unique reagents in a number of synthetic operations. Their ability to displace even relatively poor leaving groups such as carboxylates, alkoxides and amines from carbon enable them to carry out the cleavage of O— or N—alkyl bonds in esters, lactones, epoxides, ethers and amines. Liotta and coworkers[761,762] demonstrated that the reactivity of selenolates is highly dependent on their degree of solvation, the nature of the counter ion and the method of preparation, which must therefore be chosen with care. (For instance, the popular procedure for preparing NaSePh from PhSeSePh and NaBH$_4$ in ethanol probably affords a borane-selenolate complex with considerably suppressed nucleophilic strength[762]. This method should therefore be avoided if a more potent selenolate nucleophile is required.)

Several other reagents which either liberate selenolates *in situ* or act as their equivalents have been introduced recently. These include the silyl selenide PhSeSiMe$_3$ (54), its tellurium analog PhTeSiMe$_3$ (101), the aluminum selenolates Me$_2$AlSeMe (102) and *i*-Bu$_2$AlSeMe (103), and the selenoboranes B(SeMe)$_3$ (104) and B(SePh)$_3$ (105).

A. Cleavage of Esters and Lactones

Selenolates attack esters and lactones at the softer alkyl rather than the harder acyl carbon atom, resulting in the displacement of the carboxylate anion (equation 254). Reagents include LiSeMe in DMF[763], NaSePh in DMF[204,764,765] or THF[766], usually with added HMPA[177,761,762,767–771], as well as the more reactive potassium salt KSePh[769,770]. The silyl selenide 54[654,772,773] or telluride 101[774] can be used in a similar capacity in the presence of KF and 18-crown-6[772], ZnI$_2$[773,774] or TiCl$_4$[654]. The reaction is sensitive to steric hindrance and so methyl esters can be cleaved in the presence of others[762]. In contrast to the above reagents, the aluminum selenolate 102 attacks esters and lactones at the acyl carbon atom to afford high yields of selenoesters[718,719] (equation 254).

$$\underset{\substack{\parallel \\ RCOR^1}}{\overset{O}{}} \xrightarrow{\text{PhSe}^-} RCO_2^- + R^1SePh$$

$$\xrightarrow[\text{or PhTeSiMe}_3 \text{ (101)}]{\text{PhSeSiMe}_3 \text{ (54)}} \underset{\substack{\parallel \\ RCOSiMe_3}}{\overset{O}{}} + R^1SePh \text{ or } R^1TePh \quad (254)$$

$$\xrightarrow{\text{Me}_2\text{AlSeMe (102)}} \underset{\substack{\parallel \\ RCSeMe}}{\overset{O}{}} + Me_2AlOR^1$$

Several examples which illustrate further transformations used in concert with selenolate ring opening are given in equations 255[771], 256[765] and 257[768]. These include selenoxide elimination, Claisen rearrangement and decarboxylation, respectively.

(255)

(256)

(257)

B. Cleavage of 2-Oxazolines and 2-Oxazines

2-Methyl-2-oxazolines and 2-methyl-2-oxazines[775,776] undergo ring opening with NaSePh in DMF or with the silyl selenide 54. A synthetic route to secondary carboxamides was reported on the basis of prior N-alkylation of the oxazoline 106, ring opening and degradation of the resulting β-selenoethyl substituent[776] (equation 258).

C. Cleavage of Epoxides

The cleavage of epoxides with a selenolate was first reported by Sharpless and Lauer[26] and provides an excellent preparative route to allylic alcohols via equation 259. When the β-hydroxy selenides thus formed are subjected to reductive deselenization (see equation 209), the method constitutes an efficient procedure for the stereospecific deoxygenation of epoxides[655,681,684].

(260)

Effective reagents for epoxide opening include selenolates[49,61,204,531-534,655,777-779], NaTePh[780], the reagents 54[772,781], 101[774], 102[718,719], 103[48,782], 104[783] and 105[783] and benzeneselenol (PhSeH) in the presence of alumina[784]. Attack by the selenolate generally occurs at the less hindered epoxide carbon and is *anti* stereospecific. In cyclic systems, a strong preference for approach from the axial direction may outweigh other factors, as in the example in equation 260[61]. The selenoborane reagents 104 and 105[783] and the silyl selenide 54[781] produce mixtures of regioisomers which in the case of the latter can be regulated with appropriate catalysts. In related work, α,β-epoxy sulfoxides[779] and α,β-epoxy ketones[785] afforded desulfurized ketones and β-hydroxy ketones, respectively, with NaSePh and NaHTe.

D. Cleavage of Ethers and Amines

Aryl methyl ethers[786-789] and thioethers[788] were demethylated with selenolates or with the silyl telluride 101[774] to give phenols and thiophenols, respectively (equation 261).

$$\begin{array}{c} ArOMe \\ or \\ ArSMe \end{array} \xrightarrow{NaSeR} \begin{array}{c} ArOH \\ or \\ ArSH \end{array} + RSeMe \qquad (261)$$

Quaternary ammonium salts were demethylated with NaSePh[790] while amines were similarly dealkylated in the presence of ruthenium catalyst[791]. Selenols are also effective reagents for amine dealkylations as they are sufficiently acidic to protonate the amine, thereby activating it toward C—N cleavage[792] (equation 262).

$$R_3N + PhSeH \longrightarrow R_3\overset{+}{N}H \ ^-SePh \longrightarrow R_2NH + RSePh \qquad (262)$$

Primary amines can be deaminated by first converting them into their bis-*N*-tosyl derivatives followed by C—N cleavage with NaSePh or NaSPh[793] (equation 263).

$$RNH_2 \longrightarrow RNTs_2 \xrightarrow[\text{or}]{\substack{NaSePh \\ NaSPh}} RSePh \ or \ RSPh \qquad (263)$$

E. Cleavage of Cyclopropanes

Cyclopropanes which contain activating substituents (ketone[764,794,795], ester[794,796], cyano[764,794]) ring open with selenolates to provide γ-selenides. These compounds serve as precursors of β-γ-unsaturated compounds by selenoxide elimination (e.g. equation 264[796]).

$$(264)$$

XIII. TRANSFORMATIONS OF ALCOHOLS VIA SELENIDES

Alcohols are readily converted into selenides by the displacement of their tosylates or mesylates with selenolates, or by their direct reaction with selenols in the presence of H_2SO_4 or $ZnCl_2$[797]. Subsequent oxidation and elimination produce the corresponding olefins, thus achieving the overall dehydration of the alcohol. This procedure generally avoids the rearrangements and other side reactions which frequently accompany classical dehydration procedures. Similarly, alkyl halides can be dehydrohalogenated via their selenides. Numerous examples of both processes have appeared in the literature since the early work of Grieco and coworkers[98,99,798-800] and others demonstrated their synthetic utility (equation 265).

$$R\diagdown\diagup\diagdown\diagup^{OH} \longrightarrow R\diagdown\diagup\diagdown\diagup^{X} \xrightarrow{ArSe^-} R\diagdown\diagup\diagdown\diagup^{SeAr} \xrightarrow{OX.} R\diagdown\diagup\diagdown\diagup$$

$$X=OMs, OTs,$$
$$halide$$

$$(265)$$

An alternative procedure for the direct transformation of primary or secondary alcohols to selenides was reported by Grieco and coworkers[39,173,801-803] and it obviates the need for intermediate tosylates, mesylates or halides. The alcohol is treated with an aryl selenocyanate (ArSeCN; Ar is usually o-nitrophenyl) and tributylphosphine in solvents such as pyridine or THF. Selenoxide elimination then completes the dehydration process as usual (equation 266). More recently, N-PSP (34) has been used in place of aryl selenocyanates. This reagent works effectively for primary alcohols[286,804-807], but in the case of a secondary alcohol the formation of the corresponding alkylphthalimide occurred instead of the expected selenide[808]. Alcohols can also be converted into tellurides with PhTeCN and tributylphosphine and then subjected to telluroxide elimination[809].

$$R\diagdown\diagup\diagdown\diagup^{OH} \xrightarrow[Bu_3P]{ArSeCN\ or\ N\text{-}PSP\ (34)} R\diagdown\diagup\diagdown\diagup^{SeAr} \xrightarrow{OX.} R\diagdown\diagup\diagdown\diagup \quad (266)$$

Since selenide formation in equation 266 occurs with inversion of configuration at the α-carbon, subsequent brominolysis of the product via equation 117 (where inversion also takes place) provides an overall method for the conversion of chiral alcohols into alkyl bromides with overall retention of configuration[430].

In a closely related variation of this work, it was found that the treatment of carboxylic acids with PhSeCN[810] or N-PSP[286,804] and tri-butylphosphine affords selenoesters (equation 267). Other selenium electrophiles which have been employed for this purpose are PhSeCl[811], PhSeSePh[811], $Bu_3P^+SeMe^-OSO_2R$[812] and PhSeNMeAc[147]. When N-PSP was used in the presence of primary or secondary amines, the corresponding carboxamides were formed in high yield[804].

$$RCO_2H \begin{cases} \xrightarrow[Bu_3P]{ArSeCN\ or\ N\text{-}PSP(34)} RC\underset{\overset{\|}{O}}{}SeAr \\ \\ \xrightarrow[\substack{Bu_3P, \\ R_2'NH}]{N\text{-}PSP} RC\underset{\overset{\|}{O}}{}NR_2' \end{cases} \quad (267)$$

The deoxygenation of alcohols and carboxylic acids via their selenides and selenoesters is discussed in the following section.

XIV. REDUCTIVE DESELENIZATION AND DETELLURIZATION

A. Reagents

Many selenium- or tellurium-based transformations require the reductive removal of the selenium or tellurium residue after it has served its purpose. A number of procedures have been developed for this reduction. Deselenizing reagents include Raney nickel[78,395,477,493,513,645,813], nickel boride[112,395,566,814], lithium triethylborohydride[815] and lithium in ethylamine[645]. Free radical deselenizations with tributyl[285,480,816] or triphenyltin hydride[525,780,817] have proved especially useful. Detellurizations have been carried out similarly with tin hydrides[483,499,780] and Raney nickel[415].

B. Deoxygenation of Alcohols

Since alcohols are efficiently converted to selenides via equations 265 and 266, subsequent reductive deselenization[645,780,817] results in their overall deoxygenation to alkanes (equation 268).

$$ROH \longrightarrow RSeAr \xrightarrow{\substack{\text{reductive} \\ \text{deselenization}}} RH \qquad (268)$$

C. Deoxygenation of Aldehydes and Ketones

Selenoacetals are readily available from their parent aldehydes or ketones[631]. Reductive deselenization then completes the deoxygenation of the carbonyl compound to the corresponding hydrocarbon[634,645,780,817] (equation 269). The procedure is therefore an attractive alternative to the Wolff–Kishner and Clemmensen reductions. During detailed studies of the utility of triphenyltin hydride in this respect, Clive and coworkers[780,817] also demonstrated that the corresponding tin deuteride made possible the preparation of deuterium-labelled hydrocarbons.

$$(269)$$

D. Reduction of Selenoesters and Telluroesters

1. Se-Phenyl selenoesters and selenocarbonates

Se-Phenyl selenoesters reacted with tributyltin hydride to afford aldehydes and alkanes[818-820] whose relative amounts were determined by the nature of the substrates and conditions (equation 270). High temperatures and branched selenoesters favored decarbonylation to alkanes, whereas mild reduction conditions favored the aldehydes. Selenocarbonates produced formates, alcohols and alkanes by deselenization, decarbonylation and decarboxylation, respectively[818] (equation 271).

$$
\underset{\substack{\| \\ RCSePh}}{O} \xrightarrow[\substack{AIBN, \\ \Delta \text{ or } h\nu}]{Bu_3SnH} RCHO + RH \tag{270}
$$

$$
\underset{\substack{\| \\ ROCSePh}}{O} \xrightarrow[\substack{AIBN, \\ \Delta \text{ or } h\nu}]{Bu_3SnH} \underset{\substack{\| \\ ROCH}}{O} + ROH + RH \tag{271}
$$

2. O-Alkyl seleno- and telluro-esters

The selenoester **107** afforded cholestene as the principal product after tin hydride reduction[821] (equation 272), and O-alkyl telluroesters produced monomeric and dimeric ethers[628,822] with NaHTe (equation 273).

(272)

(273)

XV. REDUCTIONS WITH SELENIUM AND TELLURIUM COMPOUNDS

Selenolates and tellurolates, and also inorganic species such as NaHSe and NaHTe, function as efficient and sometimes highly selective reducing agents for many organic functionalities. In many cases the reducing species can be formed *in situ* in catalytic amounts in the presence of a less expensive co-reductant.

A. Reduction of Halides

Vicinal dihalides and also β-chloro- and β-bromo-selenides undergo reductive elimination to olefins with NaHSe[823], NaSePh[824], NaSeMe[824], Na_2Te[825], NaHTe[826,827], KTeAr[828] and the tellurolate **108**[829] (equation 274). The products are often formed stereospecifically by *anti*-elimination. Conjugated dienes were regenerated from their 1,4-dibromo adducts with reagent **108**[830]. The sequence of bromination–debromination can therefore be used in the protection of olefins and dienes. Further reduction of the olefin product was observed with excess of NaHTe in the case of styrene derivatives[827].

$$(274)$$

(108)

α-Halo ketones[831-834], esters[833], amides[832,833] and carboxylic acids[832] were de-halogenated with PhSeH[834], NaHTe[833], the tellurolate **108**[832] or the tellurophosphate **109**[831] (equation 275). In some cases α-acetoxy, α-mesyloxy or α-phenylthio substituents were similarly reduced[832].

$$(275)$$

$$\underset{\textbf{(109)}}{(EtO)_2\overset{\displaystyle O}{\overset{\|}{P}}TeNa}$$

The selective monodebromination of *gem*-dibromocyclopropanes with NaHTe was also reported recently[835] (equation 276).

$$(276)$$

B. Reduction of Epoxides

The stereospecific deoxygenation of epoxides with triphenylphosphine selenide and trifluoroacetic acid provides olefins with retention of configuration[836,837] via the pathway shown in equation 277. Other reagents which were later employed in a similar manner include the more reactive phosphine selenides **110** and **111**[838], the selenoamides **112**[839]

$$(277)$$

(110)   **(111)**   **(112)**   **(113)**

and 113[840], the tellurophosphate 109[841] and KSeCN[842]. Alternatively, the deoxygenation of epoxides can be carried out by ring opening with a selenolate followed by reductive elimination (see Section XII.C).

Potassium selenocyanate (KSeCN) was reported to effect the $E \rightleftharpoons Z$ isomerization of olefins via their bromohydrins in a process resembling equation 277[843]. This provides an alternative to the $TeCl_4$ -mediated isomerization shown in equation 112.

C. Reduction of Carbonyl Compounds

Aldehydes and ketones are efficiently reduced to alcohols with hydrogen telluride produced *in situ* from the hydrolysis of Al_2Te_3[844] or by photolysis with hydrogen selenide[844] (equation 278). Non-enolizable aldehydes afford primary alcohols with PhSeH[845] or with the magnesium selenolate PhSeMgBr[846]. Enones and other α,β-unsaturated carbonyl compounds undergo preferential reduction of the carbon—carbon double with NaHTe[847], H_2Te[844] or photochemically with PhSeH[848] (equation 279).

$$\underset{R^1}{\overset{R}{>}}=O \xrightarrow[\text{or } H_2Se, h\upsilon]{H_2Te} \underset{R^1}{\overset{R}{>}}\underset{OH}{\overset{H}{<}} \qquad (278)$$

$$R\diagdown\diagup\overset{O}{\underset{\|}{C}}\diagdown R^1 \xrightarrow[\text{PhSeH}, h\upsilon]{\underset{H_2Te \text{ or}}{NaHTe}} R\diagdown\diagup\overset{O}{\underset{\|}{C}}\diagdown R^1 \qquad (279)$$

D. Reduction of Nitrogen Compounds

Selenium and tellurium reducing agents perform several types of synthetically useful transformations of nitrogen compounds. These generally involve reduction of the N—O, N—N, N=N,—$\overset{+}{N}\equiv$N or C=N bonds. Examples are summarized in Table 2.

E. Reduction of Sulfoxides

Sulfoxides were efficiently deoxygenated to sulfides with selenols[861], the selenoboranes 104 and 105[862,863], the selenophosphate 114[864] and the silyl selenides 54[865] and 115–117[866]. The last reagents were also used to deoxygenate selenoxides and telluroxides (equation 280).

$$\underset{R}{\overset{O}{\underset{\|}{S}}}R^1 \xrightarrow{\text{Se,Te reagent}} RSR^1 \qquad (280)$$

$$\overset{O}{\underset{\|}{(EtO)_2PSeNa}}$$
$$(114)$$

$$Me_3SiXSiMe_3$$
$$(115) \ X=S$$
$$(116) \ X=Se$$
$$(117) \ X=Te$$

XVI. REARRANGEMENTS

A. [2, 3] Sigmatropic Rearrangements of Allylic Selenoxides

The facile [2, 3] shifts of allylic selenoxides provide an efficient method for introducing new allylic oxygen functions into an organic substrate. Several examples have already been noted in previous sections in connection with other overall transformations (see equations 70, 138, 207, 214 and 215). In general, [2,3] sigmatropic rearrangements of

TABLE 2. Reduction of nitrogen compounds

Nitrogen compound	Product	Reagent	References
ArNO$_2$	ArNH$_2$	H$_2$Se	849, 850
"	"	H$_2$Te	851
"	"	NaHTe	845, 852
"	"	PhTeH	845, 853
ArNO$_2$	ArN=$\overset{\overset{\displaystyle O^-}{\mid}}{N}$Ar	NaHTe	852
RNO$_2$	RNH$_2$	PhSeH–DABCO	854
RNO$_2$	(RNO)$_2$	NaHTe	852
R-$\overset{\overset{\displaystyle O^-}{\mid}}{N}\overset{+}{=}$CHR'	R-NHCH$_2$R'	NaHTe (pH 6)	855
R-$\overset{\overset{\displaystyle O^-}{\mid}}{N}\overset{+}{=}$CHR'	R-N=CHR'	NaHTe (pH 10–11)	855
R$_3$$\overset{+}{N}$-$\overset{-}{O}$	R$_3$N	NaHTe	855
ArN=O	ArNH$_2$	H$_2$Se	850
"	"	PhSeH–DABCO	854
PhN=O	PhNHNHPh	H$_2$Te	851
ArNHOH	ArNH$_2$	PhSeH–DABCO	854
"	"	H$_2$Se	850
"	"	H$_2$Te	851
ArN=$\overset{\overset{\displaystyle O^-}{\mid}}{N}$Ar	ArNHNHAr	H$_2$Te	851
"	"	NaHTe	845
ArN=$\overset{\overset{\displaystyle O^-}{\mid}}{N}$Ar	ArNH$_2$	PhSeH–DABCO	854
ArN=NAr	ArNHNHAr	H$_2$Te	851
ArN=NAr	ArNH$_2$	PhSeH–DABCO	854
RN$_3$	RNH$_2$	NaHTe	856
ArN$_2$$^+BF_4$$^-$	ArNHNH$_2$	PhSeH–CH$_2$Cl$_2$	857
ArN$_2$$^+BF_4$$^-$	ArSeH + ArH	PhSeH–acetone	857
ArNHNHAr	ArNH$_2$	PhSeH–DABCO	854
R$_2$C=N-R'	R$_2$CHNHR'	PhSeH	848, 858
"	"	NaHTe	845, 859
"	"	PhTeH	845
R$_2$C=N-X (X = OH or NR$_2'$)	R$_2$CHNHX	PhSeH	848
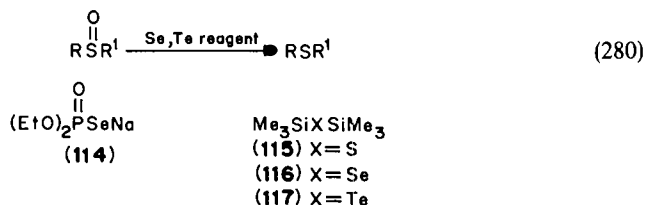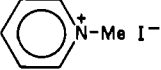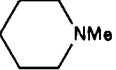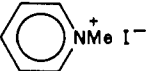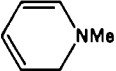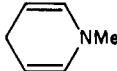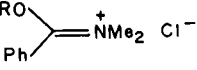
		NaHTe (pH 6)	859

2 : 1

		NaHTe (pH 10–11)	859

	PhCH$_2$OR	NaHTe	821, 860

selenoxides are stereospecific and more rapid than competing selenoxide eliminations. However, if the rearrangement is impeded by steric or conformational effects, then diene products resulting from elimination can become dominant[37,138].

Kametani and coworkers[374,375] and Clive and coworkers[867] independently developed an allylic alcohol transposition process based on conversion of the initial alcohol to a selenide with Grieco and coworkers' ArSeCN–Bu$_3$P reagent, followed by oxidation and rearrangement (equation 281). Several recent applications are depicted in equations 282[808], 283[868] and 284[123].

(281)

65–80%

49% (282)

92%

68% (283)

$$\text{(284)}$$
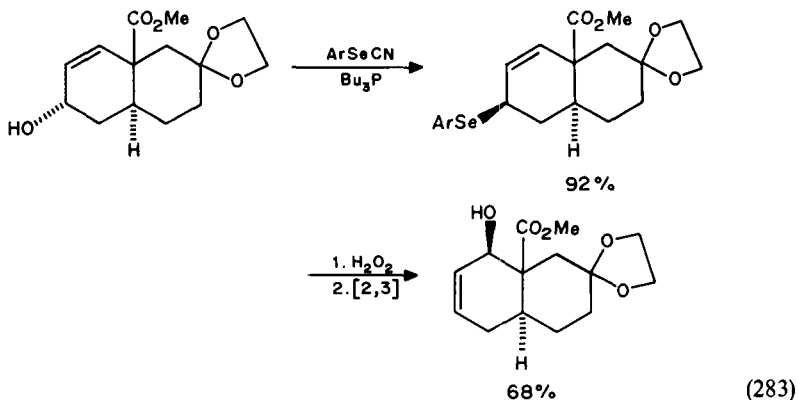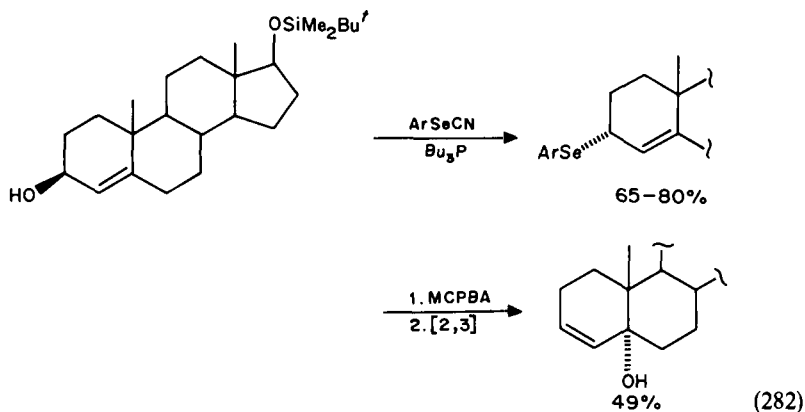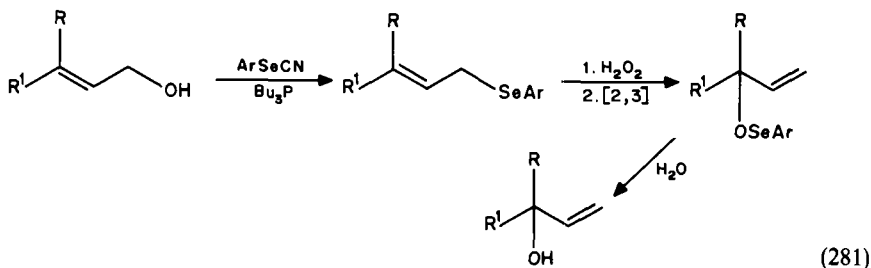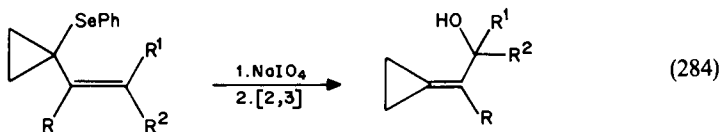
Oxaziridines are particularly effective reagents for the oxidation step[88] and chiral oxaziridines resulted in chirality transfer to the product allylic alcohol with enantiomeric excesses of up to 12.8%[89]. Allylic telluroxides undergo similar [2,3] shifts, but the products sometimes undergo further oxidation to enones and are accompanied by unrearranged byproducts[869].

The reverse of the [2,3] rearrangement of allylic selenoxides to selenenic esters (i.e. intramolecular addition of the ester to an olefin), followed by selenoxide elimination, was studied by Reich and coworkers[66,870,871] in an effort to prepare dienes from allylic alcohols (equation 285). However, sulfenate esters proved more efficacious for this purpose because the equilibrium in the rearrangement step favours the sulfoxide vs. its sulfenate ester isomer, whereas the contrary is true for the less favorable selenium system[872].

$$\text{(285)}$$
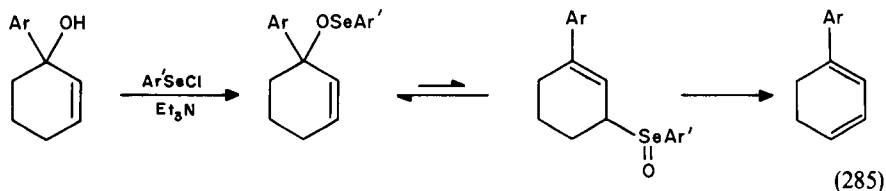
In some cases, vinyl selenoxides produce unrearranged allylic alcohols by base-catalysed double bond isomerization followed by [2,3] rearrangement[112,222,693]. An example is shown in equation 286[112,222].

$$\text{(286)}$$
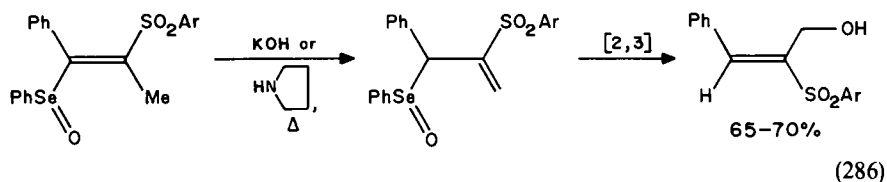
Allenic alcohols were prepared from conjugated dienyl selenides as shown in equation 287[406], while allenic selenides were converted into propargyl ketones[460,873] or alcohols[874] as in the example given in equation 288[873].
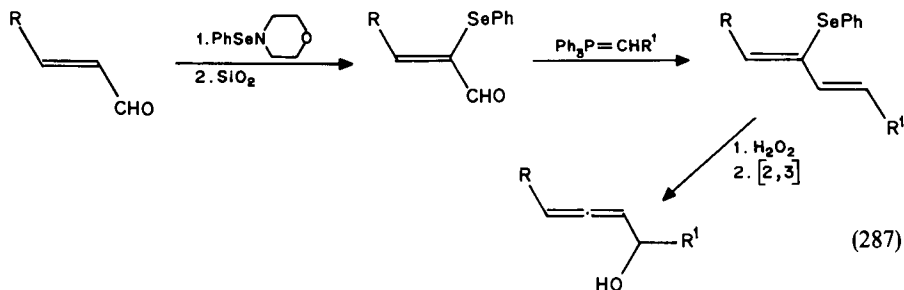
$$\text{(287)}$$
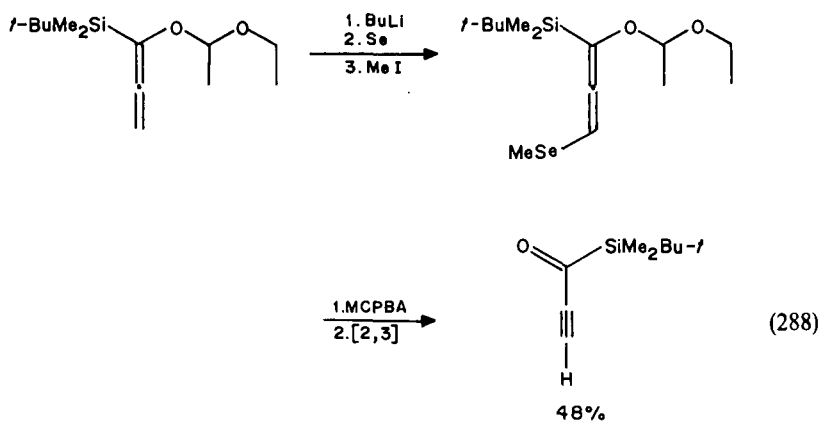
Allyl silanes serve as convenient precursors of rearranged alcohols[875-877]. For example, silanes **118** were treated with PhSeCl and SnCl$_2$ to afford the selenides **119**, which in turn produced rearranged alcohols on oxidation and [2,3] shift, as shown in equation 289[877]. An added feature of the method is that sulfenyl chlorides can be similarly employed but give the isomeric unrearranged allylic alcohols via sulfides **120**.
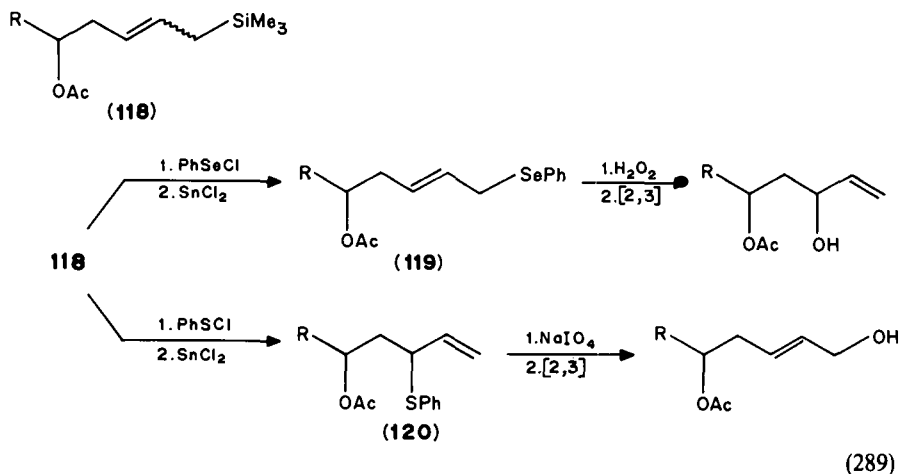
A different reaction in which an allyl silane was transformed into an unrearranged alcohol is illustrated in equation 290[878].
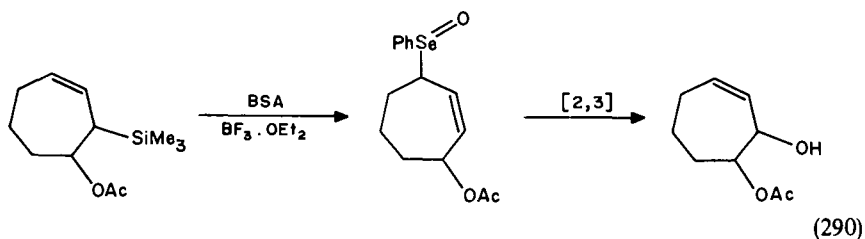
B. Other Sigmatropic Reactions

Sharpless and Lauer[879] reported that allyl phenyl selenides undergo reversible [1,3] shifts in which the arylseleno residue migrates to the less substituted position. An example where such a process is used on conjunction with a [2,3] selenoxide rearrangement to obtain the corresponding allylic alcohol is provided in equation 291[692]. Examples of [1,5] and [2,3] sigmatropic rearrangements of dienyl selenides (see equation 217) and allylic diselenides[879], respectively, are also known, as well as [2,3] rearrangements of allylic[880-882] or benzylic[883] selenium ylides. Although these latter reactions have synthetic potential, they have remained relatively unexploited.

$$\text{(291)}$$
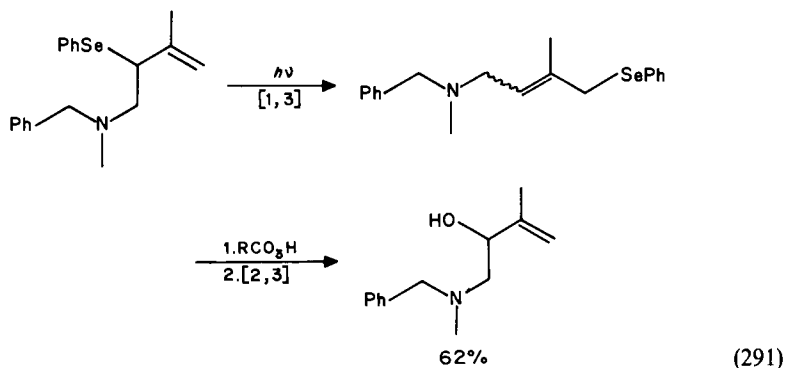
A sigmatropic rearrangement in which the selenium does not participate directly is shown in equation 292, where 3-(phenylseleno)orthopropionate (121) reacts with allylic alcohols and undergoes Claisen orthoester rearrangement. Selenoxide elimination then affords unsaturated esters or lactones, including α-methylene-γ-butyrolactones[884]. Also, sigmatropic rearrangements involving selenium imides are useful amination procedures as described previously in Section VI.A.2.

$$\text{(292)}$$
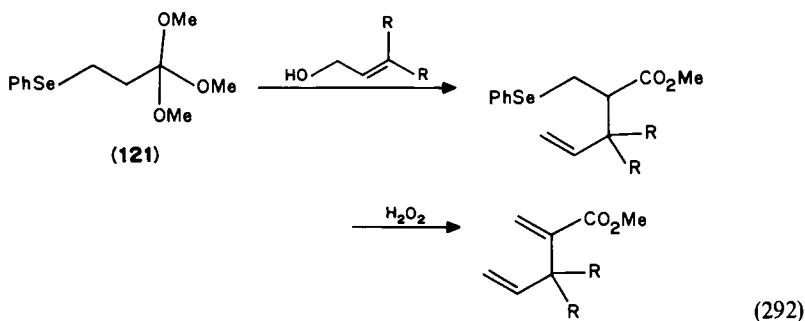
C. Ring Expansions and Contractions

1. Ring expansions

The condensation products 122 of metalated cyclopropyl selenides and ketones or aldehydes undergo ring expansion to cyclobutanes when subjected to acid catalysis[668,670,671] (equation 293). The cyclopropyl selenides 123 behave similarly[661]. The

procedure can be employed in an iterative manner as the product cyclobutanones[670,671] as well as cyclic ketones of larger ring sizes[667,669], are themselves easily converted into β-hydroxy selenides capable of ring expansion. Several related selenium-mediated ring expansions of cyclopropyl[94,777] and cyclobutylcarbinols[701] were also reported and one example is given in equation 294[94]. A different type of ring expansion of cyclic dithioketals is shown in equation 295[885]. A ring expansion of cyclic enones is described in Section XVII.A (see equation 300).

(293)

88%

65%

(294)

$n = 1 : 74\%$
$n = 2 : 56\%$

(295)
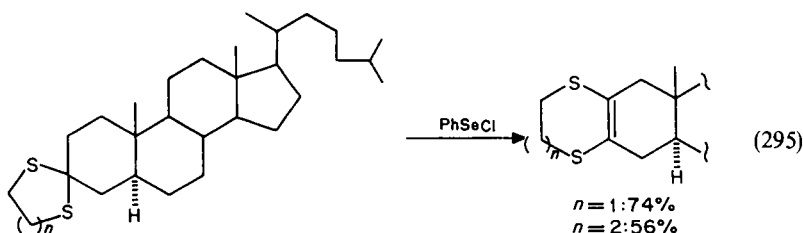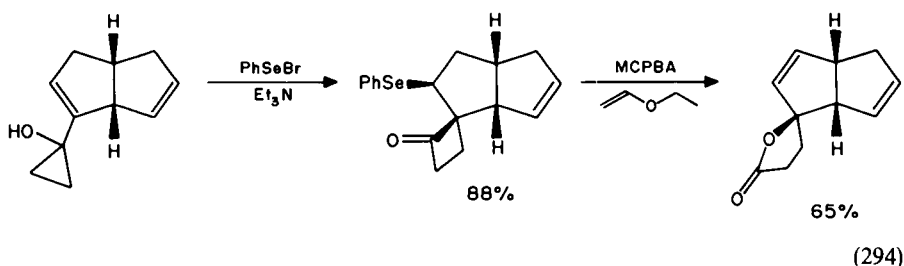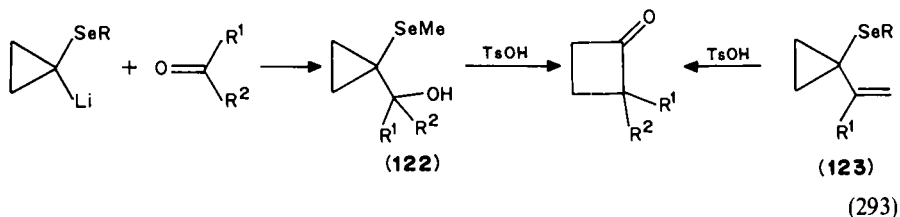
2. Ring contractions

The ring contraction of β-methoxycycloalkyl selenides 124[283,387] and tellurides 125[117,283] is promoted by oxidation to the corresponding selenones and tellurones with MCPBA (equation 296). Selenoxide elimination was observed instead when hydrogen peroxide was used as the oxidant, presumably because oxidation beyond the selenoxide or telluroxide level proceeds more slowly than elimination.

(124) X = Se
(125) X = Te

$n = 1,2$

(296)
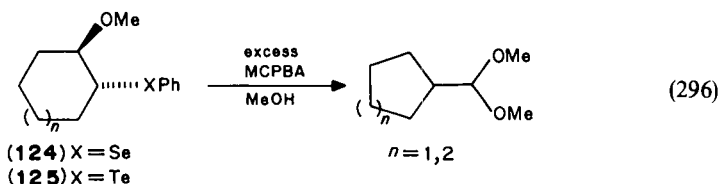
D. Other Rearrangements

Several examples of isolated cases of selenium-induced rearrangements with synthetic potential are provided in equations 297[886], 298[887] and 299[888].

$$\text{(297)}$$

$$\text{(298)}$$

$$\text{(299)}$$
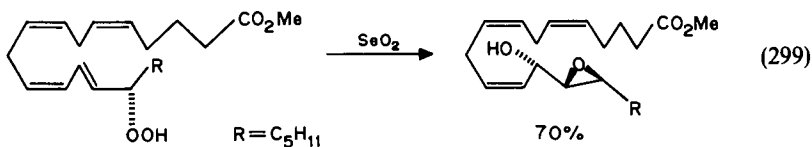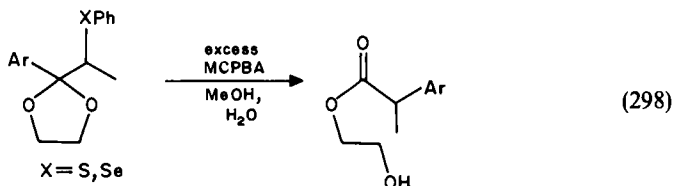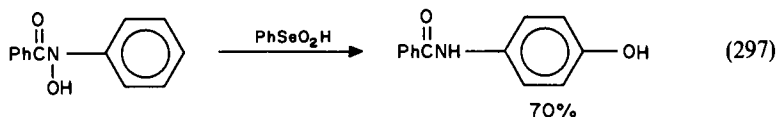
XVII. TRANSFORMATIONS OF ALDEHYDES, KETONES AND ENONES

A. Via α-Selenenylated Derivatives

Selenenium-based methodology has furnished many convenient procedures for effecting key transformations of carbonyl compounds. Aldehydes and ketones are readily selenenylated by the methods described in Section III.A.1 and act as key intermediates in the preparation of other classes of compounds. These processes are summarized in Scheme 2.

The synthesis of enones by selenoxide elimination is indicated in path a and was discussed in detail in Section III.A.1. The acidifying effect of the selenium residue permits the regioselective alkylation of α-seleno ketones via their enolates[212,311,799,802,803,880,889] (path b). The alkylated products can be further converted to exo-[889] or endo-cyclic enones[799,802,803] (path c).

The treatment of α-seleno ketones with 0.5 equivalent of LDA in THF containing HMPA results in the transselenenylation of the selenium moiety from the α to the α'-position, if it is less substituted than the α-position[889,890] (path d). Similar trans-selenenylation were noted in α-seleno-β-ketoesters and their enamines[891]. Selenoxide elimination of the rearranged products affords α', β'-unsaturated ketones via path e[212,890].

α-Seleno ketones are reductively deselenized with LiSePh[892], PhSH[311,694,695] or HBr[893] (path f), or converted into α-silyl ketones by reduction of their enol silyl ethers with lithium and dimethylaminonaphthalene[894] (path g).

Addition reactions to the carbonyl group of α-seleno aldehydes and ketones occur with LiAlH$_4$[895] or with carbon nucleophiles such as Grignard reagents[214,221,321,895], Me$_3$SiCH$_2$Li[896,897] (followed by dehydroxysilylation and PhSe migration) and enolates[898-901] to furnish β-hydroxy selenides (path h). The diastereoselectivity of such
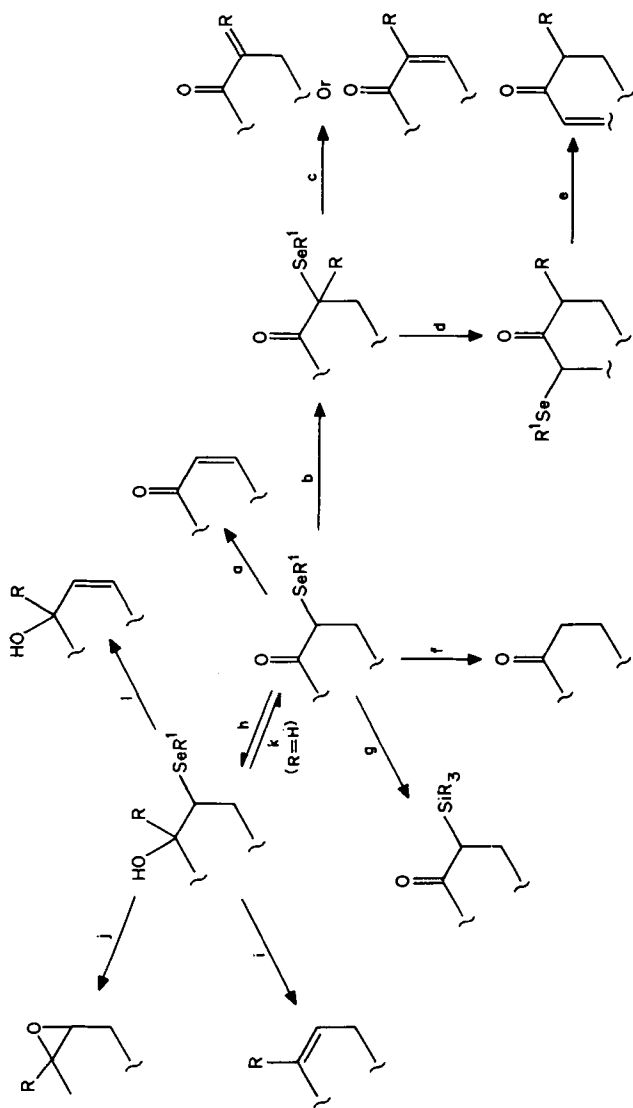
SCHEME 2

additions favors *threo* products with LiAlH$_4$ (i.e. R = H in path h) and *erythro* isomers with Grignard reagents[895]. The products in turn afford olefins by reductive elimination[321,895] (path i) or epoxides via the corresponding selenonium salts[214,221,321,895] (see equation 205) as in path j.

α-Phenylselenoacetaldehyde (36) is an especially useful α-seleno carbonyl compound[321,898-901]. Its reaction with enolates, followed by reductive elimination, provides a convenient synthesis of β,γ-unsaturated ketones[898-901]. An interesting iterative ring expansion based on this reaction used in conjunction with Cope and oxy-Cope rearrangements was reported by Clive and coworkers[899,901] and an illustrative example is shown in equation 300[901].

β-Hydroxy selenides were selectively oxidized to ketones or aldehydes without affecting the selenium residue using DDQ[321], NCS–Me$_2$S–Et$_3$N[92,321], Ar$_3$BiCO$_3$[902] and CCl$_3$CHO–Al$_2$O$_3$[903] (path k). Most other oxidants produce allylic alcohols instead (path l), and Jones reagent oxidizes both the alcohol and selenide groups to give enones[91,92].

Several other less general reactions of α-seleno carbonyl compounds are displayed in equations 301 and 302. α-Selenocyclopropyl ketones (126) afford γ-iodo ketones with P$_2$I$_4$[904], and α-selenopropanoyl chloride (127) was employed in the *in situ* formation and cycloaddition of the corresponding ketene 128 in a synthesis of α-methylene-β-lactams[905].

(300)

(301)

(302)
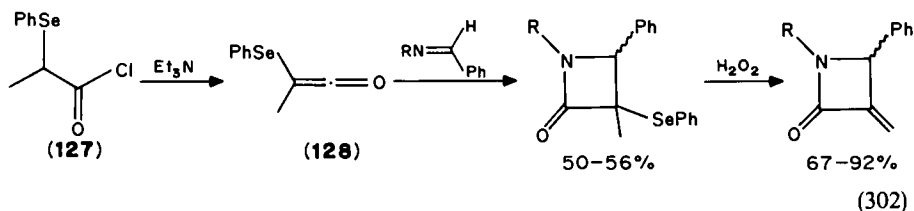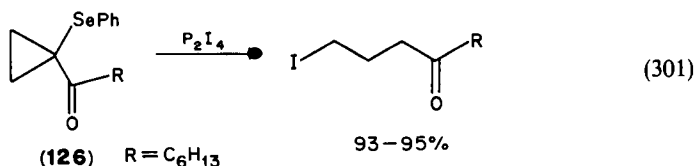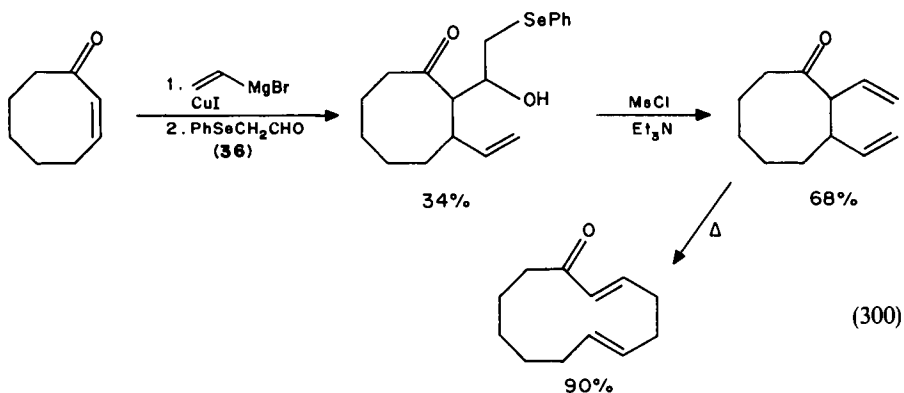
B. Reactions of Enones

Synthetically useful selenium-mediated transformations of enones are described in Scheme 3. Enones[91,906-908] (and also α,β-unsaturated lactones[906,909-913], propargylic esters[914,915] and nitroolefins[916]) act as Michael acceptors of selenols and selenolates (path a). Since the reaction can be easily reversed by selenoxide elimination (path b) the procedure serves as a protective method for sensitive functionalities such as α-methylene lactones[909] and α-methylene cyclic ketones[908]. Selenols add to cyclohexenones in the presence of $(-)$-cinchonidine to afford optically active β-seleno ketones with an enantiomeric excess of 11–43%[917]. The β-seleno ketones obtained by path a react with hydride-reducing agents[907] or with Grignard reagents[91] to afford the corresponding alcohols (or lactols from β-seleno lactones[910]), as shown in path c.

Michael additions to enones were also studied with the silyl selenide 54[68,446,772,918,919], the aluminum selenolate 102[718,719,920,921] and a selenoborane[922]. In some cases, reagents 54 and 102 were used to deliver the equivalent of the selenolate anion RSe^- to the enone to give β-seleno ketones in much the same manner as path a[718,719,772,919]. The silyl selenide 54 also afforded isolable β-seleno enol silyl ethers from enones in the presence of Ph_3P[918] or iodine[446] (path d; $X = SiMe_3$). In other instances, the corresponding enol aluminates[920,921] (path d; $X = AlMe_2$) and enol boronates[922] (path d; $X = BR_2^2$) were employed in subsequent aldol condensations (path e). The enol silyl ethers also condensed with ketals and orthoformates in the presence of trimethylsilyl triflate[68]. Finally, selenoxide elimination of the aldol condensation products afforded the corresponding α-substituted enones (path e).

Cyclohexenone reacted with PhSeCN and tributylphosphine in a similar manner to the above reagents to furnish the γ-seleno-α,β-unsaturated nitrile product shown in path f in 50% yield[704].

In work related to that shown in paths d and f, simple aldehydes were converted into silylated hemiselenoacetals with the silyl selenide 54[446,918] and to α-seleno nitriles with ArSeCN and tributylphosphine[704], thus providing an alternative route to these compounds to the selenenylation of nitriles. These reactions are shown separately in equation 303.

The Michael additions of various carbon nucleophiles to enones generate enolates which can be trapped with selenenylating agents such as PhSeCl or PhSeBr (path g). The nucleophiles include organocuprates[133,134,923-926], Grignard reagents in the presence of Cu^I salts[927-930] and organozirconium[931] and organoaluminum reagents[931]. In most such examples, the selenenylation step was followed by selenoxide elimination, resulting in the overall β-alkylation of the original enone, or by reductive deselenization to the saturated ketone (path h).

Enones can be converted into α-seleno enones with selenenamides (see equation 106) or with PhSeCl in pyridine[932] as shown in path i. The related α-selenenylation of α,β-unsaturated esters was similarly carried out with LDA and PhSeBr[933]. The α-seleno enones are in turn useful as dienophiles in Diels–Alder reactions[934]. They can also be reconverted into their parent enones by treatment with NaSePh followed by oxidation with H_2O_2[695] (path j), or subjected to Michael addition with organocuprates via path k[694,695,889,892] followed by oxidative or reductive removal of selenium as indicated in path h. A brief review of the transformations of α-seleno enones has recently appeared[934].

Two other useful transformations of enones are worthy of note. A selenium-based enone transposition sequence (path l) was reported by Liotta and coworkers[935,936] and is shown in more detail in equation 304. The α-halogenation of enones with PhSeBr and PhSeCl (path m) was described earlier (see equation 110).

$X = SiMe_3, BR^2_2, AlMe_2$

SCHEME 3

(303)

(304)
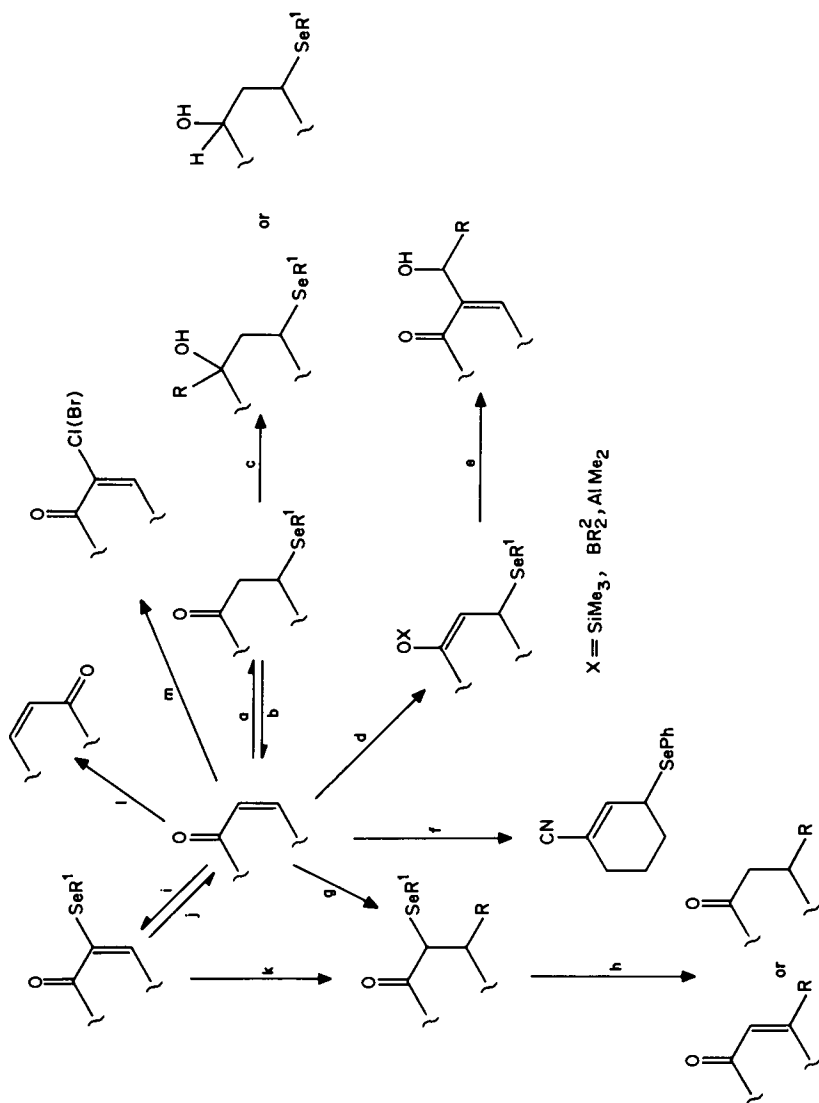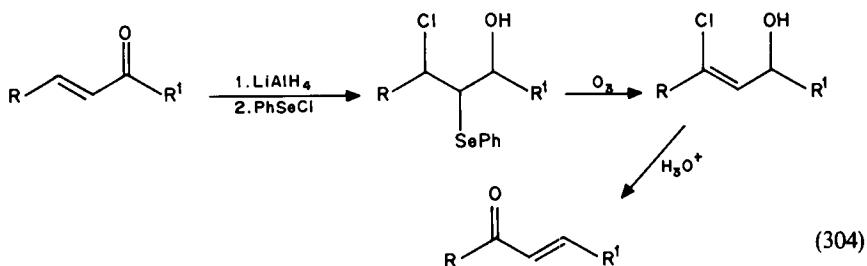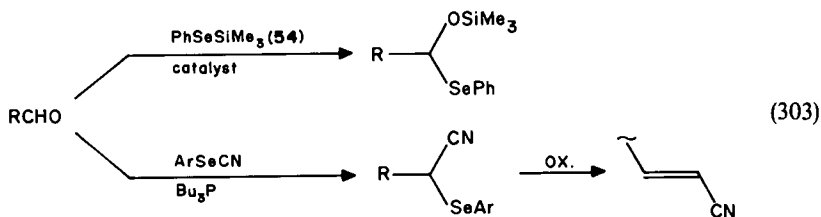
XVIII. TRANSFORMATIONS OF DIAZO COMPOUNDS

Several types of selenium and tellurium compounds undergo insertion reactions by the carbon atom of a diazo compound, with concomitant loss of nitrogen. It is thus possible to introduce a selenium or tellurium moiety, together with an additional functional group, to the diazo carbon atom. Although formally related, such reactions proceed via a number of different pathways, including ionic, carbene or carbenoid, and free-radical mechanisms, depending on the nature of the reactants and the conditions.

A. Diazoalkanes

Diazomethane and other diazoalkanes insert into the Se—Se, Te—Te, Se—Br or Se—X linkage of diselenides[937], ditellurides[937,664], selenenyl bromides[263,665] and various selenenyl pseudohalides[463] as shown in equation 305, while a selenosulfonate afforded an anomalous double-insertion product with diazomethane under photochemical conditions[271] (equation 306).

$$CH_2N_2 + ArSeX \longrightarrow ArSeCH_2X$$
$$X = ArSe, Br, NCS,$$ (305)
$$NCSe, phthalimido$$

$$CH_2N_2 + p\text{-}TolSO_2SePh \xrightarrow{h\nu} p\text{-}TolSO_2CH_2CH_2SePh$$ (306)
(excess)   60%
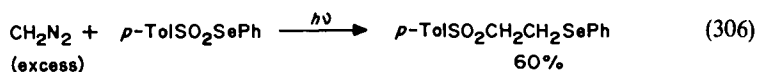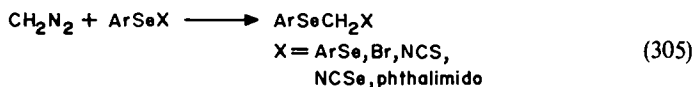
B. α-Diazo Ketones and α-Diazo Esters

Cyclic and acyclic α-diazo ketones were conveniently converted into α-substituted enones by their reaction with selenenyl halides or pseudohalides, followed by selenoxide elimination or dehydrohalogenation[938,939] (equation 307).

(307)
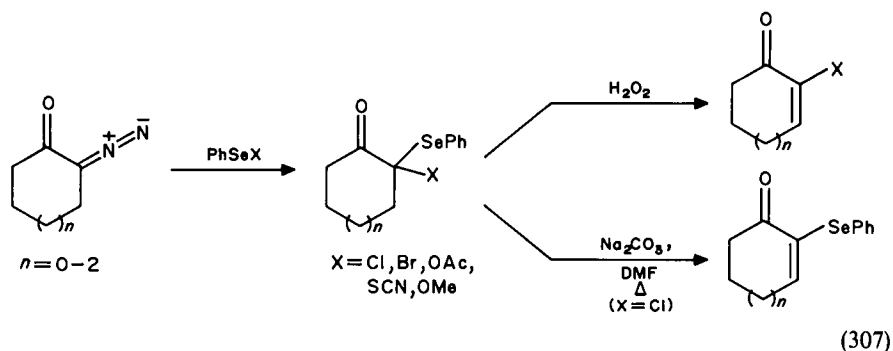
α-Diazo esters afforded similar insertion products with PhSeSePh[940], ArSeSCN[463], ArSeSeCN[463] or N-PSP (34)[463], but eliminated spontaneously to vinyl selenides in some cases where a β-hydrogen atom was present in the diazo compound[463] (equation 308 and 309).

$X = SePh, NCS + SCN,$
$NCSe, phthalimido$ (308)

$X = I, NHAc, phthalimido$ (309)

(310)
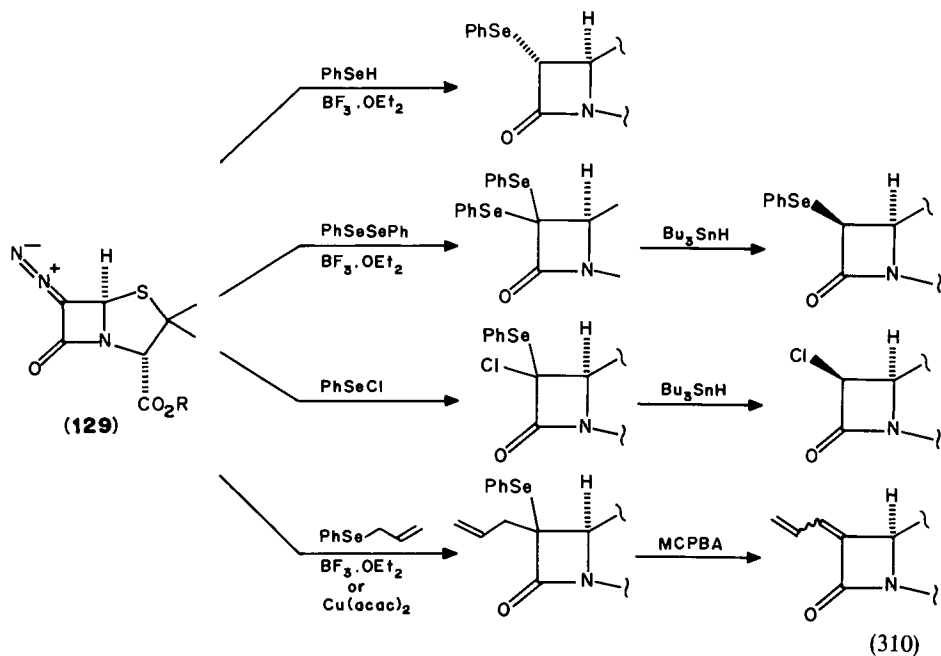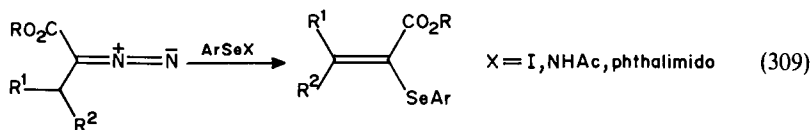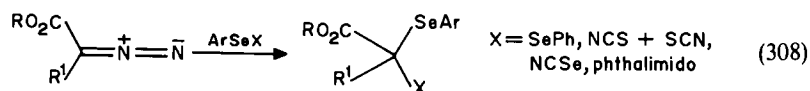
C. Diazopenicillinates

The diazopenicillinates **129** were transformed into a variety of selenium-containing products, often stereoselectively, as shown in equation 310[881,882,941].

D. Reaction with Selenoesters

The copper-catalysed insertion of diazomethane into the acyl—selenium linkage of selenoesters provides access to α-seleno ketones[893,942] via equation 311. When a workup with aqueous HBr is performed, the α-seleno ketones are further converted into methyl ketones in high yield[893].

$$\underset{\substack{\| \\ RCSeR^1}}{O} \xrightarrow[\substack{Cu \text{ or} \\ Cu^I}]{CH_2N_2} \underset{\substack{\| \\ RCCH_2SeR^1}}{O} \xrightarrow{HBr} \underset{\substack{\| \\ RCMe}}{O} \qquad (311)$$
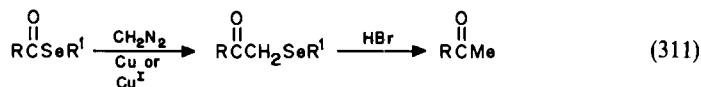
XIX. CARBONYLATIONS

A method for the carbonylation of nucleophilic compounds such as amines, alcohols and thiols was developed by Sonoda and coworkers and involves treating the organic substrate with carbon monoxide and elemental selenium, often in the presence of a base such as Et_3N or DBU. The results are summarized in Table 3. Carbonyl selenide (Se=C=O) is believed to function as an intermediate in these processes and may be prepared separately from carbon monoxide and selenium[961]. The selenium can be employed catalytically in carbonylations in the presence of oxygen, which reoxidizes the byproduct hydrogen selenide back to the fee element. The carbonylation of amines was also reported with tellurium instead of selenium[962,963]. Formamide byproducts were produced unless nitrobenzene was added to suppress their formation[963].

The carbonylations of aryltellurium chlorides and of vinyl and alkyl tellurides were effected with nickel carbonyl[964] or with carbon monoxide and $PdCl_2$–LiCl catalyst[965] to afford principally carboxylic acid products.

XX. MISCELLANEOUS SYNTHETIC APPLICATIONS

A. Decarboxylations

Barton and coworkers[102] reported a general decarboxylation method in which acid chlorides or mixed anhydrides are converted into the selenohydroxamic esters **130**, which fragment on pyrolysis or photolysis according to equation 312. The product selenides can then be further transformed oxidatively or otherwise. Similarly, the thiohydroxamic esters **131** and **132** decarboxylated to afford sulfides, selenides or tellurides when heated in the presence of disulfides, diselenides or ditellurides, respectively[966].

(130)   (312)

(131)   (132)
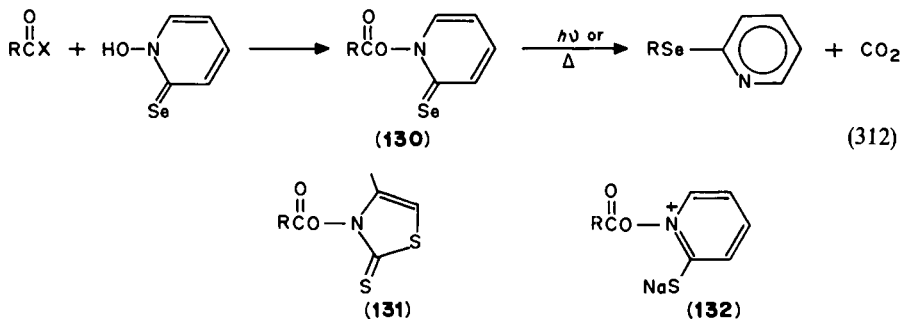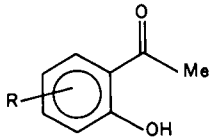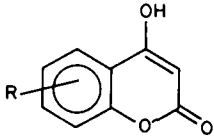
TABLE 3. Carbonylations with carbon monoxide and selenium

Starting materials	Carbonylation products	Ref.
RNH_2(or $ArNH_2$)	$RNHCNHR$ (C=O)	943–946
R_2NH	R_2NCNR_2 (C=O)	947
$ArNH_2$	$ArNHCHO$	948
$RNH_2 + R'SSR'$	$RNHCSR'$ (C=O)	949
$R_2NH + R'X$	R_2NCSeR' (C=O)	950
$RNH_2 + R'OH$	$RNHCOR'$ (C=O)	951
Me_2NNH_2	$Me_2NNHCNHNMe_2$ (C=O)	952
$RONa$	$ROCOR$ (C=O)	953,954

(X,Y = NH,O,S) 945,955,956

(X = NH,O) 955

957,958

| $R_2NCHO + NaOR'$ | R_2NCOR' (C=O) | 959 |
| $ROCHO + NaOR'$ | $ROCOR'$ (C=O) | 960 |

B. Alkylations with Trimethylselenonium Hydroxide

The selenonium hydroxide **133** is a strong methylating agent which converts carboxylic acids into methyl esters, alcohols and phenols to methyl ethers, thiols to methyl sulfides, and amines and azoles to their N-methyl derivatives[967,968] (equation 313).

$$
\left.\begin{array}{l} RCO_2H \\ ROH \\ RSH \\ RNH_2 \end{array}\right\} + Me_3\overset{+}{Se}\,\overset{-}{O}H \longrightarrow \left\{\begin{array}{l} RCO_2Me \\ ROMe \\ RSMe \\ RNHMe \end{array}\right. \tag{313}
$$

(**133**)
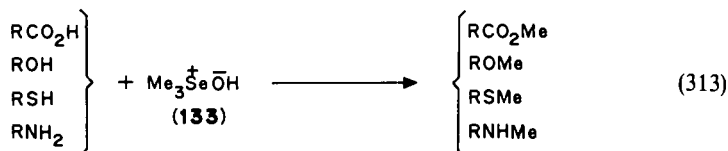
C. Telluroxides as Aldol Catalysts

Telluroxides are effective catalysts for aldol condensations[969,970], as illustrated by the example in equation 314[969].

$$
PhCHO + Ph\overset{O}{\overset{\|}{C}}Me \xrightarrow{Ar_2Te=O \text{ (70)}} Ph \overset{O}{\diagup}\diagdown Ph \tag{314}
$$

94%
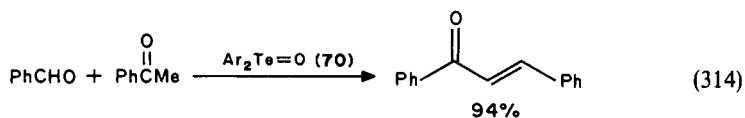
D. Protecting Group for Alcohols

The β-phenylselenoethyl group was recently employed as an alcohol protective group[971]. It can be introduced via the β-bromoethyl selenide **134** and removed by oxidation and hydrolysis (equation 315). The protected alcohol withstands ⁻OH, NaBH₄, LiAlH₄ and Grignard reagents. The similarly protected dienol ether **135** has recently found application in Diels–Alder reactions[972].

$$
PhSe\diagdown\diagup Br \text{ (134)} \tag{315}
$$

ROH
AgNO₃, MeCN
80–90%

RO⌒⌒SePh

1. H₂O₂
2. HCl
65–70%

(**135**)
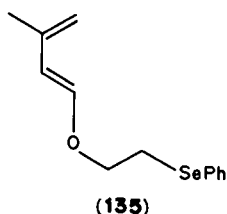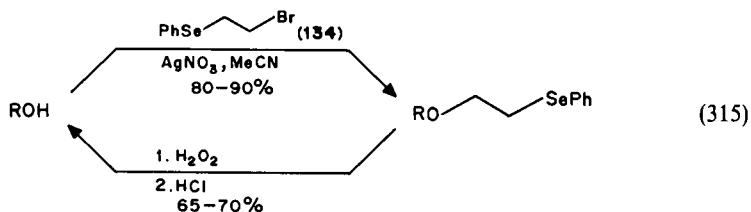
XXI. REFERENCES

1. D. L. Klayman and W. H. H. Gunther, (Eds.), *Organic Selenium Compounds: Their Chemistry and Biology,*. Wiley–Interscience, New York, 1973.
2. K. J. Irgolic and M. V. Kudchadker, in *Selenium* (Eds. R. A. Zingaro and W. C. Cooper), Van Nostrand Reinhold, New York, 1974, Ch. 8.
3. K. B. Sharpless, K. M. Gordon, R. F. Lauer, D.W. Patrick, S. P. Singer and M. W. Young, *Chem. Scr.*, **8A**, 9 (1975).
4. H. J. Reich, in *Oxidation in Organic Chemistry, Part C* (Ed. W. S. Trahanovsky), Academic Press, New York, 1978, Ch. 1.
5. H. J. Reich, *Acc. Chem. Res.*, **12**, 22 (1979).
6. D. L. J. Clive, *Tetrahedron*, **34**, 1049 (1978).
7. D. L. J. Clive, *Aldrichim. Acta*, **11**, 43 (1978).
8. P. D. Magnus, in *Comprehensive Organic Chemistry* (Eds. D. H. R. Barton and W. D. Ollis), Vol. 3, Part 12, Pergamon Press, Oxford, 1979.
9. S. V. Ley, *Annu. Rep. Chem. Soc., Sect. B*, **77**, 233 (1980).
10. D. Liotta, *Acc. Chem. Res.*, **17**, 28 (1984).
11. D. Liotta, (Ed.), *Recent Aspects of Organoselenium Chemistry*, Tetrahedron Symposium-in-Print, *Tetrahedron*, **41**, 4727–4889 (1985).
12. D. Liotta (Ed.), Organoselenium Chemistry, Wiley, New York, in press.
13. K. C. Nicolaou and N. A. Petasis, *Selenium in Natural Products Synthesis*, CIS, Philadelphia, 1984.
14. K. J. Irgolic, *The Organic Chemistry of Tellurium*, Gordon and Breach, New York, 1974.
15. K. J. Irgolic, *J. Organomet. Chem.*, **103**, 91 (1973).
16. K. J. Irgolic, *J. Organomet. Chem.*, **130**, 411 (1977).
17. K. J. Irgolic, *J. Organomet. Chem.*, **158**, 235 (1978).
18. K. J. Irgolic, *J. Organomet. Chem.*, **158**, 267 (1978).
19. K. J. Irgolic, *J. Organomet. Chem.*, **189**, 65 (1980).
20. K. J. Irgolic, *J. Organomet. Chem.*, **203**, 367 (1980).
21. S. Uemura, *Kagaku (Kyoto)*, **36**, 381 (1981).
22. L. Engman, *Acc. Chem. Res.*, **18**, 274 (1985).
23. J. L. Huguet, *Adv. Chem. Ser.*, No. 76, 345 (1967).
24. D. N. Jones, D. Mundy and R. D. Whitehouse, *J. Chem. Soc., Chem. Commun.*, 86 (1970).
25. R. Walter and J. Roy, *J. Org. Chem.*, **36**, 2561 (1971).
26. K. B. Sharpless and R. F. Lauer, *J. Am. Chem. Soc.*, **95**, 2697 (1973).
27. K. B. Sharpless, R. F. Lauer and A. Y. Teranishi, *J. Am. Chem. Soc.*, **95**, 6137 (1973).
28. K. B. Sharpless, M. W. Young and R. F. Lauer, *Tetrahedron Lett.*, 1979 (1973).
29. H. J. Reich, I. L. Reich and J. M. Renga, *J. Am. Chem. Soc.*, **95**, 5813 (1973).
30. D. L. J. Clive, *J. Chem. Soc., Chem. Commun.*, 695 (1973).
31. S. Uemura and A, Toshimitsu, *Bull. Inst. Chem. Res., Kyoto Univ.*, **62**, 105 (1984).
32. P. A. Grieco and M. Miyashita, *J. Org. Chem.*, **39**, 120 (1974).
33. H. J. Reich and S. K. Shah, *J. Am. Chem. Soc.*, **97**, 3250 (1975).
34. H. J. Reich, S. K. Shah and F. Chow, *J. Am. Chem. Soc.*, **101**, 6648 (1979).
35. R. H. Mitchell, *J. Chem. Soc., Chem. Commun.*, 990 (1974).
36. N. Zylber, J. Zylber and A. Gaudemer, *J. Chem. Soc., Chem. Commun.*, 1084 (1978).
37. W. G. Salmond, M. A. Barta, A. M. Cain and M. C. Sobala, *Tetrahedron Lett.*, 1683 (1977).
38. H. J. Reich, S. Wollowitz, J. E. Trend, F. Chow and D. F. Wendelborn, *J. Org. Chem.*, **43**, 1697 (1978).
39. P. A. Grieco, S. Gilman and M. Nishizawa, *J. Org. Chem.*, **41**, 1485 (1976).
40. K. B. Sharpless and R. F. Lauer, *J. Org. Chem.*, **39**, 429 (1974).
41. B. M. Trost and D. M. T. Chan, *J. Org. Chem.*, **48**, 3346 (1983).
42. P. Rollin, V. V. Bencomo and P. Sinaÿ, *Synthesis.*, 134 (1984).
43. K. Furuichi, S. Yogai and T. Miwa, *J. Chem. Soc., Chem. Commun.*, 66 (1980).
44. M. Petrzilka, *Helv. Chim. Acta*, **61**, 2286 (1978).
45. M. Petrzilka, *Helv. Chim. Acta*, **61**, 3075 (1978).
46. R. Pitteloud and M. Petrzilka, *Helv. Chim. Acta*, **62**, 1319 (1979).
47. P. Metz and H. -J. Schäfer, *Tetrahedron Lett.*, **23**, 4067 (1982).

48. P. A. Bartlett and P. M. Chouinard, *J. Org. Chem.*, **48**, 3854 (1983).
49. T. Arunachalam and E. Caspi, *J. Org. Chem.*, **46**, 3415 (1981).
50. B. Umezawa, O. Hoshino, S. Sawaki, H. Sashida, K. Mori, Y. Hamada, K. Kotera and Y. Iitaka, *Tetrahedron*, **40**, 1783 (1984).
51. G. Jaurand, J. -M. Beau and P. Sinaÿ, *J. Chem. Soc., Chem. Commun.*, 701 (1982).
52. A. Toshimitsu, H. Owada, T. Aoai, S. Uemura and M. Okano, *J. Chem. Soc., Chem. Commun.*, 546 (1981).
53. A. Toshimitsu, T. Aoai, H. Owada, S. Uemura and M. Okano, *J. Org. Chem.*, **46**, 4727 (1981).
54. U. Schmidt, A. Lieberknecht, H. Bökens and H. Griesser, *J. Org. Chem.*, **48**, 2680 (1983).
55. J. V. Heck and B. G. Christensen, *Tetrahedron Lett.*, **22**, 5027 (1981).
56. S. Danishefsky, E. M. Berman, M. Ciufolini, S. J. Etheredge and B. E. Segmuller, *J. Am. Chem. Soc.*, **107**, 3891 (1985).
57. C. G. Chavdarian, *J. Org. Chem.*, **48**, 1529 (1983).
58. H. J. Reich and J. M. Renga, *J. Org. Chem.*, **40**, 3313 (1975).
59. J. N. Denis, J. Vicens and A. Krief, *Tetrahedron Lett.*, 2697 (1979).
60. A. Toshimitsu, S. Uemura, M. Okano and N. Watanabe, *J. Org. Chem.*, **48**, 5246 (1983).
61. R. W. Rickards and W. P. Watson, *Aust. J. Chem.*, **33**, 451 (1980).
62. S. Raucher, *Tetrahedron Lett.*, 3909 (1977).
63. P. -T. Ho and R. J. Kolt, *Can. J. Chem.*, **60**, 663 (1982).
64. J. -M. Beau, S. Aburaki, J. -R. Pougny and P. Sinaÿ, *J. Am. Chem. Soc.*, **105**, 621 (1983).
65. M. Miyano, *J. Org. Chem.*, **46**, 1846 (1981).
66. I. L. Reich and H. J. Reich, *J. Org. Chem.*, **46**, 3721 (1981).
67. V. J. Jephcote and E. J. Thomas, *Tetrahedron Lett.*, **26**, 5327 (1985).
68. M. Suzuki, T. Kawagishi and R. Noyori, *Tetrahedron Lett.*, **22**, 1809 (1981).
69. K. M. Nsunda and L. Hevesi, *Tetrahedron Lett.*, **25**, 4441 (1984).
70. T. G. Back and S. Collins, *Tetrahedron Lett.*, **21**, 2215 (1980).
71. T. G. Back and S. Collins, *J. Org. Chem.*, **46**, 3249 (1981).
72. R. A. Gancarz and J. L. Kice, *Tetrahedron Lett.*, **21**, 4155 (1980).
73. R. A. Gancarz and J. L. Kice, *J. Org. Chem.*, **46**, 4899 (1981).
74. L. A. Paquette and W. A. Kinney, *Tetrahedron Lett.*, **23**, 5127 (1982).
75. L. A. Paquette and G. D. Crouse, *J. Org. Chem.*, **48**, 141 (1983).
76. W. A. Kinney, G. D. Crouse and L. A. Paquette, *J. Org. Chem.*, **48**, 4986 (1983).
77. K. C. Nicolaou, W. E. Barnette and R. L. Magolda, *J. Am. Chem. Soc.*, **103**, 3486 (1981).
78. K. C. Nicolaou, R. L. Magolda, W. J. Sipio, W. E. Barnette, Z. Lysenko and M. M. Joullie, *J. Am. Chem. Soc.*, **102**, 3784 (1980).
79. T. Hayama, S. Tomoda, Y. Takeuchi and Y. Nomura, *Chem. Lett.*, 1109 (1982).
80. T. Hayama, S. Tomoda, Y. Takeuchi and Y. Nomura, *Tetrahedron Lett.*, **23**, 4733 (1982).
81. S. Tomoda, Y. Takeuchi and Y. Nomura, *J. Chem. Soc., Chem. Commun.*, 871 (1982).
82. T. Hori and K. B. Sharpless, *J. Org. Chem.*, **43**, 1689 (1978).
83. D. Labar, L. Hevesi, W. Dumont and A. Krief, *Tetrahedron Lett.*, 1141 (1978).
84. M. R. Detty, *J. Org. Chem.*, **45**, 274 (1980).
85. E. Vedejs, M. J. Mullins, J. M. Renga and S. P. Singer, *Tetrahedron Lett.*, 519 (1978).
86. Y. Nagao, M. Ochiai, K. Kaneko, A. Maeda, K. Watanabe and E. Fujita, *Tetrahedron Lett.*, 1345 (1977).
87. G. Lesma, G. Palmisano and S. Tollari, *J. Chem. Soc., Perkin Trans. 1*, 1593 (1984).
88. F. A. Davis, O. D. Stringer and J. M. Billmers, *Tetrahedron Lett.*, **24**, 1213 (1983).
89. F. A. Davis, O. D. Stringer and J. P. McCauley Jr., *Tetrahedron*, **41**, 4747 (1985).
90. L. Hevesi and A. Krief, *Angew. Chem., Int. Ed. Engl*, **15**, 381 (1976).
91. M. Sevrin and A. Krief, *Tetrahedron Lett.*, 187 (1978).
92. J. Lucchetti and A. Krief, *C. R. Acad. Sci., Ser. C*, **288**, 537 (1979).
93. H. J. Reich and J. E. Trend, *J. Org. Chem.*, **41**, 2503 (1976).
94. B. M. Trost, J. M. Balkovec and M. K. -T. Mao, *J. Am. Chem. Soc.*, **105**, 6755 (1983).
95. P. E. Eaton, G. D. Andrews, E. -P. Krebs and A. Kunai, *J. Org. Chem.*, **44**, 2824 (1979).
96. A. Toshimitsu, H. Owada, K. Terao, S. Uemura and M. Okano, *J. Org. Chem.*, **49**, 3796 (1984).
97. K. B. Sharpless and M. W. Young, *J. Org. Chem.*, **40**, 947 (1975).
98. P. A. Grieco, K. Hiroi, J. J. Reap and J. A. Noguez, *J. Org. Chem.*, **40**, 1450 (1975).
99. P. A. Grieco, Y. Masaki and D. Boxler, *J. Am. Chem. Soc.*, **97**, 1597 (1975)..

100. A. Toshimitsu, H. Owada, S. Uemura and M. Okano, *Tetrahedron Lett.*, **21**, 5037 (1980).
101. A. Toshimitsu, H. Owada, K. Terao, S. Uemura and M. Okano, *J. Chem. Soc., Perkin Trans. 1*, 373 (1985).
102. D. H. R. Barton, D. Crich, Y. Hervé, P. Potier and J. Thierry, *Tetrahedron*, **41**, 4347 (1985).
103. R. D. Clark and C. H. Heathcock, *J. Org. Chem.*, **41**, 1396 (1976).
104. J. E. Baldwin, N. V. Reed and E. J. Thomas, *Tetrahedron*, **37**, 263 (1981).
105. H. O. House, W. A. Kleschick and E. J. Zaiko, *J. Org. Chem.*, **43**, 3653 (1978).
106. P. E. Eaton, W. H. Bunnelle and P. Engel, *Can. J. Chem.*, **62**, 2612 (1984).
107. R. M. Williams and J. -S. Dung, *Tetrahedron Lett.*, **26**, 37 (1985).
108. H. J. Reich and W. W. Willis, Jr., *J. Am. Chem. Soc.*, **102**, 5967 (1980).
109. T. Miura and M. Kobayashi, *J. Chem. Soc., Chem. Commun.*, 438 (1982).
110. T. G. Back and S. Collins, *Tetrahedron Lett.*, **22**, 5111 (1981).
111. T. G. Back, S. Collins and R. G. Kerr, *J. Org. Chem.*, **48**, 3077 (1983).
112. T. G. Back, S. Collins, U. Gokhale and K. -W. Law, *J. Org. Chem.*, **48**, 4776 (1983).
113. H. Lee and M. P. Cava, *J. Chem. Soc., Chem. Commun.*, 277 (1981).
114. K. B. Sharpless, K. M. Gordon, R. F. Lauer, D. W. Patrick, S. P. Singer and M. W. Young, *Chem. Scr.*, **8A**, 9 (1975).
115. T. Otsubo, F. Ogura, H. Yamaguchi, H. Higuchi, Y. Sakata and S. Misumi, *Chem. Lett.*, 447 (1981).
116. S. Uemura, S. Fukuzawa, A. Toshimitsu and M. Okano, *Tetrahedron Lett.*, **23**, 1177 (1982).
117. S. Uemura and S. Fukuzawa, *Tetrahedron Lett.*; **24**, 4347 (1983).
118. S. Uemura and S. Fukuzawa, *J. Am. Chem. Soc.*, **105**, 2748 (1983).
119. S. Uemura, S. Fukuzawa and A. Toshimitsu, *J. Organomet. Chem.*, **250**, 203 (1983).
120. S. Uemura, K. Ohe and S. Fukuzawa, *Tetrahedron Lett.*, **26**, 895 (1985).
121. S. Halazy and A. Krief, *Tetrahedron Lett.*, 4233 (1979).
122. S. Halazy and A. Krief, *Tetrahedron Lett.*, **21**, 1997 (1980).
123. S. Halazy and A. Krief, *Tetrahedron Lett.*, **22**, 2135 (1981).
124. M. Clarembeau, J. L. Bertrand and A. Krief, *Isr. J. Chem.*, **24**, 125 (1984).
125. M. Sevrin, W. Dumont and A. Krief, *Tetrahedron Lett.*, 3835 (1977).
126. J. N. Denis and A. Krief, *Tetrahedron Lett.*, **23**, 3407 (1982).
127. K. M. Nsunda and L. Hevesi, *J. Chem. Soc., Chem. Commun.*, 1000 (1985).
128. Y. Tsuda, S. Hosoi, A. Nakai, T. Ohshima, Y. Sakai and F. Kiuchi, *J. Chem. Soc., Chem. Commun.*, 1216 (1984).
129. Y. Tsuda and S. Hosoi, *Chem. Pharm. Bull.*, **33**, 1745 (1985).
130. P. A. Grieco, T. Oguri, S. Burke, E. Rodriguez, G. T. DeTitta and S. Fortier, *J. Org. Chem.*, **43**, 4552 (1978).
131. I. Iijima, K. C. Rice and J. V. Silverton, *Heterocycles*, **6**, 1157 (1977).
132. D. D. Weller and H. Rapoport, *J. Med. Chem.*, **19**, 1171 (1976).
133. H. J. Reich, J. M. Renga and I. L. Reich, *J. Org. Chem.*, **39**, 2133 (1974).
134. H. J. Reich, J. M. Renga and I. L. Reich, *J. Am. Chem. Soc.*, **97**, 5434 (1975).
135. D. L. Snitman, R. J. Himmelsbach and D. S. Watt, *J. Org. Chem.*, **43**, 4758 (1978).
136. J. Blumbach, D. A. Hammond and D. A. Whiting, *Tetrahedron Lett.*, **23**, 3949 (1982).
137. L. F. Tietze, G. V. Kiedrowski and B. Berger, *Tetrahedron Lett.*, **23**, 51 (1982).
138. A. B. Smith, III, P. A. Levenberg, P. J. Jerris, R. M. Scarborough, Jr., and P. M. Wovkulich, *J. Am. Chem. Soc.*, **103**, 1501 (1981).
139. G. Quinkert, G. Dürner, E. Kleiner, F. Adam, E. Haupt and D. Leibfritz, *Chem. Ber.*, **113**, 2227 (1980).
140. C. Romming and P. E. Hansen, *Acta Chem. Scand., Ser. A*, **33**, 265 (1979).
141. C. H. Heathcock, C. M. Tice and T. C. Gemroth, *J. Am. Chem. Soc.*, **104**, 6081 (1982).
142. J. R. Williams and J. D. Leber, *Synthesis*, 425 (1977).
143. V. Balogh, J. -C. Beloeil and M. Fetizon, *Tetrahedron*, **33**, 1321 (1977).
144. M. Jefson and J. Meinwald, *Tetrahedron Lett.*, **22**, 3561 (1981).
145. C. Paulmier and P. Lerouge, *Tetrahedron Lett.*, **23**, 1557 (1982).
146. P. Lerouge and C. Paulmier, *Tetrahedron Lett.*, **25**, 1983 (1984).
147. S. Tomoda, Y. Takeuchi and Y. Nomura, *Synthesis*, 212 (1985).
148. K. Hiroi and S. Sato, *Synthesis*, 635 (1985).
149. A. Toshimitsu, H. Owada, S. Uemura and M. Okano, *Tetrahedron Lett.*, **23**, 2105 (1982).

150. R. Michels, M. Kato and W. Heitz, *Makromol. Chem.*, **177**, 2311 (1976).
151. D. Liotta, G. Zima, C. Barnum and M. Saindane, **21**, 3643 (1980).
152. N. Petragnani, J. V. Comasseto, R. Rodrigues and T. J. Brocksom, *J. Organomet. Chem.*, **124**, 1 (1977).
153. N. Miyoshi, T. Yamamoto, N. Kambe, S. Murai and N. Sonoda, *Tetrahedron Lett.*, **23**, 4813 (1982).
154. S. Torii, K. Uneyama and K. Handa, *Tetrahedron Lett.*, **21**, 1863 (1980).
155. A. L. Cossey, L. Lombardo and L. N. Mander, *Tetrahedron Lett.*, **21**, 4383 (1980).
156. L. Lombardo, L. N. Mander and J. V. Turner, *J. Am. Chem. Soc.*, **102**, 6626 (1980).
157. L. Lombardo and L. N. Mander, *J. Org. Chem.*, **48**, 2298 (1983).
158. G. Ohloff, W. Giersch, K. H. Schulte-Elte and C. Vial, *Helv. Chim. Acta*, **59**, 1140 (1976).
159. J. Tsuji, K. Masaoka, T. Takahashi, A. Suzuki and N. Miyaura, *Bull. Chem. Soc. Jpn.*, **50**, 2507 (1977).
160. S. P. Singer and K. B. Sharpless, *J. Org. Chem.*, **43**, 1448 (1978).
161. W. Oppolzer and K. Thirring, *J. Am. Chem. Soc.*, **104**, 4978 (1982).
162. E. Pfaff and H. Plieninger, *Chem. Ber.*, **115**, 1967 (1982).
163. A. B. Smith, III, and R. E. Richmond, *J. Am. Chem. Soc.*, **105**, 575 (1983).
164. M. F. Semmelhack and S. Tomoda, *J. Am. Chem. Soc.*, **103**, 2427 (1981).
165. M. F. Semmelhack, S. Tomoda, H. Nagaoka, S. D. Boettger and K. M. Hurst, *J. Am. Chem. Soc.*, **104**, 747 (1982).
166. A. R. Battersby, A. L. Gutman, C. J. R. Fookes, H. Günther and H. Simon, *J. Chem. Soc., Chem. Commun.*, 645 (1981).
167. N. Ikota and B. Ganem, *J. Org. Chem.*, **43**, 1607 (1978).
168. M. J. Pearson, *J. Chem. Soc., Perkin Trans. 1*, 2544 (1981).
169. E. Gipstein, C. G. Willson and H. S. Sachdev, *J. Org. Chem.*, **45**, 1486 (1980).
170. W. A. Kleschick and C. H. Heathcock, *J. Org. Chem.*, **43**, 1256 (1978).
171. B. B. Snider and G. B. Phillips, *J. Org. Chem.*, **48**, 3685 (1983).
172. P. A. Grieco and M. Nishizawa, *J. Chem. Soc., Chem. Commun.*, 582 (1976).
173. P. A. Grieco and M. Nishizawa, *J. Org. Chem.*, **42**, 1717 (1977).
174. K. Yamakawa, K. Nishitani and T. Tominaga, *Tetrahedron Lett.*, 2829 (1975).
175. K. Yamakawa, T. Tominaga and K. Nishitani, *Tetrahedron Lett.*, 4137 (1975).
176. P. A. Grieco, C. S. Pogonowski and S. Burke, *J. Org. Chem.*, **40**, 542 (1975).
177. T. R. Hoye and A. J. Caruso, *J. Org. Chem.*, **46**, 1198 (1981).
178. C. A. Wilson, II, and T. A. Bryson, *J. Org. Chem.*, **40**, 800 (1975).
179. E. Vedejs, S. Larsen and F. G. West, *J. Org. Chem.*, **50**, 2170 (1985).
180. J. Tsuji, K. Masaoka and T. Takahashi, *Tetrahedron Lett.*, 2267 (1977).
181. P. A. Zoretic and P. Soja, *J. Org. Chem.*, **41**, 3587 (1976).
182. P. A. Zoretic and P. Soja, *J. Heterocycl. Chem.*, **14**, 681 (1977).
183. Y. Ohfune and M. Tomita, *J. Am. Chem. Soc.*, **104**, 3511 (1982).
184. Y. Tsuda, A. Nakai, K. Ito, F. Suzuki and M. Haruna, *Heterocycles*, **22**, 1817 (1984).
185. J. Ficini, A. Guingant and J. d'Angelo, *J. Am. Chem. Soc.*, **101**, 1318 (1979).
186. A. P. Kozikowski and A. Ames, *J. Am. Chem. Soc.*, **103**, 3923 (1981).
187. K. K. Mahalanabis, M. Mumtaz and V. Snieckus, *Tetrahedron Lett.*, **23**, 3971 (1982).
188. J. A. Oakleaf, M. T. Thomas, A. Wu and V. Snieckus, *Tetrahedron Lett.*, 1645 (1978).
189. M. Majewski, G. B. Mpango, M. T. Thomas, A. Wu and V. Snieckus, *J. Org. Chem.*, **46**, 2029 (1981).
190. K. Ito, F. Suzuki and M. Haruna, *J. Chem. Soc., Chem. Commun.*, 733 (1978).
191. J. M. Renga and H. J. Reich, *Org. Synth.*, **59**, 58 (1980).
192. D. Liotta, C. Barnum, R. Puleo, G. Zima, C. Bayer and H. S. Kezar, III, *J. Org. Chem.*, **46**, 2920 (1981).
193. D. J. Goldsmith and H. S. Kezar, III, *Tetrahedron Lett.*, **21**, 3543 (1980).
194. S. C. Welch, C. P. Hagan, D. H. White, W. P. Fleming and J. W. Trotter, *J. Am. Chem. Soc.*, **99**, 549 (1977).
195. M. L. Durrant and E. J. Thomas, *J. Chem. Soc., Perkin Trans. 1*, 901 (1984).
196. R. L. Sobczak, M. E. Osborn and L. A. Paquette, *J. Org. Chem.*, **44**, 4886 (1979).
197. R. Bloch and P. Orvane, *Synth. Commun.*, **11**, 913 (1981).
198. R. F. C. Brown, K. J. Coulston, F. W. Eastwood, B. M. Gatehouse, L. W. Guddatt, M.

Pfenninger and I. Rainbow, *Aust. J. Chem.*, **37**, 2509 (1984).
199. D. Liotta, M. Saindane, C. Barnum, H. Ensley and P. Balakrishnan, *Tetrahedron Lett.*, **22**, 3043 (1981).
200. M. R. Roberts and R. H. Schlessinger, *J. Am. Chem. Soc.*, **103**, 724 (1981).
201. T. Ishida and K. Wada, *J. Chem. Soc., Chem. Commun.*, 337 (1977).
202. T. Ishida and K. Wada, *J. Chem. Soc., Perkin Trans. 1*, 323 (1979).
203. G. M. Ksander, J. E. McMurry and M. Johnson, *J. Org. Chem.*, **42**, 1180 (1977).
204. M. Arita, K. Adachi, Y. Ito, H. Sawai and M. Ohno, *J. Am. Chem. Soc.*, **105**, 4049 (1983).
205. S. Torii, K. Uneyama and M. Ono, *Tetrahedron Lett.*, **21**, 2741 (1980).
206. S. Torii, K. Uneyama, M. Ono and T. Bannou, *J. Am. Chem. Soc.*, **103**, 4606 (1981).
207. F. G. Bordwell, J. E. Bares, J. E. Bartmess, G. E. Drucker, J. Gerhold, G. J. McCollum, M. Van Der Puy, N. R. Vanier and W. S. Mathews, *J. Org. Chem.*, **42**, 326 (1977).
208. A. Toshimitsu, T. Aoai, H. Owada, S. Uemura and M. Okano, *J. Chem. Soc., Chem. Commun.*, 412 (1980).
209. I. Ryu, S. Murai, I. Niwa and N. Sonoda, *Synthesis*, 874 (1977).
210. S. Danishefsky, R. Zamboni, M. Kahn and S. J. Etheredge, *J. Am. Chem. Soc.*, **102**, 2097 (1980).
211. S. Danishefsky, R. Zamboni, M. Kahn and S. J. Etheredge, *J. Am. Chem. Soc.*, **103**, 3460 (1981).
212. J. Olliver and J. Salaün, *J. Chem. Soc., Chem. Commun.*, 1269 (1985).
213. P. A. Grieco, H. L. Sham, J. Inanaga, H. Kim and P. A. Tuthill, *J. Chem. Soc., Chem. Commun.*, 1345 (1984).
214. G. D. Crouse and L. A. Paquette, *J. Org. Chem.*, **46**, 4272 (1981).
215. S. Danishefsky and C. F. Yan, *Synth. Commun.*, **8**, 211 (1978).
216. S. Danishefsky, C. F. Yan and P. M. McCurry, Jr., *J. Org. Chem.*, **42**, 1819 (1977).
217. S. Danishefsky, C. F. Yan, R. K. Singh, R. B. Gammill, P. M. McCurry, Jr., N. Fritsch and J. Clardy, *J. Am. Chem. Soc.*, **101**, 7001 (1979).
218. H. -U. Reissig and I. Reichelt, *Tetrahedron Lett.*, **25**, 5879 (1984).
219. D. R. Williams and K. Nishitani, *Tetrahedron Lett.*, **21**, 4417 (1980).
220. D. R. Williams, B. A. Barner, K. Nishitani and J. G. Phillips, *J. Am. Chem. Soc.*, **104**, 4708 (1982).
221. L. A. Paquette, M. J. Coghlan and P. C. Hayes, *J. Org. Chem.*, **49**, 4516 (1984).
222. T. G. Back, S. Collins and K. -W. Law, *Can. J. Chem.*, **63**, 2313 (1985).
223. T. G. Back, N. Ibrahim and D. J. McPhee, *J. Org. Chem.*, **47**, 3283 (1982).
224. J. Hooz and J. Oudenes, *Synth. Commun.*, **10**, 667 (1980).
225. K. C. Nicolaou, R. L. Magolda and W. J. Sipio, *Synthesis*, 982 (1979).
226. M. F. Semmelhack and A. Zask, *J. Am. Chem. Soc.*, **105**, 2034 (1983).
227. A. G. González, C. Betancor, C. G. Francisco, R. Hernández, J. A. Salazar and E. Suárez, *Tetrahedron Lett.*, 2959 (1977).
228. G. R. Waitkins and C. W. Clark, *Chem. Rev.*, **36**, 235 (1945).
229. N. Rabjohn, *Org. React.*, **5**, 331 (1949).
230. N. Rabjohn, *Org. React.*, **24**, 261 (1976).
231. E. N. Trachtenberg, in *Oxidation* (Ed. R. L. Augustine), Vol. 1, Marcel Dekker, New York, 1969, Ch. 3.
232. R. A. Jerussi, in *Selective Organic Transformations* (Ed. B. S. Thyagarajan), Vol. 1, Wiley, New York, 1970, p. 301.
233. T. Laitalainen, *Ann. Acad. Sci. Fenn., Ser. A2*, 195 (1982).
234. E. R. Koft and A. B. Smith, III, *J. Am. Chem. Soc.*, **104**, 2659 (1982).
235. N. A. Shams, *J. Prakt. Chem.*, **327**, 536 (1985).
236. M. Cain, O. Campos, F. Guzman and J. M. Cook, *J. Am. Chem. Soc.*, **105**, 907 (1983).
237. H. Nagaoka, G. Schmid, H. Iio and Y. Kishi, *Tetrahedron Lett.*, **22**, 899 (1981).
238. D. H. R. Barton, D. J. Lester and S. V. Ley, *J. Chem. Soc., Chem. Commun.*, 130 (1978).
239. D. H. R. Barton, D. J. Lester and S. V. Ley, *J. Chem. Soc., Perkin Trans. 1*, 2209 (1980).
240. D. H. R. Barton, A. G. Brewster, R. A. H. F. Hui, D. J. Lester, S. V. Ley and T. G. Back, *J. Chem. Soc., Chem. Commun.*, 952 (1978).
241. D. H. R. Barton, J. W. Morzycki, W. B. Motherwell and S. V. Ley, *J. Chem. Soc., Chem. Commun.*, 1044 (1981).
242. D. H. R. Barton C. R. A. Godfrey, J. W. Morzycki, W. B. Motherwell and S. V. Ley, *J. Chem. Soc., Perkin Trans. 1*, 1947 (1982).
243. K. Yamakawa, T. Satoh, N. Ohba, R. Sakaguchi, S. Takita and N. Tamura, *Tetrahedron*, **37**, 473 (1981).

244. S. J. Foster, C. W. Rees and D. J. Williams, *J. Chem. Soc., Perkin Trans. 1*, 711 (1985).
245. D. H. R. Barton, R. A. H. F. Hui, D. J. Lester and S. V. Ley, *Tetrahedron Lett.*, 3331 (1979).
246. D. H. R. Barton, R. A. H. F. Hui, S. V. Ley and D. J. Williams, *J. Chem. Soc., Perkin Trans. 1*, 1919 (1982).
247. N. Khoi and J. Polonsky, *Helv. Chim. Acta*, **64**, 1540 (1981).
248. T. Matsui, S. Tahara and M. Nakayama, *Bull. Chem. Soc. Jpn.*, **57**, 3355 (1984).
249. T. G. Back, *J. Chem. Soc., Chem. Commun.*, 278 (1978).
250. T. G. Back, *J. Org. Chem.*, **46**, 1442 (1981).
251. D. H. R. Barton, W. B. Motherwell, J. Wozniak and S. Z. Zard, *J. Chem. Soc., Perkin Trans. 1*, 1865 (1985).
252. V. I. Erashko, O. M. Sazonova, A. A. Tishaninova and A. A. Fainzil'berg, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 161 (1982); *Chem. Abstr.*, **96**, 142370b (1982).
253. T. Sakakibara, I. Takai, E. Ohara and R. Sudoh, *J. Chem. Soc., Chem. Commun.*, 261 (1981).
254. T. Sakakibara, S. Ikuta and R. Sudoh, *Synthesis*, 261 (1982).
255. T. Sakakibara, M. D. Manandhar and Y. Ishido, *Synthesis*, 920 (1983).
256. D. Seebach and D. Enders, *J. Med. Chem.*, **17**, 1225 (1974).
257. R. Kupper and C. J. Michejda, *J. Org. Chem.*, **44**, 2326 (1979).
258. A. I. Meyers, P. D. Edwards, T. R. Bailey and G. E. Jagdmann, Jr., *J. Org. Chem.*, **50**, 1019 (1985).
259. D. N. Brattesani and C. H. Heathcock, *Tetrahedron Lett.*, 2279 (1974).
260. D. N. Barattesani and C. H. Heathcock, *J. Org. Chem.*, **40**, 2165 (1975).
261. Y. Masuyama, Y. Ueno and M. Okawara, *Chem. Lett.*, 835 (1977).
262. H. E. Zimmerman and D. R. Diehl, *J. Am. Chem. Soc.*, **101**, 1841 (1979).
263. N. Petragnani, R. Rodrigues and J. V. Comasseto, *J. Organomet. Chem.*, **114**, 281 (1976).
264. A. L. Braga, J. V. Comasseto and N. Petragnani, *Synthesis*, 240 (1984).
265. G. Saleh, T. Minami, Y. Ohshiro and T. Agawa, *Chem. Ber.*, **112**, 355 (1979).
266. T. Minami, H. Sako, T. Ikehira, T. Hanamoto and I. Hirao, *J. Org. Chem.*, **48**, 2569 (1983).
267. H. Schmidbaur, C. Zybill, C. Krüger and H. -J. Kraus, *Chem. Ber.*, **116**, 1955 (1983).
268. M. Mikolajczyk, S. Grzejszczak and K. Korbacz, *Tetrahedron Lett.*, **22**, 3097 (1981).
269. J. V. Comasseto and N. Petragnani, *J. Organomet. Chem.*, **152**, 295 (1978).
270. M. Isobe, Y. Ichikawa and T. Goto, *Tetrahedron Lett.*, **22**, 4287 (1981).
271. T. G. Back, *J. Org. Chem.*, **46**, 5443 (1981).
272. B. Harirchian and P. Magnus, *J. Chem. Soc., Chem. Commun.*, 522 (1977).
273. D. Labar, A. Krief and L. Hevesi, *Tetrahedron Lett.*, 3967 (1978).
274. D. Labar and A. Krief, *Bull. Soc. Chim. Belg.*, **93**, 1005 (1984).
275. D. L. J. Clive, *J. Chem. Soc., Chem. Commun.*, 100 (1974).
276. H. J. Reich, *J. Org. Chem.*, **39**, 428 (1974).
277. H. J. Reich, W. W. Willis, Jr., and S. Wollowitz, *Tetrahedron Lett.*, **23**, 3319 (1982).
278. J. L. Kice, F. McAfee and H. Slebocka-Tilk, *Tetrahedron Lett.*, **23**, 3323 (1982).
279. R. A. Gancarz and J. L. Kice, *Tetrahedron Lett.*, **22**, 1661 (1981).
280. D. G. Garratt and A. Kabo, *Can. J. Chem.*, **58**, 1030 (1980).
281. M. Perrier and R. Rouessac, *C. R. Acad. Sci., Ser. II*, **295**, 729 (1982).
282. A. Toshimitsu, S. Uemura and M. Okano, *J. Chem. Soc., Chem. Commun.*, 965 (1982).
283. S. Uemura and S. Fukuzawa, *J. Chem. Soc., Perkin Trans. 1*, 471 (1985).
284. R. K. Boeckman, Jr., and S. S. Ko, *J. Am. Chem. Soc.*, **102**, 7146 (1980).
285. K. C. Nicolaou, D. A. Claremon, W. E. Barnette and S. P. Seitz, *J. Am. Chem. Soc.*, **101**, 3704 (1979).
286. K. C. Nicolaou, N. A. Petasis and D. A. Claremon, *Tetrahedron*, **41**, 4835 (1985).
287. P. S. Liu, V. E. Marquez, J. A. Kelley and J. S. Driscoll, *J. Org. Chem.*, **45**, 5225 (1980).
288. K. Katsuura and V. Snieckus, *Tetrahedron Lett.*, **26**, 9 (1985).
289. A. B. Smith, III, B. H. Toder, R. E. Richmond and S. J. Branca, *J. Am. Chem. Soc.*, **106**, 4001 (1984).
290. A. Toshimitsu, S. Uemura and M. Okano, *J. Chem. Soc., Chem. Commun.*, 166 (1977).
291. A. Toshimitsu, T. Aoai, S. Uemura and M. Okano, *J. Org. Chem.*, **45**, 1953 (1980).
292. S. Torii, K. Uneyama and M. Ono, *Tetrahedron Lett.*, **21**, 2653 (1980).
293. K. Uneyama, M. Ono and S. Torii, *Phosphorus Sulfur*, **16**, 35 (1983).
294. N. Miyoshi, Y. Ohno, K. Kondo, S. Murai and N. Sonoda, *Chem. Lett.*, 1309 (1979).
295. K. Isobe, J. Taga and Y. Tsuda, *Tetrahedron Lett.*, 2331 (1976).
296. L. A. Paquette, T. J. Nitz, R. J. Ross and J. P. Springer, *J. Am. Chem. Soc.*, **106**, 1446 (1984).

297. T. Kametani, K. Suzuki, H. Kurobe and H. Nemoto, *J. Chem. Soc., Chem. Commun.*, 1128 (1979).
298. T. Kametani, K. Suzuki, H. Kurobe and H. Nemoto, *Chem. Pharm. Bull.*, **29**, 105 (1981).
299. D. G. Garratt, M. D. Ryan and A. Kabo, *Can. J. Chem.*, **58**, 2329 (1980).
300. N. Miyoshi, Y. Takai, S. Murai and N. Sonoda, *Bull. Chem. Soc. Jpn.*, **51**, 1265 (1978).
301. N. Miyoshi, S. Furui, S. Murai and N. Sonoda, *J. Chem. Soc., Chem. Commun.*, 293 (1975).
302. N. Sonoda, N. Miyoshi and S. Murai, *Chem. Scr.*, **8A**, 109 (1975).
303. N. Miyoshi, S. Murai and N. Sonoda, *Tetrahedron Lett.*, 851 (1977).
304. D. Seebach, G. Calderari and P. Knochel, *Tetrahedron*, **41**, 4861 (1985).
305. J. Bergman and L. Engman, *J. Organomet. Chem.*, **181**, 335 (1979).
306. M. Shimizu, R. Takeda and I. Kuwajima, *Tetrahedron Lett.*, 419 (1979).
307. M. Shimizu, R. Takeda and I. Kuwajima, *Tetrahedron Lett.*, 3461 (1979).
308. M. Shimizu, and I. Kuwajima, *Bull. Chem. Soc. Jpn.*, **54**, 3100 (1981).
309. M. Shimizu, R. Takeda and I. Kuwajima, *Bull. Chem. Soc. Jpn.*, **54**, 3510 (1981).
310. I. Kuwajima and M. Shimizu, *Tetrahedron Lett.*, 1277 (1978).
311. T. Takahashi, H. Nagashima and J. Tsuji, *Tetrahedron Lett.*, 799 (1978).
312. S. Raucher, *Tetrahedron Lett.*, 2261 (1978).
313. A. Toshimitsu, Y. Kozawa, S. Uemura and M. Okano, *J. Chem. Soc., Perkin Trans. 1*, 1273 (1978).
314. S. Uemura, A. Toshimitsu, M. Okano and K. Ichikawa, *Bull. Chem. Soc. Jpn.*, **48**, 1925 (1975).
315. A. P. Kozikowski, K. L. Sorgi and R. J. Schmiesing, *J. Chem. Soc., Chem. Commun.*, 477 (1980).
316. A. P. Kozikowski, R. J. Schmiesing and K. L. Sorgi, *J. Am. Chem. Soc.*, **102**, 6580 (1980).
317. M. Isobe, M. Kitamura and T. Goto, *Tetrahedron Lett.*, **22**, 239 (1981).
318. M. Kitamura, M. Isobe, Y. Ichikawa and T. Goto, *J. Org. Chem.*, **49**, 3517 (1984).
319. G. Bérubé, E. Luce and K. Jankowski, *Bull. Soc. Chim. Fr., Ser. 2*, 109 (1983).
320. G. Jaurand, J. -M. Beau and P. Sinaÿ, *J. Chem. Soc., Chem. Commun.*, 572 (1981).
321. R. Baudat and M. Petrzilka, *Helv. Chim. Acta*, **62**, 1406 (1979).
322. H. J. Bestmann and P. Ermann, *Justus Liebigs Ann. Chem.*, 1740 (1984).
323. N. Satyanarayana and U. R. Nayak, *Synth. Commun.*, **15**, 331 (1985).
324. S. F. Martin, S. R. Desai, G. W. Phillips and A. C. Miller, *J. Am. Chem. Soc.*, **102**, 3294 (1980).
325. H. Ogawa, H. Morita, S. Suemura, T. Imoto, Y. Nogami, T. Koga, Y. Sakurgai, I. Miyamoto, H. Kato and Y. Taniguchi, *Tetrahedron Lett.*, **26**, 5567 (1985).
326. A. Guillemonat, *Ann. Chim. (Paris)*, **11**, 143 (1939).
327. K. B. Sharpless and R. F. Lauer, *J. Am. Chem. Soc.*, **94**, 7154 (1972).
328. D. Arigoni, A. Vasella, K. B. Sharpless and H. B. Jensen, *J. Am. Chem. Soc.*, **95**, 7917 (1973).
329. H. P. Jensen and K. B. Sharpless, *J. Org. Chem.*, **40**, 264 (1975).
330. M. A. Warpehoski, B. Chabaud and K. B. Sharpless, *J. Org. Chem.*, **47**, 2897 (1982).
331. L. M. Stephenson and D. R. Speth, *J. Org. Chem.*, **44**, 4683 (1979).
332. W. -D. Woggon, F. Ruther and H. Egli, *J. Chem. Soc., Chem. Commun.*, 706 (1980).
333. M. A. Umbreit and K. B. Sharpless, *J. Am. Chem. Soc.*, **99**, 5526 (1977).
334. O. Campos and J. M. Cook, *Tetrahedron Lett.*, 1025 (1979).
335. M. Haruna and K. Ito, *J. Chem. Soc., Chem. Commun.*, 483 (1981).
336. W. C. Still and D. Mobilio, *J. Org. Chem.*, **48**, 4785 (1983).
337. D. R. Williams, M. L. Bremmer, D. L. Brown and J. D'Antuono, *J. Org. Chem.*, **50**, 2807 (1985).
338. B. B. Snider and Y. S. Kulkarni, *Tetrahedron Lett.*, **26**, 5675 (1985).
339. B. R. Chhabra, K. Hayano, T. Ohtsuka, H. Shirahama and T. Matsumoto, *Chem. Lett.*, 1703 (1981).
340. F. Camps, J. Coll and A. Parente, *Synthesis*, 215 (1978).
341. Y. -W. Lee, E. Lee and K. Nakanishi, *Tetrahedron Lett.*, **21**, 4323 (1980).
342. H. -J. Bestmann and R. Schobert, *Angew. Chem., Int. Ed. Engl.*, **24**, 791 (1985).
343. O. Campos, M. DiPierro, M. Cain, R. Mantei, A. Gawish and J. M. Cook, *Heterocycles*, **14**, 975 (1980).
344. B. Chabaud and K. B. Sharpless, *J. Org. Chem.*, **44**, 4202 (1979).
345. D. H. R. Barton and D. Crich, *Tetrahedron*, **41**, 4359 (1985).
346. A. S. Kende, D. P. Lorah and R. J. Boatman, *J. Am. Chem. Soc.*, **103**, 1271 (1981).
347. T. Sakamoto, T. Sakasai and H. Yamanaka, *Chem. Pharm. Bull.*, **29**, 2485 (1981).
348. T. K. Liao, P. J. Wittek and C. C. Cheng, *J. Heterocycl. Chem.*, **13**, 1283 (1976).
349. P. J. Wittek, T. K. Liao and C. C. Cheng, *J. Org. Chem.*, **44**, 870 (1979).
350. D. H. R. Barton, R. A. H. F. Hui and S. V. Ley, *J. Chem. Soc., Perkin Trans. 1*, 2179 (1982).

351. L. Syper and J. Mlochowski, *Synthesis*, 747 (1984).
352. J. Bergman and L. Engman, *Tetrahedron Lett.*, 3279 (1978).
353. J. Bergman and L. Engman, *J. Org. Chem.*, **47**, 5191 (1982).
354. D. H. R. Barton, A. G. Brewster, S. V. Ley and M. N. Rosenfeld, *J. Chem. Soc., Chem. Commun.*, 985 (1976).
355. D. H. R. Barton, A. G. Brewster, S. V. Ley, C. M. Read and M. N. Rosenfeld, *J. Chem. Soc., Perkin Trans. 1*, 1473 (1981).
356. D. H. R. Barton, P. D. Magnus and M. N. Rosenfeld, *J. Chem. Soc., Chem. Commun.*, 301 (1975).
357. D. H. R. Barton, S. V. Ley, P. D. Magnus and M. N. Rosenfeld, *J. Chem. Soc., Perkin Trans. 1*, 567 (1977).
358. K. B. Sukumaran and R. G. Harvey, *J. Am. Chem. Soc.*, **101**, 1353 (1979).
359. K. B. Sukumaran and R. G. Harvey, *J. Org. Chem.*, **45**, 4407 (1980).
360. P. W. Jeffs and D. G. Lynn, *Tetrahedron Lett.*, 1617 (1978).
361. R. T. Taylor and L. A. Flood, *J. Org. Chem.*, **48**, 5160 (1983).
362. K. B. Sharpless and K. M. Gordon, *J. Am. Chem. Soc.*, **98**, 300 (1976).
363. I. Simiti, A. Mureson and M. Coman, *Arch. Pharm.*, **314**, 744 (1981).
364. K. Yamakawa, T. Satoh, N. Ohba and R. Sakaguchi, *Chem. Lett.*, 763 (1979).
365. K. Yamakawa and T. Satoh, *Heterocycles*, **15**, 337 (1981).
366. P. A. Grieco, Y. Yokoyama, S. Gilman and Y. Ohfune, *J. Chem. Soc., Chem. Commun.*, 870 (1977).
367. S. R. Dutta and B. P. Pradhan, *Indian J. Chem., Sect. B*, **21**, 575 (1982).
368. S. R. Dutta and B. P. Pradhan, *Indian J. Chem., Sect. B*, **22**, 680 (1983).
369. B. P. Pradhan and S. R. Dutta, *Indian J. Chem., Sect. B*, **23**, 565 (1984).
370. V. Anjaneyulu and G. S. Rao, *Indian J. Chem., Sect. B*, **23**, 663 (1984).
371. E. E. Gilbert, *Synth. Commun.*, **15**, 53 (1985).
372. P. A. Grieco, Y. Yokoyama, S. Gilman and M. Nishizawa, *J. Org. Chem.*, **42**, 2034 (1977).
373. H. J. Reich, F. Chow and S. L. Peake, *Synthesis*, 299 (1978).
374. T. Kametani, H. Nemoto and K. Fukumoto, *Heterocycles*, **6**, 1365 (1977).
375. T. Kametani, H. Nemoto and K. Fukumoto, *Biorg. Chem.*, **7**, 215 (1978).
376. A. G. Abatjoglou and D. R. Bryant, *Tetrahedron Lett.*, **22**, 2051 (1981).
377. a) S. Uemura, S. Fukuzawa and M. Okano, *Tetrahedron Lett.*, **22**, 5331 (1981). b) S. Uemura, S. Fukuzawa, S. R. Patil and M. Okano, *J. Chem. Soc., Perkin Trans. 1*, 499 (1985).
378. B. P. Mundy and W. G. Bornmann, *J. Org. Chem.*, **49**, 5264 (1984).
379. T. Fukuyama, B. D. Robins and R. A. Sachleben, *Tetrahedron Lett.*, **22**, 4155 (1981).
380. J. A. Marshall and R. D. Royce, Jr., *J. Org. Chem.*, **47**, 693 (1982).
381. S. L. Schreiber and C. Santini, *J. Am. Chem. Soc.*, **106**, 4038 (1984).
382. T. G. Back and N. Ibrahim, *Tetrahedron Lett.*, 4931 (1979).
383. H. J. Reich and S. K. Shah, *J. Org. Chem.*, **42**, 1773 (1977).
384. W. Dumont, D. Van Ende and A. Krief, *Tetrahedron Lett.*, 485 (1979).
385. K. Sachdev and H. S. Sachdev, *Tetrahedron Lett.*, 4223 (1976).
386. D. Van Ende, W. Dumont and A. Krief, *J. Organomet. Chem.*, **149**, C10 (1978).
387. S. Uemura, S. Fukuzawa and A. Toshimitsu, *J. Chem. Soc., Chem. Commun.*, 1501 (1983).
388. J. V. Comasseto, *J. Organomet. Chem.*, **253**, 131 (1983).
389. G. R. Krow and D. A. Shaw, *Synth. Commun.*, **12**, 313 (1982).
390. W. Dumont, M. Sevrin and A. Krief, *Tetrahedron Lett.*, 183 (1978).
391. J. N. Denis and A. Krief, *Tetrahedron Lett.*, **23**, 3411 (1982).
392. A. Cravador and A. Krief, *J. Chem. Soc., Chem. Commun.*, 951 (1980).
393. A. Toshimitsu, T. Aoai, S. Uemura and M. Okano, *J. Chem. Soc., Chem. Commun.*, 1041 (1980).
394. A. Bewick, D. E. Coe, G. B. Fuller and J. M. Mellor, *Tetrahedron Lett.*, **21**, 3827 (1980).
395. D. H. R. Barton, M. R. Britten-Kelly and D. Ferreira, *J. Chem. Soc., Perkin Trans. 1*, 1682 (1978).
396. K. B. Sharpless, T. Hori, L. K. Truesdale and C. O. Dietrich, *J. Am. Chem. Soc.*, **98**, 269 (1976).
397. K. B. Sharpless and S. P. Singer, *J. Org. Chem.*, **41**, 2504 (1976).
398. J. E. Fankhauser, R. M. Peevey and P. B. Hopkins, *Tetrahedron Lett.*, **25**, 15 (1984).
399. J. N. Fitzner, R. G. Shea, J. E. Fankhauser and P. B. Hopkins, *Synth. Commun.*, **14**, 605 (1984).
400. R. G. Shea, J. N. Fitzner, J. E. Fankhauser and P. B. Hopkins, *J. Org. Chem.*, **49**, 3647 (1984).
401. J. N. Fitzner, D. V. Pratt and P. B. Hopkins, *Tetrahedron Lett.*, **26**, 1959 (1985).
402. J. N. Fitzner, R. G. Shea, J. E. Fankhauser and P. B. Hopkins, *J. Org. Chem.*, **50**, 417 (1985).

403. D. H. R. Barton, A. G. Brewster, S. V. Ley and M. N. Rosenfeld, *J. Chem. Soc., Chem. Commun.*, 147 (1977).
404. J. S. E. Holker, E. O'Brien and B. K. Park, *J. Chem. Soc., Perkin Trans. 1*, 1915 (1982).
405. I. Perina, N. Bregant and K. Balenovic, *Bull. Sci. Cons. Acad. Sci. Arts RSF Yougosl., Sect. A*, **18**, 3 (1973); *Chem. Abstr.*, **79**, 5096b (1973).
406. P. Lerouge and C. Paulmier, *Tetrahedron Lett.*, **25**, 1987 (1984).
407. H. J. Reich, J. M. Renga and J. E. Trend, *Tetrahedron Lett.*, 2217 (1976).
408. S. Raucher, *J. Org. Chem.*, **42**, 2950 (1977).
409. D. Liotta and G. Zima, *Tetrahedron Lett.*, 4977 (1978).
410. G. H. Schmid and D. G. Garratt, in *The Chemistry of Double-Bonded Functional Groups. Supplement A, Part 2* (Ed. S. Patai), Wiley, Chichester, 1977, Ch. 9.
411. D. G. Garratt and G. H. Schmid, *J. Org. Chem.*, **42**, 1776 (1977).
412. J. -E. Bäckvall, J. Bergman and L. Engman, *J. Org. Chem.*, **48**, 3918 (1983).
413. S. V. Ley and A. J. Whittle, *Tetrahedron Lett.*, **22**, 3301 (1981).
414. R. S. Brown, S. C. Eyley and P. J. Parsons, *J. Chem. Soc., Chem. Commun.*, 438 (1984).
415. L. Engman, *J. Am. Chem. Soc.*, **106**, 3977 (1984).
416. J. E. Bäckvall and L. Engman, *Tetrahedron Lett.*, **22**, 1919 (1981).
417. L. Engman, *J. Org. Chem.*, **49**, 3559 (1984).
418. G. H. Schmid, in *The Chemistry of the Carbon—Carbon Triple Bond* (Ed. S. Patai), Wiley, Chichester, 1978, Ch. 8.
419. A. J. Bridges and J. W. Fischer, *Tetrahedron Lett.*, **24**, 445 (1983).
420. A. J. Bridges and J. W. Fischer, *Tetrahedron Lett.*, **24**, 447 (1983).
421. A. J. Bridges and J. W. Fischer, *J. Org. Chem.*, **49**, 2954 (1984).
422. C. N. Filer, D. Ahern, R. Fazio and E. J. Shelton, *J. Org. Chem.*, **45**, 1313 (1980).
423. D. G. Garratt, P. L. Beaulieu and V. M. Morisset, *Can. J. Chem.*, **59**, 927 (1981).
424. G. Himbert and M. Feustel, *J. Chem. Res. (S)*, 240 (1984).
425. S. Tomoda, Y. Takeuchi and Y. Nomura, *Chem. Lett.*, 1715 (1981).
426. T. Hori and K. B. Sharpless, *J. Org. Chem.*, **44**, 4204 (1979).
427. T. Hori and K. B. Sharpless, *J. Org. Chem.*, **44**, 4208 (1979).
428. M. Sevrin, W. Dumont, L. Hevesi and A. Krief, *Tetrahedron Lett.*, 2647 (1976).
429. M. Sevrin and A. Krief, *Tetrahedron Lett.*, **21**, 585 (1980).
430. M. Sevrin and A. Krief, *J. Chem. Soc., Chem. Commun.*, 656 (1980).
431. M. Sevrin, J. N. Denis and A. Krief, *Angew. Chem., Int. Ed. Engl.*, **17**, 526 (1978).
432. L. Hevesi, M. Sevrin and A. Krief, *Tetrahedron Lett.*, 2651 (1976).
433. A. M. Morella and A. D. Ward, *Tetrahedron Lett.*, **25**, 1197 (1984).
434. T. Kauffmann, H. Ahlers, H. -J. Tilhard and A. Woltermann, *Angew. Chem., Int. Ed. Engl.*, **16**, 710 (1977).
435. K. Chikamatsu, T. Otsubo, F. Ogura and H. Yamaguchi, *Chem. Lett.*, 1081 (1982).
436. S. Uemura and S. Fukuzawa, *Chem. Lett.*, 943 (1980).
437. S. Uemura and S. Fukuzawa, *J. Organomet. Chem.*, **268**, 223 (1984).
438. S. Uemura and S. Fukuzawa, *J. Chem. Soc., Chem. Commun.*, 1033 (1980).
439. S. Uemura, S. Fukuzawa, M. Wakasugi and M. Okano, *J. Organomet. Chem.*, **214**, 319 (1981).
440. S. Uemura, H. Miyoshi and M. Okano, *Chem. Lett.*, 1357 (1979).
441. F. O. Ayorinde, *Tetrahedron Lett.*, **24**, 2077 (1983).
442. M. Albeck and S. Shaik, *J. Chem. Soc., Perkin Trans. 1*, 1223 (1975).
443. M. Albeck, T. Tamari and M. Sprecher, *J. Org. Chem.*, **48**, 2276 (1983).
444. G. A. Olah, M. Nojima and I. Kerekes, *J. Am. Chem. Soc.*, **96**, 925 (1974).
445. Y. A. Sedov, *Khim. Geterotsikl. Soedin.*, 265 (1983).
446. M. R. Detty, *Tetrahedron Lett.*, 4189 (1979).
447. M. R. Detty and M. D. Seidler, *J. Org. Chem.*, **46**, 1283 (1981).
448. S. Raucher, M. R. Hansen and M. A. Colter, *J. Org. Chem.*, **43**, 4885 (1978).
449. E. G. Kataev, T. G. Mannafov, A. B. Remizov and O. A. Komarovskaya, *Zh. Org. Khim.*, **11**, 2322 (1975).
450. E. G. Kataev, T. G. Mannafov, E. A. Berdnikov and O. A. Komarovskaya, *Zh. Org. Khim.*, **9**, 1983 (1973).
451. A. E. Feiring, *J. Org. Chem.*, **45**, 1958 (1980).
452. A. E. Feiring, *J. Org. Chem.*, **45**, 1962 (1980).

453. Z. Janousek, S. Piettre, F. Gorissen-Hervens and H. G. Viehe, *J. Organomet. Chem.*, **250**, 197 (1983).
454. S. Piettre, Z. Janousek, R. Merenyi and H. G. Viehe, *Tetrahedron*, **41**, 2527 (1985).
455. M. J. Crimmin, P. J. O'Hanlon and N. H. Rogers, *J. Chem. Soc., Perkin Trans. 1*, 541 (1985).
456. K. Uneyama, K. Takano and S. Torii, *Tetrahedron Lett.*, **23**, 1161 (1982).
457. J. Hooz and R. Mortimer, *Tetrahedron Lett.*, 805 (1976).
458. J. Hooz and R. D. Mortimer, *Can. J. Chem.*, **56**, 2786 (1978).
459. H. J. Reich, J. J. Rusek and R. E. Olson, *J. Am. Chem. Soc.*, **101**, 2225 (1979).
460. H. J. Reich, M. J. Kelly, R. E. Olson and R. C. Holtan, *Tetrahedron*, **39**, 949 (1983).
461. D. G. Garratt, M. D. Ryan and M. Ujjainwalla, *Can. J. Chem.*, **57**, 2145 (1979).
462. D. G. Garratt, *Can. J. Chem.*, **57**, 2180 (1979).
463. T. G. Back and R. G. Kerr, *J. Organomet. Chem.*, **286**, 171 (1985).
464. S. Tomoda, Y. Takeuchi and Y. Nomura, *Tetrahedron Lett.*, **23**, 1361 (1982).
465. S. Tomoda, Y. Takeuchi and Y. Nomura, *Chem. Lett.*, 1733 (1982).
466. T. Hayama, S. Tomoda, Y. Takeuchi and Y. Nomura, *J. Org. Chem.*, **49**, 3235 (1984).
467. Y. -H. Kang and J. L. Kice, *J. Org. Chem.*, **49**, 1507 (1984).
468. T. Toru, T. Seko and E. Maekawa, *Tetrahedron Lett.*, **26**, 3263 (1985).
469. Y. -H. Kang and J. L. Kice, *Tetrahedron Lett.*, **23**, 5373 (1982).
470. J. L. Kice and Y. -H. Kang, *Tetrahedron*, **41**, 4739 (1985).
471. D. L. J. Clive, G. Chittattu, N. J. Curtis, W. A. Kiel and C. K. Wong, *J. Chem. Soc., Chem. Commun.*, 725 (1977).
472. D. L. J. Clive, C. G. Russell, G. Chittattu and A. Singh, *Tetrahedron*, **36**, 1399 (1980).
473. K. C. Nicolaou, *Tetrahedron*, **37**, 4097 (1981).
474. (a) K. C. Nicolaou, S. P. Seitz, W. J. Sipio and J. F. Blount, *J. Am. Chem. Soc.*, **101**, 3884 (1979); (b) K. C. Nicolaou, W. J. Sipio, R. L. Magolda and D. A. Claremon, *J. Chem. Soc., Chem. Commun.*, 83 (1979).
475. D. L. J. Clive and V. N. Kalè, *J. Org. Chem.*, **46**, 231 (1981).
476. E. J. Corey, G. E. Keck and I. Székely, *J. Am. Chem. Soc.*, **99**, 2006 (1977).
477. D. L. J. Clive, G. Chittattu and C. K. Wong, *Can. J. Chem.*, **55**, 3894 (1977).
478. K. C. Nicolaou and Z. Lysenko, *Tetrahedron Lett.*, 1257 (1977).
479. K. C. Nicolaou and W. E. Barnette, *J. Chem. Soc., Chem. Commun.*, 331 (1977).
480. K. C. Nicolaou, W. E. Barnette, R. L. Magolda, P. A. Grieco, W. Owens, C. -L. J. Wang, J. B. Smith, M. Ogletree and A. M. Lefer, *Prostaglandins*, **16**, 789 (1978).
481. K. C. Nicolaou, W. E. Barnette and R. L. Magolda, *J. Am. Chem. Soc.*, **103**, 3480 (1981).
482. Y. Naruta, H. Uno and K. Maruyama, *J. Chem. Soc., Chem. Commun.*, 1277 (1981).
483. J. Bergman and L. Engman, *J. Am. Chem. Soc.*, **103**, 5196 (1981).
484. K. Uneyama, S. Fujibayashi and S. Torii, *Tetrahedron Lett.*, **26**, 4637 (1985).
485. F. M. Hauser and R. P. Rhee, *J. Am. Chem. Soc.*, **101**, 1628 (1979).
486. P. L. Beaulieu, V. M. Morisset and D. G. Garratt, *Tetrahedron Lett.*, **21**, 129 (1980).
487. P. G. Williard and S. E. de Laszlo, *J. Org. Chem.*, **50**, 3738 (1985).
488. K. Suzuki and T. Mukaiyama, *Chem. Lett.*, 683 (1982).
489. S. Current and K. B. Sharpless, *Tetrahedron Lett.*, 5075 (1978).
490. S. V. Ley and B. Lygo, *Tetrahedron Lett.*, **23**, 4625 (1982).
491. A. M. Doherty, S. V. Ley, B. Lygo and D. J. Williams, *J. Chem. Soc., Perkin Trans. 1*, 1371 (1984).
492. M. de Moura Campos and N. Petragnani, *Chem. Ber.*, **93**, 317 (1960).
493. K. C. Nicolaou and Z. Lysenko, *J. Am. Chem. Soc.*, **99**, 3185 (1977).
494. D. L. J. Clive and G. Chittattu, *J. Chem. Soc., Chem. Commun.*, 484 (1977).
495. D. Goldsmith, D. Liotta, C. Lee and G. Zima, *Tetrahedron Lett.*, 4801 (1979).
496. A. Rouessac, F. Rouessac and H. Zamarlik, *Tetrahedron Lett.*, **22**, 2641 (1981).
497. S. W. Rollinson, R. A. Amos and J. A. Katzenellenbogen, *J. Am. Chem. Soc.*, **103**, 4114 (1981).
498. T. Toru, S. Fujita and E. Maekawa, *J. Chem. Soc., Chem. Commun.*, 1082 (1985).
499. J. V. Comasseto and N. Petragnani, *Synth. Commun.*, **13**, 889 (1983).
500. G. B. Gill and M. S. H. Idris, *Tetrahedron Lett.*, **26**, 4811 (1985).
501. D. P. Curran and D. M. Rakiewicz, *J. Am. Chem. Soc.*, **107**, 1448 (1985)
502. D. L. J. Clive, C. K. Wong, W. A. Kiel and S. M. Menchen, *J. Chem. Soc., Chem. Commun.*, 379 (1978).

503. D. L. J. Clive, V. Farina, A. Singh, C. K. Wong, W. A. Kiel and S. M. Menchen, *J. Org. Chem.*, **45**, 2120 (1980).
504. R. P. Webb, II and S. Danishefsky, *Tetrahedron Lett.*, **24**, 1357 (1983).
505. A. Toshimitsu, K. Terao and S. Uemura, *Tetrahedron Lett.*, **25**, 5917 (1984).
506. S. R. Wilson and R. A. Sawicki, *J. Org. Chem.*, **44**, 287 (1979).
507. J. E. Baldwin, S. B. Haber and J. Kitchin, *J. Chem. Soc., Chem. Commun.*, 790 (1973).
508. K. C. Nicolaou, W. E. Barnette and R. L. Magolda, *J.. Am. Chem. Soc.*, **100**, 2567 (1978).
509. C. M. Angelov, *Heterocycles*, **20**, 791 (1983).
510. K. M. Angelov and C. Tancheva, *Zh. Obshch. Khim.*, **55**, 53 (1985).
511. W. P. Jackson, S. V. Ley and J. A. Morton, *J. Chem. Soc., Chem. Commun.*, 1028 (1980).
512. W. P. Jackson, S. V. Ley and J. A. Morton, *Tetrahedron Lett.*, **22**, 2601 (1981).
513. S. V. Ley and P. J. Murray, *J. Chem. Soc., Chem. Commun.*, 1252 (1982).
514. S. V. Ley, B. Lygo, H. Molines and J. A. Morton, *J. Chem. Soc., Chem. Commun.*, 1251 (1982).
515. S. V. Ley, B. Lygo and H. Molines, *J. Chem. Soc., Perkin Trans. 1*, 2403 (1984).
516. S. V. Ley, P. J. Murray and B. D. Palmer, *Tetrahedron*, **41**, 4765 (1985).
517. M. Alderdice and L. Weiler, *Can. J. Chem.*, **59**, 2239 (1981).
518. W. P. Jackson, S. V. Ley and A. J. Whittle, *J. Chem. Soc., Chem. Commun.*, 1173 (1980).
519. D. Gravel, R. Déziel and L. Bordeleau, *Tetrahedron Lett.*, **24**, 699 (1983).
520. S. Uemura, A. Toshimitsu, T. Aoai and M. Okano, *Chem. Lett.*, 1359 (1979).
521. (a) S. Uemura, A. Toshimitsu, T. Aoai and M. Okano, *J. Chem. Soc., Chem. Commun.*, 610 (1979); (b) A. Toshimitsu, T. Aoai, S. Uemura and M. Okano, *J. Org. Chem.*, **46**, 3021 (1981).
522. A. Toshimitsu, S. Uemura and M. Okano, *J. Chem. Soc., Perkin Trans. 1*, 1206 (1979).
523. S. Uemura, A. Toshimitsu, T. Aoai and M. Okano, *Tetrahedron Lett.*, **21**, 1533 (1980).
524. R. M. Scarborough, Jr., A. B. Smith, III, W. E. Barnette and K. C. Nicolaou, *J. Org. Chem.*, **44**, 1742 (1979).
525. D. L. J. Clive, G. Chittattu and C. K. Wong, *J. Chem. Soc., Chem. Commun.* 441 (1978).
526. R. V. Stevens and K. F. Albizati, *J. Org. Chem.*, **50**, 632 (1985).
527. A. Toshimitsu, S. Uemura and M. Okano, *J. Chem. Soc., Chem. Commun.*, 87 (1982).
528. F. Rouessac and H. Zamarlik, *Tetrahedron Lett.*, **22**, 2643 (1981).
529. H. Zamarlik, N. Gnonlonfoun and F. Rouessac, *Can. J. Chem.*, **62**, 2326 (1984).
530. A. Rouessac and F. Rouessac, *Tetrahedron*, **37**, 4165 (1981).
531. T. Kametani, H. Kurobe and H. Nemoto, *J. Chem. Soc., Chem. Commun.*, 762 (1980).
532. T. Kametani, K. Fukumoto, H. Kurobe and H. Nemoto, *Tetrahedron Lett.*, **22**, 3653 (1981).
533. T. Kametani, H. Kurobe and H. Nemoto, *J. Chem. Soc., Perkin Trans. 1*, 756 (1981).
534. T. Kametani, H. Kurobe, H. Nemoto and K. Fukumoto, *J. Chem. Soc., Perkin Trans. 1*, 1085 (1982).
535. S. D. Burke, W. F. Fobare and D. M. Armistead, *J. Org. Chem.*, **47**, 3348 (1982).
536. L. Set, D. R. Cheshire and D. L. J. Clive, *J. Chem. Soc., Chem. Commun.*, 1205 (1985).
537. D. L. J. Clive and P. L. Beaulieu, *J. Chem. Soc., Chem. Commun.*, 307 (1983).
538. (a) M. D. Bachi and C. Hoornaert, *Tetrahedron Lett.*, **22**, 2693 (1981); (b) M. D. Bachi, F. Frolow and C. Hoornaert, *J. Org. Chem.*, **48**, 1841 (1983).
539. D. A. Burnett, J.-K. Choi, D. J. Hart and Y.-M. Tsai, *J. Am. Chem. Soc.*, **106**, 8201 (1984).
540. A. G. Angoh and D. L. J. Clive, *J. Chem. Soc., Chem. Commun.*, 980 (1985).
541. A. G. Angoh and D. L. J. Clive, *J. Chem. Soc., Chem. Commun.*, 941 (1985).
542. M. Shimizu and I. Kuwajima, *J. Org. Chem.*, **45**, 4063 (1980).
543. M. Shimizu, R. Ando and I. Kuwajima, *J. Org. Chem.*, **49**, 1230 (1984).
544. M. Shimizu, R. Ando and I. Kuwajima, *J. Org. Chem.*, **46**, 5246 (1981).
545. M. Shimizu and I. Kuwajima, *Tetrahedron Lett.*, 2801 (1979).
546. M. Shimizu, H. Urabe and I. Kuwajima, *Tetrahedron Lett.*, **22**, 2183 (1981).
547. I. Kuwajima, M. Shimizu and H. Urabe, *J. Org. Chem.*, **47**, 837 (1982).
548. F. Ogura, T. Otsubo, K. Ariyoshi and H. Yamaguchi, *Chem. Lett.*, 1833 (1983).
549. L. Engman and M. P. Cava, *J. Chem. Soc., Chem. Commun.*, 164 (1982).
550. K. Takaki, M. Yasumura and K. Negoro, *J. Org. Chem.*, **48**, 54 (1983).
551. D. H. R. Barton, S. V. Ley and C. A. Meerholz, *J. Chem. Soc., Chem. Commun.*, 755 (1979).
552. F. Ogura, H. Yamaguchi, T. Otsubo and H. Tanaka, *Bull. Chem. Soc. Jpn.*, **55**, 641 (1982).
553. J. P. Marino and A. Schwartz, *Tetrahedron Lett.*, 3253 (1979).
554. K. Balenovic, N. Bregant and I. Perina, *Synthesis*, 172 (1973).

555. I. Perina, N. Bregant and K. Balenovic, *Bull. Sci. Cons. Acad. Sci. Arts RSF Yougosl., Sect. A*, **18**, 4 (1973); *Chem. Abstr.*, **78**, 160007w (1973).
556. M. R. Czarny, *J. Chem. Soc., Chem. Commun.*, 81 (1976).
557. D. H. R. Barton, A. Billion and J. Boivin, *Tetrahedron Lett.*, **26**, 1229 (1985).
558. D. H. R. Barton, X. Lusinchi and P. Milliet, *Tetrahedron*, **41**, 4727 (1985).
559. J. P. Marino and R. D. Larsen, Jr., *J. Am. Chem. Soc.*, **103**, 4642 (1981).
560. M. R. Czarny, *Synth. Commun.*, **6**, 285 (1976).
561. V. I. Naddaka, V. P. Garkin and V. I. Minkin, *Zh. Org. Khim.*, **12**, 2481 (1976).
562. M. Poje and K. Balenovic, *Bull. Sci. Cons. Acad. Sci. Arts RSF Yougosl., Sect. A*, **20**, 1 (1975); *Chem. Abstr.*, **83**, 43558u (1975).
563. T. Kobayashi and T. Hiraoka, *Bull. Chem. Soc. Jpn.*, **52**, 3366 (1979).
564. D. H. R. Barton, X. Lusinchi and P. Milliet, *Tetrahedron Lett.*, **23**, 4949 (1982).
565. I. Ninomiya, T. Kiguchi, C. Hashimoto, D. H. R. Barton, X. Lusinchi and P. Milliet, *Tetrahedron Lett.*, **26**, 4183 (1985).
566. I. Ninomiya, C. Hashimoto, T. Kiguchi, D. H. R. Barton, X. Lusinchi and P. Milliet, *Tetrahedron Lett.*, **26**, 4187 (1985).
567. T. G. Back, S. Collins and R. G. Kerr, *J. Org. Chem.*, **46**, 1564 (1981).
568. K. Kondo, S. Murai and N. Sonoda, *Tetrahedron Lett.*, 3727 (1977).
569. D. H. R. Barton, D. J. Lester and S. V. Ley, *J. Chem. Soc., Chem. Commun.*, 276 (1978).
570. D. H. R. Barton, D. J. Lester and S. V. Ley, *J. Chem. Soc., Perkin Trans. 1*, 1212 (1980).
571. S. V. Ley, C. A. Meerholz and D. H. R. Barton, *Tetrahedron*, **37**, Suppl. 1, 213 (1981).
572. J. Bergman and L. Engman, *Z. Naturforsch., Teil B*, **35**, 882 (1980).
573. K. Balenovic, R. Lazic, V. Polak and P. Stern, *Bull. Sci. Cons. Acad. Sci. Arts RSF Yougosl., Sect. A*, **17**, 147 (1972); *Chem. Abstr.*, **77**, 139499c (1972).
574. T. G. Back and S. Collins, *Tetrahedron Lett.*, 2661 (1979).
575. T. G. Back and S. Collins, *Tetrahedron Lett.*, **21**, 2213 (1980).
576. N. Bregant, I. Perina and K. Balenovic, *Bull. Sci. Cons. Acad. Sci. Arts RSF Yougosl., Sect. A*, **17**, 148 (1972); *Chem. Abstr.*, **77**, 152092j (1972).
577. (a) T. G. Back, *J. Chem. Soc., Chem. Commun.*, 530 (1981); (b) T. G. Back and R. G. Kerr, *Can. J. Chem.*, **60**, 2711 (1982).
578. D. H. R. Barton, X. Lusinchi and J. S. Ramirez, *Tetrahedron Lett.*, **24**, 2995 (1983).
579. D. H. R. Barton, D. J. Lester and S. V. Ley, *J. Chem Soc., Chem. Commun.*, 445 (1977).
580. D. H. R. Barton, G. Bashiardes and J. -L. Fourrey, *Tetrahedron Lett.*, **25**, 1287 (1984).
581. I. Lalezari, A. Shafiee and M. Yalpani, *Angew. Chem., Int. Ed. Engl.*, **9**, 464 (1970).
582. I. Lalezari, A. Shafiee and M. Yalpani, *J. Org. Chem.*, **36**, 2836 (1971).
583. I. Lalezari, A. Shafiee and M. Yalpani, *J. Heterocycl. Chem.*, **9**, 1411 (1972).
584. I. Lalezari, A. Shafiee, F. Rabet and M. Yalpani, *J. Heterocycl. Chem.*, **10**, 953 (1973).
585. I. Lalezari, A. Shafiee and H. Golgolab, *J. Heterocycl. Chem.*, **10**, 655 (1973).
586. H. Golgolab and I. Lalezari, *J. Heterocycl. Chem.*, **12**, 801 (1975).
587. I. Lalezari, A. Shafiee, J. Khorrami and A. Soltani, *J. Pharm. Sci.*, **67**, 1336 (1978).
588. A. Shafiee, S. Toghraie, F. Aria and G. Mortezaei-Zandjani, *J. Heterocycl. Chem.*, **19**, 1305 (1982).
589. I. Lalezari, *Synthesis*, 660 (1984).
590. H. Meier and I. Menzel, *J. Chem. Soc., Chem. Commun.*, 1059 (1971).
591. H. Meier and E. Voigt, *Tetrahedron*, **28**, 187 (1972).
592. H. Meier and I. Menzel, *Tetrahedron Lett.*, 445 (1972).
593. H. Meier, M. Layer and A. Zetzsche, *Chem. Ztg.*, **98**, 460 (1974).
594. H. Meier, S. Schniepp and W. Combrink, *Chem. Ztg.*, **99**, 461 (1975).
595. H. Meier and H. Gugel, *Synthesis*, 338 (1976).
596. H. Meier, M. Layer, W. Combrink and S. Schniepp, *Chem. Ber.*, **109**, 1650 (1976).
597. H. Meier, T. Echter and H. Petersen, *Angew. Chem., Int. Ed. Engl.*, **17**, 942 (1978).
598. J. Zountsas and H. Meier, *Justus Liebigs Ann. Chem.*, 1366 (1982).
599. N. Hanold and H. Meier, *Chem. Ber.*, **118**, 198 (1985).
600. B. A. Keay and R. Rodrigo, *J. Am. Chem. Soc.*, **104**, 4725 (1982).
601. S. N. Dhawan and J. Kagan, *J. Lebelled Compd. Radiopharm.*, **19**, 331 (1982).
602. G. Sosnovsky and J. A. Krogh, *Synthesis*, 703 (1978).
603. G. Sosnovsky, J. A. Krogh and S. G. Umhoefer, *Synthesis*, 722 (1979).
604. A. G. H. Wee, A. Y. L. Shu, E. Bunnenberg and C. Djerassi, *J. Org. Chem.*, **49**, 3327 (1984).

605. C. L. Pedersen, *Acta Chem. Scand., Ser. B*, **30**, 675 (1976).
606. G. Sosnovsky and J. A. Krogh, *Z. Naturforsch., Teil B*, **34**, 511 (1979).
607. G. Sosnovsky and J. A. Krogh, *Synthesis*, 654 (1980).
608. B. Nakhdjavan and G. Klar, *Justus Liebigs Ann. Chem.*, 1683 (1977).
609. L. G. Faehl and J. L. Kice, *J. Org. Chem.*, **44**, 2357 (1979).
610. K. C. Nicolaou, R. L. Magolda and W. E. Barnette, *J. Chem. Soc., Chem. Commun.*, 375 (1978).
611. K. C. Nicolaou, D. A. Claremon, D. P. Papahatjis and R. L. Magolda, *J. Am. Chem. Soc.*, **103**, 6969 (1981).
612. K. C. Nicolaou, D. P. Papahatjis, D. A. Claremon, R. L. Magolda and R. E. Dolle, *J. Org. Chem.*, **50**, 1440 (1985).
613. M. P. Edwards, S. V. Ley, S. G. Lister and B. D. Palmer, *J. Chem. Soc., Chem. Commun.*, 630 (1983).
614. M. P. Edwards, S. V. Ley, S. G. Lister, B. D. Palmer and D. J. Williams, *J. Org. Chem.*, **49**, 3503 (1984).
615. J. Drabowicz and M. Mikolajczyk, *Synthesis*, 758 (1978).
616. J. Drabowicz, P. Lyzwa and M. Mikolajczyk, *Phosphorus Sulfur*, **17**, 169 (1983).
617. D. H. R. Barton, N. J. Cussans and S. V. Ley, *J. Chem. Soc., Chem. Commun.*, 751 (1977).
618. N. J. Cussans, S. V. Ley and D. H. R. Barton, *J. Chem. Soc., Perkin Trans. 1*, 1654 (1980).
619. D. H. R. Barton, M. T. Bielska, J. M. Cardoso, N. J. Cussans and S. V. Ley, *J. Chem. Soc., Perkin Trans. 1*, 1840 (1981).
620. J. -C. Barrière, A. Chiaroni, J. Cléophax, S. D. Géro, C. Riche and M. Vuilhorgne, *Helv. Chim. Acta*, **64**, 1140 (1981).
621. D. VanEnde, A. Cravador and A. Krief, *J. Organomet. Chem.*, **177**, 1 (1979).
622. A. Burton, L. Hevesi, W. Dumont, A. Cravador and A. Krief, *Synthesis*, 877 (1979).
623. D. H. R. Barton, N. J. Cussans and S. V. Ley, *J. Chem. Soc., Chem. Commun.*, 393 (1978).
624. N. J. Cussans, S. V. Ley and D. H. R. Barton, *J. Chem. Soc., Perkin Trans. 1*, 1650 (1980).
625. S. Tamagaki, I. Hatanaka and S. Kozuka, *Bull. Chem. Soc. Jpn.*, **50**, 3421 (1977).
626. M. Mikolajczyk and J. Luczak, *J. Org. Chem.*, **43**, 2132 (1978).
627. S. V. Ley, C. A. Meerholz and D. H. R. Barton *Tetrahedron Lett.*, **21**, 1785 (1980).
628. A. G. M. Barrett, D. H. R. Barton and R. W. Read, *J. Chem. Soc., Chem. Commun.*, 645 (1979).
629. R. A. Gancarz and J. L. Kice, *Tetrahedron Lett.*, **21**, 1697 (1980).
630. A. Krief, *Tetrahedron*, **36**, 2531 (1980).
631. M. Clarembeau, A. Cravador, W. Dumont, L. Hevesi, A. Krief, J. Lucchetti and D. Van Ende, *Tetrahedron*, **41**, 4793 (1985).
632. D. Seebach and N. Peleties, *Angew. Chem., Int. Ed. Engl.*, **8**, 450 (1969).
633. D. Seebach and N. Peleties, *Chem. Ber.*, **105**, 511 (1972).
634. J. Lucchetti and A. Krief, *Tetrahedron Lett.*, **22**, 1623 (1981).
635. B. -T. Gröbel and D. Seebach, *Chem. Ber.*, **110**, 852 (1977).
636. H. J. Reich, W. W. Willis, Jr. and P. D. Clark, *J. Org. Chem.*, **46**, 2775 (1981).
637. S. Raucher and G. A. Koolpe, *J. Org. Chem.*, **43**, 3794 (1978).
638. K. Hirai, Y. Iwano and K. Fujimoto, *Tetrahedron Lett.*, **23**, 4021 (1982).
639. D. Seebach and A. K. Beck, *Angew. Chem., Int. Ed. Engl.*, **13**, 806 (1974).
640. W. Dumont, P. Bayet and A. Krief, *Angew. Chem., Int. Ed. Engl.*, **13**, 804 (1974).
641. W. Dumont and A. Krief, *Angew. Chem., Int. Ed. Engl.*, **14**, 350 (1975).
642. A. Anciaux, A. Eman, W. Dumont, D. Van Ende and A. Krief, *Tetrahedron Lett.*, 1613 (1975).
643. D. Van Ende, W. Dumont and A. Krief, *Angew. Chem., Int. Ed. Engl.*, **14**, 700 (1975).
644. J. N. Denis, W. Dumont and A. Krief, *Tetrahedron Lett.*, 453 (1976).
645. M. Sevrin, D. Van Ende and A. Krief, *Tetrahedron Lett.*, 2643 (1976).
646. D. Van Ende and A. Krief, *Tetrahedron Lett.*, 457 (1976).
647. W. Dumont and A. Krief, *Angew. Chem., Int. Ed. Engl.*, **15**, 161 (1976).
648. S. Halazy, J. Lucchetti and A. Krief, *Tetrahedron Lett.*, 3971 (1978).
649. D. Labar, W. Dumont, L. Hevesi and A. Krief, *Tetrahedron Lett.*, 1145 (1978).
650. S. Halazy, W. Dumont and A. Krief, *Tetrahedron Lett.*, **22**, 4737 (1981).
651. D. Labar and A. Krief, *J. Chem. Soc., Chem. Commun.*, 564 (1982).
652. T. DiGiamberardino, S. Halazy, W. Dumont and A. Krief, *Tetrahedron Lett.*, **24**, 3413 (1983).
653. D. Seebach, N. Meyer and A. K. Beck, *Justus Liebigs Ann. Chem.*, 846 (1977).
654. I. Kuwajima, S. Hoshino, T. Tanaka and M. Shimizu, *Tetrahedron Lett.*, **21**, 3209 (1980).

655. L. A. Paquette, T. -H. Yan and G. J. Wells, *J. Org. Chem.*, **49**, 3610 (1984).
656. H. J. Reich, F. Chow and S. K. Shah, *J. Am. Chem. Soc.*, **101**, 6638 (1979).
657. R. H. Mitchell, *Can. J. Chem.*, **58**, 1398 (1980).
658. D. J. Goldsmith, D. C. Liotta, M. Volmer, W. Hoekstra and L. Waykole, *Tetrahedron*, **41**, 4873 (1985).
659. M. Clarembeau and A. Krief, *Tetrahedron Lett.*, **25**, 3629 (1984).
660. M. Clarembeau and A. Krief, *Tetrahedron Lett.*, **26**, 1093 (1985).
661. S. Halazy and A. Krief, *Tetrahedron Lett.*, **22**, 4341 (1981).
662. A. Anciaux, A. Eman, W. Dumont and A. Krief, *Tetrahedron Lett.*, 1617 (1975).
663. W. Dumont, M. Sevrin and A. Krief, *Angew. Chem., Int. Ed. Engl.*, **16**, 541 (1977).
664. D. Seebach and A. K. Beck, *Chem. Ber.*, **108**, 314 (1975).
665. C. A. Brandt, J. V. Comasseto, W. Nakamura and N. Petragnani, *J. Chem. Res. (S)*, 156 (1983).
666. S. Halazy and A. Krief, *Tetrahedron Lett.*, **22**, 1833 (1981).
667. J. L. Laboureur and A. Krief, *Tetrahedron Lett.*, **25**, 2713 (1984).
668. S. Halazy and A. Krief, *J. Chem. Soc., Chem. Commun.*, 1136 (1979).
669. D. Labar, J. L. Laboureur and A. Krief, *Tetrahedron Lett.*, **23**, 983 (1982).
670. S. Halazy, F. Zutterman and A. Krief, *Tetrahedron Lett.*, **23**, 4385 (1982).
671. S. Halazy and A. Krief, *J. Chem. Soc., Chem. Commun.*, 1200 (1982).
672. J. Lucchetti and A. Krief, *Tetrahedron Lett.*, 2697 (1978).
673. J. Lucchetti, W. Dumont and A. Krief, *Tetrahedron Lett.*, 2695 (1979).
674. J. Lucchetti and A. Krief, *J. Organomet. Chem.*, **194**, C49 (1980).
675. J. Lucchetti and A. Krief, *J. Chem. Soc., Chem. Commun.*, 127 (1982).
676. J. Lucchetti and A. Krief, *Synth. Commun.*, **13**, 1153 (1983).
677. W. Dumont, J. Lucchetti and A. Krief, *J. Chem. Soc., Chem. Commun.*, 66 (1983).
678. J. L. Laboureur, W. Dumont and A. Krief, *Tetrahedron Lett.*, **25**, 4569 (1984).
679. H. J. Reich and F. Chow, *J. Chem. Soc., Chem. Commun.*, 790 (1975).
680. H. J. Reich, M. C. Clark and W. W. Willis, Jr., *J. Org. Chem.*, **47**, 1618 (1982).
681. J. Rémion, W. Dumont and A. Krief, *Tetrahedron Lett.*, 1385 (1976).
682. Y. Yamamoto, Y. Saito and K. Maruyama, *Tetrahedron Lett.*, **23**, 4597 (1982).
683. J. Lucchetti and A. Krief, *Tetrahedron Lett.*, 2693 (1978).
684. J. Rémion and A. Krief, *Tetrahedron Lett.*, 3743 (1976).
685. J. N. Denis, S. Desauvage, L. Hevesi and A. Krief, *Tetrahedron Lett.*, **22**, 4009 (1981).
686. J. N. Denis, W. Dumont and A. Krief, *Tetrahedron Lett.*, 4111 (1979).
687. J. Lucchetti, J. Rémion and A. Krief, *C. R. Acad. Sci., Ser. C*, **288**, 553 (1979).
688. Y. Yamamoto, Y. Saito and K. Maruyama, *J. Org. Chem.*, **48**, 5408 (1983).
689. H. Wetter, *Helv. Chim. Acta*, **61**, 3072 (1978).
690. H. J. Reich and W. W. Willis, Jr., *J. Org. Chem.*, **45**, 5227 (1980).
691. H. J. Reich, *J. Org. Chem.*, **40**, 2570 (1975).
692. H. J. Reich, M. C. Schroeder and I. L. Reich, *Isr. J. Chem.*, **24**, 157 (1984).
693. H. J. Reich and S. K. Shah, *J. Am. Chem. Soc.*, **99**, 263 (1977).
694. H. J. Reich, P. M. Gold and F. Chow, *Tetrahedron Lett.*, 4433 (1979).
695. H. J. Reich, S. K. Shah, P. M. Gold and R. E. Olson, *J. Am. Chem. Soc.*, **103**, 3112 (1981).
696. M. R. Binns and R. K. Haynes, *J. Org. Chem.*, **46**, 3790 (1981).
697. T. Kauffmann and K. -R. Gaydoul, *Tetrahedron Lett.*, **26**, 4071 (1985).
698. T. Kauffmann and H. Ahlers, *Chem. Ber.*, **116**, 1001 (1983).
699. B. -T. Gröbel and D. Seebach, *Chem. Ber.*, **110**, 867 (1977).
700. S. Raucher and G. A. Koolpe, *J. Org. Chem.*, **43**, 4252 (1978).
701. R. C. Gadwood, *J. Org. Chem.*, **48**, 2098 (1983).
702. N. Petragnani and H. M. C. Ferraz, *Synthesis*, 476 (1978).
703. N. Petragnani, H. M. C. Ferraz and M. Yonashiro, *Synthesis*, 27 (1985).
704. P. A. Grieco and Y. Yokoyama, *J. Am. Chem. Soc.*, **99**, 5210 (1977).
705. J. N. Marx and P. J. Dobrowolski, *Tetrahedron Lett.*, **23**, 4457 (1982).
706. A. Osuka, Y. Mori, H. Shimizu and H. Suzuki, *Tetrahedron Lett.*, **24**, 2599 (1983).
707. A. Osuka and H. Suzuki, *Tetrahedron Lett.*, **24**, 5109 (1983).
708. W. Dumont, P. Bayet and A. Krief, *Angew. Chem., Int. Ed. Engl.*, **13**, 274 (1974).
709. W. W. Lotz and J. Gosselck, *Tetrahedron*, **29**, 917 (1973).
710. E. Wenkert, T. W. Ferreira and E. L. Michelotti, *J. Chem. Soc., Chem. Commun.*, 637 (1979).

711. H. Okamura, M. Miura, K. Kosugi and H. Takei, *Tetrahedron Lett.*, **21**, 87 (1980).
712. S. Uemura and S. Fukuzawa, *Tetrahedron Lett.*, **23**, 1181 (1982).
713. S. Uemura, S. Fukuzawa and S. R. Patil, *J. Organomet. Chem.*, **243**, 9 (1983).
714. T. G. Back, S. Collins and K. -W. Law, *Tetrahedron Lett.*, **25**, 1689 (1984).
715. A. F. Sviridov, M. S. Ermolenko, D. V. Yashunsky and N. K. Kochetkov, *Tetrahedron Lett.*, **24**, 4355 (1983).
716. A. F. Sviridov, M. S. Ermolenko, D. V. Yashunsky and N. K. Kochetkov, *Tetrahedron Lett.*, **24**, 4359 (1983).
717. A. P. Kozikowski and A. Ames, *J. Am. Chem. Soc.*, **102**, 860 (1980).
718. A. P. Kozikowski and A. Ames, *Tetrahedron*, **41**, 4821·(1985).
719. A. P. Kozikowski and A. Ames, *J. Org. Chem.*, **43**, 2735 (1978).
720. R. Ando, T. Sugawara and I. Kuwajima, *J. Chem. Soc., Chem. Commun.*, 1514 (1983).
721. I. Kuwajima, R. Ando and T. Sugawara, *Tetrahedron Lett.*, **24**, 4429 (1983).
722. R. Ando, T. Sugawara, M. Shimizu and I. Kuwajima, *Bull. Chem. Soc. Jpn.*, **57**, 2897 (1984).
723. M. Shimizu and I. Kuwajima, *J. Org. Chem.*, **45**, 2921 (1980).
724. A. Krief, W. Dumont and J. N. Denis, *J. Chem. Soc., Chem. Commun.*, 571 (1985).
725. J. Bergman, *Tetrahedron*, **28**, 3323 (1972).
726. J. Bergman, R. Carlsson and B. Sjöberg, *Org. Synth.*, **57**, 18 (1977).
727. J. Bergman and L. Engman, *Tetrahedron*, **36**, 1275 (1980).
728. S. Uemura, M. Wakasugi and M. Okano, *J. Organomet. Chem.*, **194**, 277 (1980).
729. J. Bergman, *Chem. Scr.*, **8A**, 116 (1975).
730. M. Albeck and T. Tamari, *J. Organomet. Chem.*, **238**, 357 (1982).
731. D. H. R. Barton, S. A. Glover and S. V. Ley, *J. Chem. Soc., Chem. Commun.*, 266 (1977).
732. S. A. Glover, *J. Chem. Soc., Perkin Trans. 1*, 1338 (1980).
733. D. L. J. Clive, P. C. Anderson, N. Moss and A. Singh, *J. Org. Chem.*, **47**, 1641 (1982).
734. T. Otsubo, F. Ogura, H. Yamaguchi, H. Higuchi and S. Misumi, *Synth. Commun.*, **10**, 595 (1980).
735. E. Cuthbertson and D. D. MacNicol, *Tetrahedron Lett.*, 1893 (1975).
736. R. H. Mitchell, *Can. J. Chem.*, **54**, 238 (1976).
737. H. Higuchi and S. Misumi, *Tetrahedron Lett.*, **23**, 5571 (1982).
738. H. Higuchi, M. Kugimiya, T. Otsubo, Y. Sakata and S. Misumi, *Tetrahedron Lett.*, **24**, 2593 (1983).
739. T. Kaneda, S. Umeda, H. Tanigawa, S. Misumi, Y. Kai, H. Morii, K. Miki and N. Kasai, *J. Am. Chem. Soc.*, **107**, 4802 (1985).
740. A. Couture, A. Lablache-Combier, R. Lapouyade and Félix, *J. Chem. Res. (S)*, 258 (1979).
741. E. Cuthbertson and D. D. MacNicol, *J. Chem. Soc., Chem. Commun.*, 498 (1974).
742. E. Cuthbertson, J. H. Gall and D. D. MacNicol, *Tetrahedron Lett.*, 3203 (1977).
743. H. Higuchi, Y. Sakata, S. Misumi, T. Otsubo, F. Ogura and H. Yamaguchi, *Chem. Lett.*, 627 (1981).
744. H. Higuchi, T. Otsubo, F. Ogura, H. Yamaguchi, Y. Sakata and S. Misumi, *Bull. Chem. Soc. Jpn.*, **55**, 182 (1982).
745. H. Ishihara and Y. Hirabayashi, *Chem. Lett.*, 1007 (1978).
746. T. G. Back, D. H. R. Barton, M. R. Britten-Kelly and F. S. Guziec, Jr., *J. Chem. Soc., Chem. Commun.*, 539 (1975).
747. T. G. Back, D. H. R. Barton, M. R. Britten-Kelly and F. S. Guziec, Jr., *J. Chem. Soc., Perkin Trans. 1*, 2079 (1976).
748. F. S. Guziec, Jr., and C. J. Murphy, *J. Org. Chem.*, **45**, 2890 (1980).
749. E. R. Cullen, F. S. Guziec, Jr., M. I. Hollander and C. J. Murphy, *Tetrahedron Lett.*, **22**, 4563 (1981).
750. E. R. Cullen, F. S. Guziec, Jr., and C. J. Murphy, *J. Org. Chem.*, **47**, 3563 (1982).
751. F. S. Guziec, Jr., C. J. Murphy and E. R. Cullen, *J. Chem. Soc., Perkin Trans. 1*, 107 (1985).
752. F. S. Guziec, Jr., L. J. San Filippo, C. J. Murphy, C. A. Moustakis and E. R. Cullen, *Tetrahedron*, **41**, 4843 (1985).
753. F. S. Guziec, Jr., and C. A. Moustakis, *J. Chem. Soc., Chem. Commun.*, 63 (1984).
754. C. C. Silveira, J. V. Comasseto and V. Catani, *Synth. Commun.*, **15**, 931 (1985).
755. R. P. Alexander and I. Paterson, *Tetrahedron Lett.*, **24**, 5911 (1983).
756. M. Renard and L. Hevesi, *Tetrahedron Lett.*, **24**, 3911 (1983).
757. S. Halazy and L. Hevesi, *J. Org. Chem.*, **48**, 5242 (1983).
758. G. E. Keck and J. B. Yates, *J. Am. Chem. Soc.*, **104**, 5829 (1982).

759. T. Kawamura, K. Kikukawa, M. Takagi and T. Matsuda, *Bull. Chem. Soc. Jpn.*, **50**, 2021 (1977).
760. J. V. Comasseto and C. A. Brandt, *J. Chem. Res. (S)*, 56 (1982).
761. D. Liotta, W. Markiewicz and H. Santiesteban, *Tetrahedron Lett.*, 4365 (1977).
762. D. Liotta, U. Sunay, H. Santiesteban and W. Markiewicz, *J. Org. Chem.*, **46**, 2605 (1981).
763. M. Tiecco, L. Testaferri, M. Tingoli, D. Chianelli, and M. Montanucci, *Synth. Commun.*, **13**, 617 (1983).
764. (a) R. M. Scarborough, Jr., and A. B. Smith, III, *Tetrahedron Lett.*, 4361 (1977); (b) R. M. Scarborough, Jr., B. H. Toder and A. B. Smith, III, *J. Am. Chem. Soc.*, **102**, 3904 (1980).
765. T. Kometani, Y. Takeuchi and E. Yoshii, *J. Org. Chem.*, **48**, 2630 (1983).
766. S. Takano, N. Tamura and K. Ogasawara, *J. Chem. Soc., Chem. Commun.*, 1155 (1981).
767. D. Liotta and H. Santiesteban, *Tetrahedron Lett.*, 4369 (1977).
768. D. J. Goldsmith and J. K. Thottathil, *Tetrahedron Lett.*, **22**, 2447 (1981).
769. P. Dowd and P. Kennedy, *Synth. Commun.*, **11**, 935 (1981).
770. T. R. Hoye and A. J. Caruso, *Tetrahedron Lett.*, 4611 (1978).
771. K. P. Lok, I. J. Jakovac and J. B. Jones, *J. Am. Chem. Soc.*, **107**, 2521 (1985).
772. M. R. Detty, *Tetrahedron Lett.*, 5087 (1978).
773. N. Miyoshi, H. Ishii, S. Murai and N. Sonoda, *Chem. Lett.*, 873 (1979).
774. K. Sasaki, Y. Aso, T. Otsubo and F. Ogura, *Tetrahedron Lett.*, **26**, 453 (1985).
775. S. Saito, H. Tamai, Y. Usui, M. Inaba and T. Moriwake, *Chem. Lett.*, 1243 (1984).
776. M. Inaba, T. Moriwake and S. Saito, *Tetrahedron Lett.*, **26**, 3235 (1985).
777. B. M. Trost and P. H. Scudder, *J. Am. Chem. Soc.*, **99**, 7601 (1977).
778. H. M. Sirat, E. J. Thomas and J. D. Wallis, *J. Chem. Soc., Perkin Trans. 1*, 2885 (1982).
779. T. Satoh, Y. Kaneko, T. Kumagawa, T. Izawa, K. Sakata and K. Yamakawa, *Chem. Lett.*, 1957 (1984).
780. D. L. J. Clive, G. J. Chittattu, V. Farina, W. A. Kiel, S. M. Menchen, C. G. Russell, A. Singh, C. K. Wong and N. J. Curtis, *J. Am. Chem. Soc.*, **102**, 4438 (1980).
781. N. Miyoshi, K. Kondo, S. Murai and N. Sonoda, *Chem. Lett.*, 909 (1979).
782. P. A. Bartlett and L. A. McQuaid, *J. Am. Chem. Soc.*, **106**, 7854 (1984).
783. A. Cravador and A. Krief, *Tetrahedron Lett.*, **22**, 2491 (1981).
784. G. H. Posner and D. Z. Rogers, *J. Am. Chem. Soc.*, **99**, 8208 (1977).
785. A. Osuka, K. Taka-Oka and H. Suzuki, *Chem. Lett.*, 271 (1984).
786. R. Ahmad, J. M. Saá and M. P. Cava, *J. Org. Chem.*, **42**, 1228 (1977).
787. Z. Ahmed and M. P. Cava, *J. Am. Chem. Soc.*, **105**, 682 (1983).
788. M. Evers and L. Christiaens, *Tetrahedron Lett.*, **24**, 377 (1983).
789. D. L. Boger and J. S. Panek, *J. Am. Chem. Soc.*, **107**, 5745 (1985).
790. V. Šimánek and A. Klásek, *Tetrahedron Lett.*, 3039 (1969).
791. S. Murahashi and T. Yano, *J. Am. Chem. Soc.*, **102**, 2456 (1980).
792. H. J. Reich and M. L. Cohen, *J. Org. Chem.*, **44**, 3148 (1979).
793. P. Müller and M. P. N. Thi, *Helv. Chim. Acta*, **63**, 2168 (1980).
794. A. B. Smith, III, and R. M. Scarborough, Jr., *Tetrahedron Lett.*, 1649 (1978).
795. S. Masamune, T. Kaiho and D. S. Garvey, *J. Am. Chem. Soc.*, **104**, 5521 (1982).
796. P. Kocienski and C. Yeates, *J. Chem. Soc., Perkin Trans. 1*, 1879 (1985).
797. M. Clarembeau and A. Krief, *Tetrahedron Lett.*, **25**, 3625 (1984).
798. P. A. Grieco, J. A. Noguez and Y. Masaki, *Tetrahedron Lett.*, 4213 (1975).
799. P. A. Grieco, M. Nishizawa, S. D. Burke and N. Marinovic, *J. Am. Chem. Soc.*, **98**, 1612 (1976).
800. P. A. Grieco, J. A. Noguez and Y. Masaki, *J. Org. Chem.*, **42**, 495 (1977).
801. G. Majetich, P. A. Grieco and M. Nishizawa, *J. Org. Chem.*, **42**, 2327 (1977).
802. P. A. Grieco, M. Nishizawa, T. Oguri, S. D. Burke and N. Marinovic, *J. Am. Chem. Soc.*, **99**, 5773 (1977).
803. M. Nishizawa, P. A. Grieco, S. D. Burke and W. Metz, *J. Chem. Soc., Chem. Commun.*, 76 (1978).
804. P. A. Grieco, J. Y. Jaw, D. A. Claremon and K. C. Nicolaou, *J. Org. Chem.*, **46**, 1215 (1981).
805. S. V. Ley, N. S. Simpkins and A. J. Whittle, *J. Chem. Soc., Chem. Commun.*, 1001 (1981).
806. S. V. Ley, D. Neuhaus, N. S. Simpkins and A. J. Whittle, *J. Chem. Soc., Perkin Trans. 1*, 2157 (1982).
807. S. V. Ley, N. S. Simpkins and A. J. Whittle, *J. Chem. Soc., Chem. Commun.*, 503 (1983).
808. T. G. Back and D. J. McPhee, *J. Org. Chem.*, **49**, 3842 (1984).
809. F. Ogura, H. Yamaguchi, T. Otsubo and K. Chikamatsu, *Synth. Commun.*, **12**, 131 (1982).
810. P. A. Grieco, Y. Yokoyama and E. Williams, *J. Org. Chem.*, **43**, 1283 (1978).

811. S. Masamune, Y. Hayase, W. Schilling, W. K. Chan and G. S. Bates, *J. Am. Chem. Soc.*, **99**, 6756 (1977).
812. R. K. Haynes and C. Indorato, *Aust. J. Chem.*, **37**, 1183 (1984).
813. B. Danieli, G. Lesma, G. Palmisano and S. Tollari, *J. Chem. Soc., Perkin Trans. 1*, 1237 (1984).
814. T. G. Back, *J. Chem. Soc., Chem. Commun.*, 1417 (1984).
815. R. O. Hutchins and K. Learn, *J. Org. Chem.*, **47**, 4380 (1982).
816. E. J. Corey, H. L. Pearce, I. Székely and M. Ishiguro, *Tetrahedron Lett.*, 1023 (1978).
817. D. L. J. Clive, G. Chittattu and C. K. Wong, *J. Chem. Soc., Chem. Commun.*, 41 (1978).
818. J. Pfenninger, C. Heuberger and W. Graf, *Helv. Chim. Acta*, **63**, 2328 (1980).
819. J. Pfenninger and W. Graf, *Helv. Chim. Acta*, **63**, 1562 (1980).
820. R. E. Ireland, D. W. Norbeck, G. S. Mandel and N. S. Mandel, *J. Am. Chem. Soc.*, **107**, 3285 (1985).
821. D. H. R. Barton and S. W. McCombie, *J. Chem. Soc., Perkin Trans. 1*, 1574 (1975).
822. A. G. M. Barrett, R. W. Read and D. H. R. Barton, *J. Chem. Soc., Perkin Trans. 1*, 2191 (1980).
823. T. K. Raja, *Indian J. Chem.*, **19B**, 812 (1980).
824. M. Sevrin, J. N. Denis and A. Krief, *Tetrahedron Lett.*, **21**, 1877 (1980).
825. H. Suzuki and M. Inouye, *Chem. Lett.*, 225 (1985).
826. K. Ramasamy, S. K. Kalyanasundaram and P. Shanmugam, *Synthesis*, 311 (1978).
827. K. Ramasamy, S. K. Kalyanasundaram and P. Shanmugam, *Synthesis*, 545 (1978).
828. H. Suzuki, A. Kondo and A. Osuka, *Bull. Chem. Soc. Jpn.*, **58**, 1335 (1985).
829. L. Engman, *Tetrahedron Lett.*, **23**, 3601 (1982).
830. L. Engman and S. E. Byström, *J. Org. Chem.*, **50**, 3170 (1985).
831. D. L. J. Clive and P. L. Beaulieu, *J. Org. Chem.*, **47**, 1124 (1982).
832. L. Engman and M. P. Cava, *J. Org. Chem.*, **47**, 3946 (1982).
833. A. Osuka and H. Suzuki, *Chem. Lett.*, 119 (1983).
834. R. Seshadri, W. J. Pegg and M. Israel, *J. Org. Chem.*, **46**, 2596 (1981).
835. A. Osuka, K. Takechi and H. Suzuki, *Bull. Chem. Soc. Jpn.*, **57**, 303 (1984).
836. D. L. J. Clive and C. A. Denyer, *J. Chem. Soc., Chem. Commun.*, 253 (1973).
837. T. H. Chan and J. R. Finkenbine, *Tetrahedron Lett.*, 2091 (1974).
838. F. Mathey and G. Muller, *C. R. Acad. Sci., Ser. C*, **281**, 881 (1975).
839. A. Ogawa, J. Miyake, S. Murai and N. Sonoda, *Tetrahedron Lett.*, **26**, 669 (1985).
840. V. Calò, L. Lopez, A. Mincuzzi and G. Pesce, *Synthesis*, 200 (1976).
841. (a) D. L. J. Clive and S. M. Menchen, *J. Chem. Soc., Chem. Commun.*, 658 (1977); (b) D. L. J. Clive and S. M. Menchen, *J. Org. Chem.*, **45**, 2347 (1980).
842. J. M. Behan, R. A. W. Johnstone and M. J. Wright, *J. Chem. Soc., Perkin Trans. 1*, 1216 (1975).
843. D. Van Ende and A. Krief, *Tetrahedron Lett.*, 2709 (1975).
844. (a) N. Kambe, K. Kondo, S. Morita, S. Murai and N. Sonoda, *Angew. Chem., Int. Ed. Engl.*, **19**, 1009 (1980); (b) N. Kambe, K. Kondo, S. Murai and N. Sonoda, *Angew. Chem., Int. Ed. Engl.*, **19**, 1008 (1980).
845. M. Akiba and M. P. Cava, *Synth. Commun.*, **14**, 1119 (1984).
846. T. Kametani, M. Aizawa, H. Kurobe, T. Matsuura, H. Nemoto and K. Fukumoto, *Chem. Pharm. Bull.*, **30**, 1493 (1982).
847. M. Yamashita, Y. Kato and R. Suemitsu, *Chem. Lett.*, 847 (1980).
848. M. J. Perkins, B. V. Smith and E. S. Turner, *J. Chem. Soc., Chem. Commun.*, 977 (1980).
849. T. Miyata, K. Kondo, S. Murai, T. Hirashima and N. Sonoda, *Angew. Chem., Int. Ed. Engl.*, **19**, 1008 (1980).
850. K. Kondo, N. Sonoda and H. Sakurai, *J. Chem. Soc., Chem. Commun.*, 42 (1975).
851. N. Kambe, K. Kondo and N. Sonoda, *Angew. Chem., Int. Ed. Engl.*, **19**, 1009 (1980).
852. A. Osuka, H. Shimizu and H. Suzuki, *Chem. Lett.*, 1373 (1983).
853. N. Ohira, Y. Aso, T. Otsubo and F. Ogura, *Chem. Lett.*, 853 (1984).
854. K. Fujimori, H. Yoshimoto and S. Oae, *Tetrahedron Lett.*, 4397 (1979).
855. D. H. R. Barton, A. Fekih and X. Lusinchi, *Tetrahedron Lett.*, **26**, 4603 (1985).
856. H. Suzuki and K. Takaoka, *Chem. Lett.*, 1733 (1984).
857. F. G. James, M. J. Perkins, O. Porta and B. V. Smith, *J. Chem. Soc., Chem. Commun.*, 131 (1977).
858. K. Fujimori, H. Yoshimoto and S. Oae, *Tetrahedron Lett.*, **21**, 3385 (1980).
859. D. H. R. Barton, A. Fekih and X. Lusinchi, *Tetrahedron Lett.*, **26**, 3693 (1985).
860. A. G. M. Barrett, R. W. Read and D. H. R. Barton, *J. Chem. Soc., Perkin Trans. 1*, 2184 (1980).

861. M. J. Perkins, B. V. Smith, B. Terem and E. S. Turner, *J. Chem. Res. (S)*, 341 (1979).
862. D. L. J. Clive and S. M. Menchen, *J. Chem. Soc., Chem. Commun.*, 168 (1979).
863. D. L. J. Clive and S. M. Menchen, *J. Org. Chem.*, **44**, 4279 (1979).
864. D. L. J. Clive, W. A. Kiel, S. M. Menchen and C. K. Wong, *J. Chem. Soc., Chem. Commun.*, 657 (1977).
865. M. R. Detty, *J. Org. Chem.*, **44**, 4528 (1979).
866. M. R. Detty and M. D. Seidler, *J. Org. Chem.*, **47**, 1354 (1982).
867. D. L. J. Clive, G. Chittattu, N. J. Curtis and S. M. Menchen, *J. Chem. Soc., Chem. Commun.*, 770 (1978).
868. P. A. Zoretic, R. J. Chambers, G. D. Marbury and A. A. Riebiro, *J. Org. Chem.*, **50**, 2981 (1985).
869. S. Uemura, S. Fukuzawa and K. Ohe, *Tetrahedron Lett.*, **26**, 921 (1985).
870. H. J. Reich, I. L. Reich and S. Wollowitz, *J. Am. Chem. Soc.*, **100**, 5981 (1978).
871. H. J. Reich and S. Wollowitz, *J. Am. Chem. Soc.*, **104**, 7051 (1982).
872. H. J. Reich, K. E. Yelm and S. Wollowitz, *J. Am. Chem. Soc.*, **105**, 2503 (1983).
873. H. J. Reich and M. J. Kelly, *J. Am. Chem. Soc.*, **104**, 1119 (1982).
874. A. Haces, E. M. G. A. van Kruchten and W. H. Okamura, *Tetrahedron Lett.*, **23**, 2707 (1982).
875. S. I. Pennanen, *Synth. Commun.*, **10**, 373 (1980).
876. H. Nishiyama, K. Itagaki, K. Sakuta and K. Itoh, *Tetrahedron Lett.*, **22**, 5285 (1981).
877. H. Nishiyama, S. Narimatsu and K. Itoh, *Tetrahedron Lett.*, **22**, 5289 (1981).
878. P. Magnus, F. Cooke and T. Sarkar, *Organometallics*, **1**, 562 (1982).
879. K. B. Sharpless and R. F. Lauer, *J. Org. Chem.*, **37**, 3973 (1972).
880. H. J. Reich and M. L. Cohen, *J. Am. Chem. Soc.*, **101**, 1307 (1979).
881. P. J. Giddings, D. I. John and E. J. Thomas, *Tetrahedron Lett.*, **21**, 395 (1980).
882. P. J. Giddings, D. I. John, E. J. Thomas and D. J. Williams, *J. Chem. Soc., Perkin Trans. 1*, 2757 (1982).
883. P. G. Gassman, T. Miura and A. Mossman, *J. Chem. Soc., Chem. Commun.*, 558 (1980).
884. S. Raucher, K. -J. Hwang and J. E. Macdonald, *Tetrahedron Lett.*, 3057 (1979).
885. C. G. Francisco, R. Freire, R. Hernández, J. A. Salazar and E. Suárez, *Tetrahedron Lett.*, **25**, 1621 (1984).
886. T. Frejd and K. B. Sharpless, *Tetrahedron Lett.*, 2239 (1978).
887. S. Uemura, S. Fukuzawa, T. Yamauchi, K. Hattori, S. Mizutaki and K. Tamaki, *J. Chem. Soc., Chem. Commun.*, 426 (1984).
888. E. J. Corey, W. Su and M. M. Mehrotra, *Tetrahedron Lett.*, **25**, 5123 (1984).
889. D. Liotta, C. S. Barnum and M. Saindane, *J. Org. Chem.*, **46**, 4301 (1981).
890. D. Liotta, M. Saindane and D. Brothers, *J. Org. Chem.*, **47**, 1598 (1982).
891. S. J. Falcone and M. E. Munk, *Synth. Commun.*, **9**, 719 (1979).
892. G. Zima, C. Barnum and D. Liotta, *J. Org. Chem.*, **45**, 2736 (1980).
893. T. G. Back and R. G. Kerr, *Tetrahedron*, **41**, 4759 (1985).
894. I. Kuwajima and R. Takeda, *Tetrahedron Lett.*, **22**, 2381 (1981).
895. A. M. Léonard-Coppens and A. Krief, *Tetrahedron Lett.*, 3227 (1976).
896. H. Nishiyama, K. Itagaki, N. Osaka and K. Itoh, *Tetrahedron Lett.*, **23**, 4103 (1982).
897. H. Nishiyama, T. Kitajima, A. Yamamoto and K. Itoh, *J. Chem. Soc., Chem. Commun.*, 1232 (1982).
898. C. J. Kowalski and J. -S. Dung, *J. Am. Chem. Soc.*, **102**, 7950 (1980).
899. D. L. J. Clive, A. G. Angoh, S. C. Suri, S. N. Rao and C. G. Russell, *J. Chem. Soc., Chem. Commun.*, 828 (1982).
900. D. L. J. Clive and C. G. Russell, *J. Chem. Soc., Chem. Commun.*, 434 (1981).
901. D. L. J. Clive, C. G. Russell and S. C. Suri, *J. Org. Chem.*, **47**, 1632 (1982).
902. D. H. R. Barton, D. J. Lester, W. B. Motherwell and M. T. B. Papoula, *J. Chem. Soc., Chem. Commun.*, 246 (1980).
903. G. H. Posner and M. J. Chapdelaine, *Tetrahedron Lett.*, 3227 (1977).
904. J. N. Denis and A. Krief, *J. Chem. Soc., Chem. Commun.*, 229 (1983).
905. T. Agawa, M. Ishida and Y. Ohshiro, *Synthesis*, 933 (1980).
906. M. Miyashita and A. Yoshikoshi, *Synthesis*, 664 (1980).
907. M. Miyashita, T. Suzuki and A. Yoshikoshi, *J. Org. Chem.*, **50**, 3377 (1985).
908. A. Nickon, A. D. Rodriguez, R. Ganguly and V. Shirhatti, *J. Org. Chem.*, **50**, 2767 (1985).
909. P. A. Grieco and M. Miyashita, *Tetrahedron Lett.*, 1869 (1974).

910. K. Mori, *Tetrahedron*, **32**, 1101 (1976).
911. J. C. Sih and D. R. Graber, *J. Org. Chem.*, **43**, 3798 (1978).
912. R. H. Wollenberg, *Tetrahedron Lett.*, **21**, 3139 (1980).
913. R. C. Nickolson and H. Vorbrüggen, *Tetrahedron Lett.*, **24**, 47 (1983).
914. D. H. Wadsworth and M. R. Detty, *J. Org. Chem.*, **45**, 4611 (1980).
915. L. A. Tsoi, A. K. Patsaev, V. Z. Ushanov and L. V. Vyaznikovtsev, *Zh. Org. Khim.*, **20**, 2081 (1984).
916. N. Shinmon, M. P. Cava and R. F. C. Brown, *J. Chem. Soc., Chem. Commun.*, 1020 (1980).
917. H. Pluim and H. Wynberg, *Tetrahedron Lett.*, 1251 (1979).
918. D. Liotta, P. B. Paty, J. Johnston and G. Zima, *Tetrahedron Lett.*, 5091 (1978).
919. N. Miyoshi, H. Ishii, K. Kondo, S. Murai and N. Sonoda, *Synthesis*, 300 (1979).
920. A. Itoh, S. Ozawa, K. Oshima and H. Nozaki, *Tetrahedron Lett.*, **21**, 361 (1980).
921. A. Itoh, S. Ozawa, K. Oshima and H. Nozaki, *Bull. Chem. Soc. Jpn.*, **54**, 274 (1981).
922. W. R. Leonard and T. Livinghouse, *J. Org. Chem.*, **50**, 730 (1985).
923. A. Pelter, R. S. Ward, D. Ohlendorf and D. H. J. Ashdown, *Tetrahedron*, **35**, 531 (1979).
924. Y. Hayashi, T. Matsumoto, T. Hyono, N. Nishikawa, M. Uemura, M. Nishizawa, M. Togami and T. Sakan, *Tetrahedron Lett.*, 3311 (1979).
925. K. Ishii, P. Mathies, T. Nishio, H. R. Wolf, B. Frei and O. Jeger, *Helv. Chim. Acta*, **67**, 1175 (1984).
926. K. Mori and S. Takechi, *Tetrahedron*, **41**, 3049 (1985).
927. H. E. Zimmerman and M. C. Hovey, *J. Org. Chem.*, **44**, 2331 (1979).
928. H. E. Zimmerman and S. A. Fleming, *J. Org. Chem.*, **50**, 2539 (1985).
929. W. Oppolzer and K. Bättig, *Helv. Chim. Acta*, **64**, 2489 (1981).
930. R. K. Hill and L. A. Renbaum, *Tetrahedron*, **38**, 1959 (1982).
931. J. Schwartz and Y. Hayasi, *Tetrahedron Lett.*, **21**, 1497 (1980).
932. G. Zima and D. Liotta, *Synth. Commun.*, **9**, 697 (1979).
933. T. A. Hase and P. Kukkola, *Synth. Commun.*, **10**, 451 (1980).
934. D. Liotta, M. Saindane, C. Barnum and G. Zima, *Tetrahedron*, **41**, 4881 (1985).
935. D. Liotta and G. Zima, *J. Org. Chem.*, **45**, 2551 (1980).
936. D. Liotta, G. Zima and M. Saindane, *J. Org. Chem.*, **47**, 1258 (1982).
937. N. Petragnani and G. Schill, *Chem. Ber.*, **103**, 2271 (1970).
938. D. J. Buckley, S. Kulkowit and A. McKervey, *J. Chem. Soc., Chem. Commun.*, 506 (1980).
939. D. J. Buckley and M. A. McKervey, *J. Chem. Soc., Perkin Trans. 1*, 2193 (1985).
940. R. Pellicciari, M. Curini, P. Ceccherelli and R. Fringuelli, *J. Chem. Soc., Chem. Commun.*, 440 (1979).
941. P. J. Giddings, D. I. John and E. J. Thomas, *Tetrahedron Lett.*, **21**, 399 (1980).
942. T. G. Back and R. G. Kerr, *Tetrahedron Lett.*, **23**, 3241 (1982).
943. N. Sonoda, T. Yasuhara, K. Kondo, T. Ikeda and S. Tsutsumi, *J. Am. Chem. Soc.*, **93**, 6344 (1971).
944. K. Kondo, N. Sonoda and S. Tsutsumi, *J. Chem. Soc., Chem. Commun.*, 307 (1972).
945. K. Kondo, S. Yokoyama, N. Miyoshi, S. Murai and N. Sonoda, *Angew. Chem. Int. Ed. Engl.*, **18**, 692 (1979).
946. K. Kondo, K. Murata, N. Miyoshi, S. Murai and N. Sonoda, *Synthesis*, 735 (1979).
947. K. Kondo, N. Sonoda, K. Yoshida, M. Koishi and S. Tsutsumi, *Chem. Lett.*, 401 (1972).
948. K. Kondo, N. Sonoda and H. Sakurai, *J. Chem. Soc., Chem. Commun.*, 853 (1973).
949. P. Koch, *Tetrahedron Lett.*, 2087 (1975).
950. K. Kondo, M. Takarada, S. Murai and N. Sonoda, *Synthesis*, 597 (1979).
951. K. Kondo, N. Sonoda and S. Tsutsumi, *Chem. Lett.*, 373 (1972).
952. K. Kondo, N. Sonoda and H. Sakurai, *Chem. Lett.*, 1429 (1974).
953. K. Kondo, N. Sonoda and S. Tsutsumi, *Tetrahedron Lett.*, 4885 (1971).
954. K. Kondo, N. Sonoda and H. Sakurai, *Bull. Chem. Soc. Jpn.*, **48**, 108 (1975).
955. P. Koch and E. Perrotti, *Tetrahedron Lett.*, 2899 (1974).
956. N. Sonoda, G. Yamamoto, K. Natsukawa, K. Kondo and S. Murai, *Tetrahedron Lett.*, 1969 (1975).
957. A. Ogawa, K. Kondo, S. Murai and N. Sonoda, *J. Chem. Soc., Chem. Commun.*, 1283 (1982).
958. A. Ogawa, N. Kambe, S. Murai and N. Sonoda, *Tetrahedron*, **41**, 4813 (1985).
959. K. Kondo, N. Sonoda and H. Sakurai, *J. Chem. Soc., Chem. Commun.*, 160 (1974).
960. K. Kondo, N. Sonoda and H. Sakurai, *Tetrahedron Lett.*, 803 (1974).
961. K. Kondo, S. Yokoyama, N. Miyoshi, S. Murai and N. Sonoda, *Angew. Chem., Int. Ed. Engl.*, **18**, 691 (1979).

962. N. Kambe, K. Kondo, H. Ishii, S. Murai and N. Sonoda, *Angew. Chem., Int. Ed. Engl.*, **18**, 547 (1979).
963. N. Kambe, K. Kondo, H. Ishii and N. Sonoda, *Bull. Chem. Soc. Jpn.*, **54**, 1460 (1981).
964. J. Bergman and L. Engman, *J. Organomet. Chem.*, **175**, 233 (1979).
965. S. Uemura, K. Ohe, J. -R. Kim, K. Kudo and N. Sugita, *J. Chem. Soc., Chem. Commun.*, 271 (1985).
966. D. H. R. Barton, D. Bridon and S. Z. Zard, *Tetrahedron Lett.*, **25**, 5777 (1984).
967. K. Yamauchi, K. Nakamura and M. Kinoshita, *Tetrahedron Lett.*, 1787 (1979).
968. K. Yamauchi, K. Hattori and M. Kinoshita, *J. Chem. Soc., Perkin Trans. 1*, 1327 (1985).
969. L. Engman and M. P. Cava, *Tetrahedron Lett.*, **22**, 5251 (1981).
970. M. Akiba, M. V. Lakshmikantham, K. Y. Jen and M. P. Cava, *J. Org. Chem.*, **49**, 4819 (1984).
971. T. -L. Ho and T. W. Hall, *Synth. Commun.*, **5**, 367 (1975).
972. T. Mandai, K. Osaka, M. Kawagishi, M. Kawada and J. Otera, *Synth. Commun.*, **14**, 797 (1984).

CHAPTER **4**

Seleno- and telluro-carbonyl compounds

FRANK S. GUZIEC, JR.

Department of Chemistry, New Mexico State University, Las Cruces, New Mexico 88003, USA

I. INTRODUCTION

A. Overview

The chemistry of the carbonyl group is well known as one of the cornerstones of organic chemistry, and that of the thiocarbonyl group has recently become much more familiar to the practising organic chemist. The corresponding selenium and tellurium compounds, however, are generally considered to be exotic and perhaps out of the mainstream of organic chemistry. While it would be easy to blame these views on pervasive 'seleno- and telluro-phobia', it is clear that these analogues are much less well known than the corresponding oxygen and sulfur compounds.

In many cases, early preparations of seleno- or telluro-carbonyl compounds involved the use of toxic and foul-smelling reagents. In addition, often the selenium and tellurium reagents used in attempted preparations of these compounds behave differently than their oxygen or sulfur analogs, leading to errors and confusion in the early literature.

Recent advances in spectroscopy, the ability to do manipulations routinely and carry out observations at low temperatures and in inert atmospheres and the use of more convenient and less hazardous procedures have opened up new areas of investigation, and have made seleno- and telluro-carbonyl compounds much more available for study.

Books by Klayman and Gunther[1] and Zingaro and Cooper[2] provide useful chapters[3-7] on the chemistry of selenocarbonyl compounds up to about 1972. Sections on tellurocarbonyl compounds appear in the books by Irgolic[3] in 1974 and that of Cooper[9] in 1971. More recent coverage of these areas can be found in the *Specialist Periodical Reports* of the Royal Society of Chemistry (London)[10] and in the Barton and Ollis compendium[11]. The use of seleno- and telluro-carbonyl compounds in heterocyclic synthesis has recently been described by Renson[12].

B. Nomenclature of Se/Te Carbonyl Compounds

A major difficulty in finding seleno- and telluro-carbonyl compounds in the literature occurs as a result of the sometimes ambiguous nomenclature associated with these compounds. For example, 'selenoketone' may refer to selenium substitution on a normal ketone in addition to the selenium analog of a ketone. Both uses for this name have appeared in recent titles and abstracts. Another major difficulty results from attempts by authors, especially in the older literature, to apply sulfur nomenclature directly to selenium compounds. For example, the selenium analogue of a thione is *not* a selenone.

$$\underset{\text{Ketone}}{\underset{\text{RCR}}{\overset{\overset{\displaystyle O}{\|}}{}}} \qquad \underset{\text{Thione}}{\underset{\text{RCR}}{\overset{\overset{\displaystyle S}{\|}}{}}} \qquad \underset{\text{Selenone}}{\underset{\overset{\displaystyle \|}{O}}{\underset{\displaystyle RSeR}{\overset{\overset{\displaystyle O}{\|}}{}}}} \qquad \underset{\text{Selone}}{\underset{\text{RCR}}{\overset{\overset{\displaystyle Se}{\|}}{}}}$$
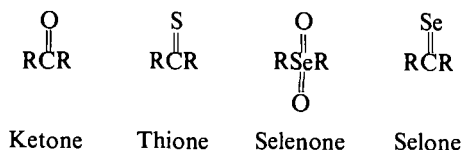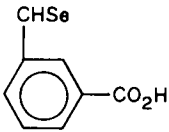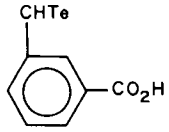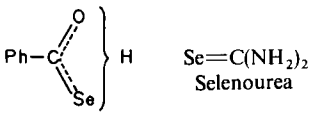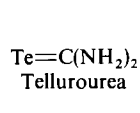
The most recent IUPAC *Nomenclature of Organic Chemistry* lists rules for naming organic selenium and tellurium compounds[13]. These rules state that 'organic compounds of

TABLE 1. Suggested functional group nomenclature of selenocarbonyl and tellurocarbonyl compounds

Functional group	Prefix	Suffix or functional group name
$\diagup\!\!\!\!-\overset{\displaystyle Se}{\underset{\displaystyle H}{C}}$	Selenoformyl-	-selenal -carboselenaldehyde
$\diagup\!\!\!\!-\overset{\displaystyle Te}{\underset{\displaystyle H}{C}}$	Telluroformyl-	-tellural -carbotelluraldehyde
$\diagup\!\!\diagdown C=Se$	Selenoxo-	-selone
$\diagup\!\!\diagdown C=Te$	Telluroxo-	—
$\diagup\!\!\!\!-\overset{\displaystyle O}{\underset{\displaystyle SeH}{C}}$	—	-carboselenoic acid

TABLE 2. Examples of selenocarbonyl and tellurocarbonyl nomenclature

$Me(CH_2)_3CHSe$	$Me(CH_2)_3CHTe$
(a) Pentaneselenal	(a) Pentanetellural
(b) 1-Butanecarboselenaldehyde	(b) 1-Butanecarbotelluraldehyde

CHSe

─CO_2H

m-Selenoformylbenzoic acid

CHTe

─CO_2H

m-Telluroformylbenzoic acid

$Ph-C$ ⎰ O / Se ⎱ H $Se{=}C(NH_2)_2$
                           Selenourea

$Te{=}C(NH_2)_2$
Tellurourea

Selenobenzoic acid

Se
‖
EtCEt

Te
‖
EtCEt

(a) 3-Selenoxopentane   3-Telluroxopentane
(b) 3-Pentaneselone

selenium are named as far as possible analogously to the corresponding sulfur compounds' and 'organic compounds of tellurium are named in the same way as those of selenium with "tellur-" in place of "selen-"'. Application of these rules to seleno- and telluro-carbonyl groups are summarized in Table 1. An additional rule states that compounds which cannot be named using the above scheme are named by placing 'seleno-' or 'telluro-' before the name of the corresponding oxygen compound. Examples of seleno- and telluro-carbonyl compounds named using these rules are listed in Table 2.

One complication arises because of the inability of this system to distinguish Se- verses O-protonated isomers of selenobenzoic or, more importantly, the Se- versus O-alkylated ester derivatives. To avoid such ambiguity, it may be worthwhile to use the term 'selone' wherever a selenocarbonyl moiety exists. For example, the O-alkylated seleno ester would be designated as a selone ester and the Se-alkylated compound would be designated as a selenol ester. Accordingly seloneamide, selonecarbonate, selonecarbamate, etc., would denote selenocarbonyl-containing compounds. One difficulty with such a proposal is that no nomenclature analogue of 'selone' has been adopted for the tellurocarbonyl group ('tellone').

Until these nomenclature problems are resolved, and consistent nomenclatures adopted in the current literature, finding seleno- and telluro-carbonyl compounds will continue to be difficult. The naming of compounds in this chapter will follow the IUPAC guidelines.

C. Carbon—Chalcogen Multiple Bonds

Recent successes in the preparations of compounds with carbon—selenium and carbon—tellurium double bonds may, at first glance, appear surprising. Poor overlap in the 2p–3p π bond of thiones has been used to explain the lowered stabilities of these

compounds relative to ketones[14]. An extension of this line of thought made the existence of selones, with even poorer $2p$–$4p\pi$ overlap, doubtful. It appeared that significant resonance interaction or metal coordination, lowering the bond order of carbon—selenium or carbon—tellurium multiple bonds, would be necessary for stability in seleno- or telluro-carbonyl compounds.

The preparation of selones with a 'pure' carbon—selenium double bond showed such stabilization was not necessary[15]. Subsequent preparation of monomeric telluroesters shows that compounds with formal $2p$–$5p\pi$ bonding can exist with only moderate resonance stabilization[16].

Comparison of the [17]O and [77]Se shifts of carbonyl and selenocarbonyl compounds indicate that the bond orders of the carbonyl and selenocarbonyl groups are similar[17]. The absorption spectra of selenocarbonyl[18] and tellurocarbonyl[16] compounds parallel those of their carbonyl and thiocarbonyl analogs. Both of these observations suggest that there is true 'double bond character' in these functional groups.

Data dealing with bonding in carbon—chalcogen double bonds are summarized in Table 3. As expected, the carbon—chalcogen double bond length increases significantly in the series O, S, Se, Te. With this increase in size comes greater polarizability. Because of this polarizability, seleno- and telluro-carbonyl compounds are weaker bases than their sulfur and oxygen analogs, but show increased nucleophilicity at the selenium and tellurium atoms. This increased polarizability can also be used to explain the increased carbon electrophilicity of the seleno- and telluro-carbonyl groups.

The polarity of the seleno- and telluro-carbonyl groups deserves special comment. Whereas the carbonyl group is highly polar, the thiocarbonyl group is much less so. Thiophilic addition—nucleophilic addition at the sulfur center of a thiocarbonyl group—was originally explained by a 'reversed polarity' of the thiocarbonyl moiety with carbon being δ^- relative to sulfur. This 'reversed polarity' should be even more pronounced in the seleno- and telluro-carbonyl groups. A comparison of orbital electronegativities suggests that this is not the case[20]. Both the σ and π components of the seleno- and telluro-carbonyl groups should show 'normal' polarity with the chalcogen being δ^- relative to carbon. A dipole moment study of 'pure' carbon—chalcogen double bonds in ketone analogues suggests 'normal polarity' for these functional groups (Section XIV.E)[21].

While many seleno- and telluro-carbonyl compounds are reasonably stable, their chemistry is best characterized by reactions which readily convert the carbon—selenium and carbon—tellurium double bonds into more stable selenium- or tellurium-containing single-bonded species, or which bring about the replacement of selenium or tellurium by oxygen, sulfur or nitrogen. These reactions often make the preparation and characteriz-

TABLE 3. Steric and electronic factors involved in carbon—chalcogen double bonds

	Covalent radii (Å)[19]				
	C	O	S	Se	Te
Single-bonded	0.77	0.74	1.04	1.17	1.37
Double-bonded	0.67	0.62	0.94	1.07	1.27

	Orbital electronegativities[20] (Pauling scale)					
		C	O	S	Se	Te
σ	sp^2	2.75	5.54	3.46	3.29	3.17
π	p	1.68	3.19	2.40	2.31	2.31

ation of seleno- and telluro-carbonyl compounds difficult. A useful tactic in increasing the stabilities of seleno- and telluro-carbonyl compounds, aside from resonance stabilization, has been to shield these group sterically, thereby eliminating some possible decomposition pathways.

D. Reagents for the Synthesis of Se/Te Carbonyl Compounds

As was previously mentioned, two of the major difficulties associated with the investigations of seleno- and telluro-carbonyl compounds are the toxicity and unpleasant odors of reagents used in their preparation.

Hydrogen selenide is a colorless gas, b.p. $-41\,°C$, with an unpleasant odor resembling that of radishes. It is extremely toxic and irritating and should be treated with great care[22]. Hydrogen selenide is a moderately strong acid[23], pK_1 3.88, $pK_2 \approx 11$. It is readily oxidized by atmospheric oxygen affording finely divided red selenium, and should be used in an inert atmosphere. Hydrogen selenide is commercially available in cylinders, or it can be generated in small quantities by hydrolysis of commercially available aluminum selenide[24]. Alternatively, hydrogen selenide can be prepared by reduction of selenium by carbon monoxide in water in the presence of triethylamine[25]. These conditions are mild enough to allow *in situ* formation of hydrogen selenide.

Although hydrogen selenide is used directly in many procedures, the generation of ethanolic solutions of sodium hydrogen selenide using the procedure of Klayman and Griffin[26] is generally far more convenient (equation 1). This procedure utilizes sodium borohydride and elemental selenium in ethanol. The triethylborate formed, in general, does not interfere with further reactions. Aqueous solutions of sodium hydrogen selenide can be prepared similarly.

$$Se + NaBH_4 \xrightarrow{\text{EtOH}} NaHSe + B(OEt)_3 + H_2 \tag{1}$$
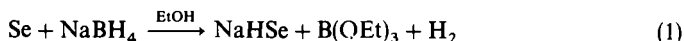
Sodium and lithium selenides can be prepared by metal reduction of selenium in liquid ammonia (equation 2)[27,28]. The diselenides can be prepared similarly with a 1:1 molar ratio of reagents (equation 3).

$$Se + 2Na \xrightarrow{\text{NH}_3} Na_2Se \tag{2}$$

$$2Se + 2Na \xrightarrow{\text{NH}_3} Na_2Se_2 \tag{3}$$

Suspensions of lithium selenide and lithium diselenide in tetrahydrofuran can be easily prepared by reaction of selenium with lithium triethylborohydride (equations 4 and 5)[29].

$$Se + 2LiEt_3BH \xrightarrow{\text{THF}} Li_2Se + 2Et_3B + H_2 \tag{4}$$

$$2Se + 2LiEt_3BH \xrightarrow{\text{THF}} Li_2Se_2 + 2Et_3B + H_2 \tag{5}$$
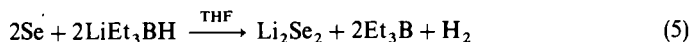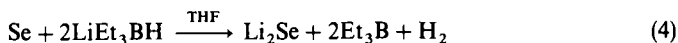
Carbon diselenide is a substance with a remarkably unpleasant odor[30]. It is commercially available and can be most conveniently prepared from carbon tetrachloride or dichloromethane and selenium at elevated temperature. An improved technique for the preparation of carbon diselenide from dichloromethane affords this reagent in ca. 85% yield (equation 6)[31,32]. While the reactions of carbon diselenide resemble those of carbon disulfide, the former is more likely to polymerize in the presence of nucleophiles[30].

$$CH_2Cl_2 + 2Se \xrightarrow{565\,°C} CSe_2 + 2HCl \tag{6}$$
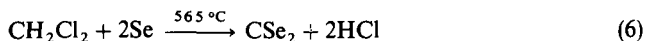
Phosphorus pentaselenide has not proved to be particularly useful in the preparation of selenocarbonyl compounds. Although phosphorus pentaselenide has not been well characterized[33], it appears to be much less soluble than its sulfur analogue, perhaps leading to lowered reactivity. Attempts to prepare the selenium analog of the well known thionating reagent p-methoxyphenylthioxophosphine sulfide dimer (1) using phosphorus pentaselenide were unsuccessful[34].

$$p\text{—MeOC}_6\text{H}_4\text{P}\begin{array}{c}\text{S}\\\parallel\end{array}\begin{array}{c}\text{S}\\\diagdown\\\diagup\\\text{S}\end{array}\begin{array}{c}\text{S}\\\parallel\\\text{P}\end{array}\text{C}_6\text{H}_4\text{OMe}\text{—}p \qquad\qquad \left[(\text{C}_6\text{H}_{11})_3\text{Sn}\right]_2\text{—Se}$$

(1)   (2)
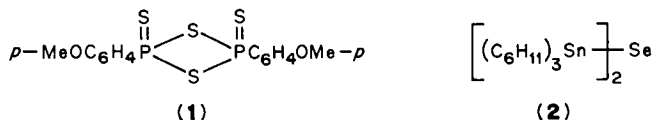
Selenium(I) bromide can be prepared by reaction of selenium dioxide, selenium, concentrated hydrobromic acid and concentrated sulfuric acid[34].

Boron triselenide can be prepared in situ in a non-aggregated form suitable for selenation by reaction of bis(tricyclohexyltin) selenide (2) with boron trichloride[35]. Compound 2 can be prepared from tricyclohexyltin chloride and sodium selenide.

Hydrogen telluride is an unstable toxic gas most easily prepared by hydrolysis of aluminum telluride[36]. It is more acidic than hydrogen selenide (pK_1 2.64, $pK_2 \approx 10.8$) and deposits elemental tellurium on exposure to air[23]. Lithium telluride and sodium hydrogen telluride can be prepared analogously to the preparations of the corresponding selenium compounds[37,38]. Carbon ditelluride has not been reported.

In general, both organo-selenium and -tellurium compounds should be considered toxic and treated with extreme care. This author finds that treatment of glassware and apparatus with permanganate solution is useful in removing persistent odors. Concentrated nitric acid or potassium hydroxide in isopropanol are useful for cleaning red selenium residues from glassware. Traps containing sodium hydroxide–hydrogen peroxide are useful in carbon diselenide work[31].

II. Se/Te KETONES AND ALDEHYDES

A. Early Reports

Although selenium and tellurium analogues of aldehydes and ketones have been described since the 1870s, many of these early reports should be viewed with skepticism since adequate analytical techniques were not available for the characterization of these compounds. Many early claims for the preparation of seleno- and telluro-aldehydes and -ketones involved the addition of hydrogen selenide or hydrogen telluride to aldehydes or ketones. Monomeric, dimeric and trimeric seleno- and telluro-carbonyl compounds were claimed to be products of these reactions[39–44].

Only the selenium reactions have been reinvestigated in detail. Margolis and Pittman[45] showed that, at least in the case of ketones, the products were red selenium and bis(dialkylmethyl) diselenides, presumably derived from an intermediate selone. They suggested that the reaction of hydrogen selenide with a carbonyl compound initially involves an addition, affording an intermediate hydroselenohydrin (3a or 3b). In the case of aldehydes, trimerization of this intermediate is rapid and no selenium is formed, the product being the trimeric cyclic triselenide 4 (equation 7)[46]. X-ray analysis subsequently confirmed the nature of trimeric 'selenoformaldehyde'[47] and 'selenoacetaldehyde'[48]; linear polymeric forms of 'selenoformaldehyde'[49,50] and trimeric 'selenobenzaldehyde'[51] have also been described.

$$R_2C{=}O + H_2Se \xrightarrow{H^+} \left[\begin{array}{c} R \\ C \\ H \end{array} \begin{array}{c} SeH \\ OH \end{array} \right] \xrightarrow{-H_2O} (4) \tag{7}$$

(3a)

$$R_2C{=}O + H_2Se \xrightarrow{H^+} \left[\begin{array}{c} R \\ C \\ R \end{array} \begin{array}{c} SeH \\ OH \end{array} \right] \xrightarrow{-H_2O} \left[R_2C{=}Se \right] \tag{8}$$

(3b)   (5)

$$\downarrow H_2Se$$

$$R_2CH{-}Se{-}Se{-}CHR_2 \xleftarrow{[O]} R_2CH{-}SeH + Se$$

(7)   (6)
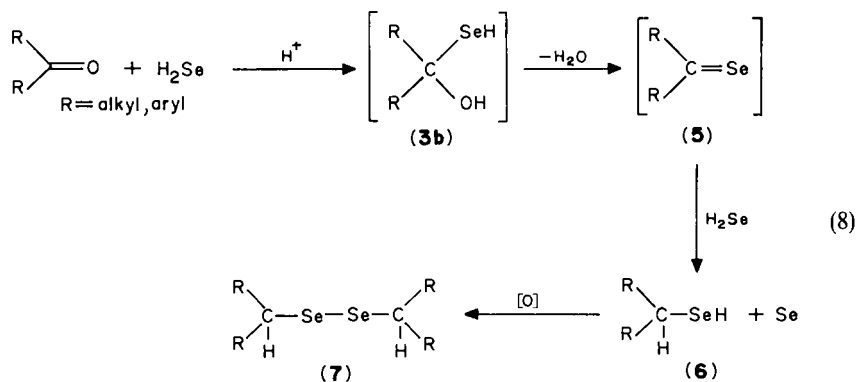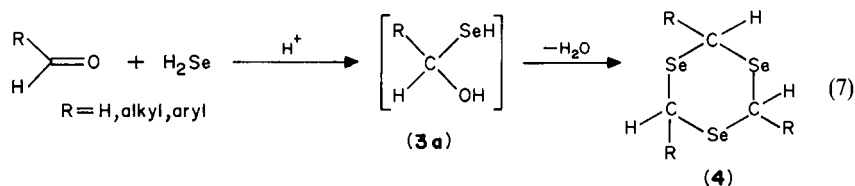
In the case of the ketones, dehydration of **3b** occurs, affording an intermediate selone which is rapidly reduced by hydrogen selenide (an excellent reducing agent) to the selenol **6**. Oxidation of **6** affords the diselenide **7** (equation 8)[45]. Although no reinvestigation of the hydrogen telluride reaction has been reported, it is unlikely that monomeric telluroketones were in fact isolated under similar conditions.

A detailed discussion of the early reports on the preparation and reactions of selenocarbonyl analogues of aldehydes and ketones (and the problems associated with these reports) has appeared previously[3].

B. Selenoketones (Selones)

1. Preparation

The first true monomeric selones isolated, not stabilized by resonance interactions or metal ligands, were di-*tert*-butylselone and selenofenchone. These were prepared by pyrolysis of a phosphoranylidine hydrazone (**8**) (prepared from the corresponding hydrazone) in the presence of selenium powder. The selone **9**, nitrogen and triphenylphosphine selenide were obtained (equation 9)[15,52]. A variety of other sterically hindered selones have been prepared using this method[53–55]. The method was subsequently applied to the preparation of sterically hindered thiones, and it was found that sulfur was more reactive than selenium in these reactions[56,57].

While the mechanism of this reaction has not been investigated in detail, it has been suggested that the first step involves cleavage of **8** to a diazo compound (**10**) and triphenylphosphine (equation 10)[21]. No selone-forming reaction is observed at temperatures below the thermal decomposition point of the phosphoranylidene hydrazone. The resulting diazo compound may react with powered selenium, or more likely, with an

$$R = R' = t\text{-Bu}$$

$$(9)$$

activated form of selenium generated on reaction of selenium with the liberated phosphine. Since there is no evidence of selenium reacting directly with carbenes or carbenoid species, a likely intermediate in the reaction is the N-selenonitrimine **11**, which loses nitrogen to afford the selone.

$$(10)$$

Among the by-products of this reaction are diazo compound decomposition products and symmetrical olefins formed by an *in situ* 'two-fold extrusion' reaction (see below). Unless the reaction conditions are carefully controlled, these by-products may predominate. These compounds are also the only isolated products from the attempted synthesis of moderately sterically hindered selones such as selenobenzophenone and selenocamphor[52].

A more convenient alternative to the phosphoranylidene hydrazone method involves the reaction of the hydrazone directly with selenium(I) bromide in the presence of a tertiary amine[34] (equation 11) or the reaction of a hydrazone dimagnesium salt with selenium(I) chloride[58]. An N-selenonitrosimine may again be an intermediate in this reaction. Again, only sterically hindered selones could be prepared using the selenium bromide method; no selones were obtained from camphor, benzophenone or fluorenone hydrazones.

A third method for the preparation of selones utilizes bis(tricyclohexyltin) selenide (**2**)–boron trichloride as an *in situ* source of non-aggregated boron selenide (equation 12)[35]. Only selenofenchone has been prepared using these conditions. A comparison of preparations of selones using these methods has recently been reported[21].

$$(11)$$

$$[(C_6H_{11})_3Sn\text{--}\tfrac{1}{2}Se + BCl_3 \longrightarrow [B_2Se_3] \longrightarrow$$

$$(12)$$

2. Reactions

All selones so far prepared are deep blue compounds. They are thermally stable up to 150 °C in an inert atmosphere and do not react in visible light provided that oxygen is excluded. Selones are easily reduced with sodium borohydride, sodium amalgam or sodium to air-sensitive selenols (12) (equation 13)[52]. Reaction of a selone with tris(dimethylamino)phosphine, tri-n-butyl phosphine or sodium potassium alloy leads to reduction to the alkane (equation 14)[52]. Selenium extrusion occurs on reaction with pentacarbonyliron.

$$(13)$$

$$(14)$$
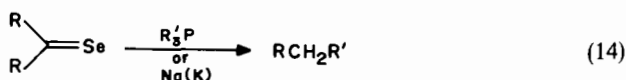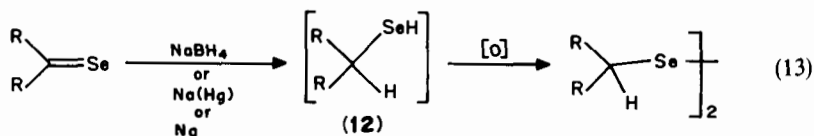
Oxidation of a selone with peracids leads to the corresponding ketone, presumably via a selenine intermediate (13) (equation 15). When a selone is heated with excess of sulfur, exchange of sulfur and selenium takes place, affording the corresponding thione[59]. This method provides a convenient route to S-labelled thiones (14), and can also be carried out on selone esters and selenoamides (equation 16).

$$\underset{R}{\overset{R}{>}}\!\!=\!\text{Se} \ + \ m\text{-ClC}_6\text{H}_4\text{CO}_3\text{H} \ \longrightarrow \ \left[\underset{R}{\overset{R}{>}}\!\!=\!\text{Se}\overset{\nearrow\text{O}}{} \right] \ \xrightarrow{-\text{Se}} \ \underset{R}{\overset{R}{>}}\!\!=\!\text{O}$$

$$\text{(13)}$$

$$(15)$$

$$\underset{R}{\overset{R}{>}}\!\!=\!\text{Se} \ + \ \text{S}^* \ \longrightarrow \ \underset{R}{\overset{R}{>}}\!\!=\!\text{S}^* \ + \ \text{Se} \qquad (16)$$

$$\text{(14)}$$
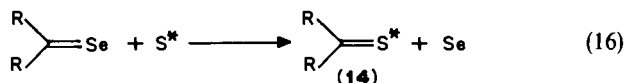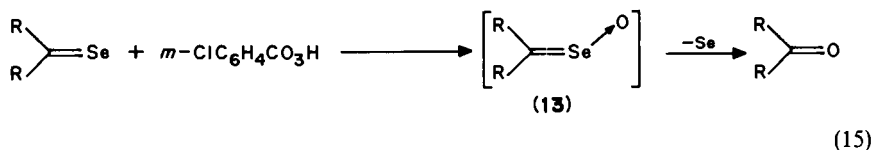
Selones are less basic than thiones. Under conditions where thiones are protonated in superacid media, selones lead only to polymeric materials[60].

Selones react with sterically hindered diazo compounds in a two-fold extrusion reaction to afford extremely sterically hindered olefins. The cycloaddition of a selone with a diazo compound is much more facile than the corresponding reaction of a thione (equation 17)[52].

$$\underset{\bigtimes}{\overset{\bigtimes}{>}}\!\!=\!\text{Se} \ + \ \underset{\bigtimes}{\overset{\bigtimes}{>}}\!\!=\!\text{S} \ + \ \text{Ph}_2\text{CN}_2 \longrightarrow \ \underset{\text{Ph}}{\overset{\text{Ph}}{>}}\!\!\overset{/\text{N=N}\diagdown\bigtimes}{\underset{\diagdown\text{Se}\diagup}{}} \qquad (17)$$

1 equiv.   1 equiv.   1 equiv.   only product observed
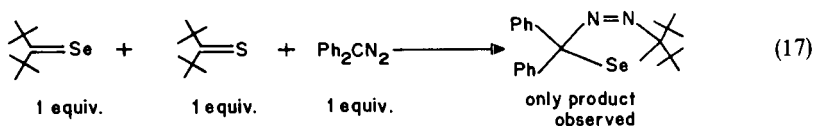
The intermediate heterocyclic selenadiazoline **15** thermally extrudes nitrogen, affording a thermally unstable episelenide, which then extrudes selenium to give the olefin (equation 18)[52].

$$\underset{R}{\overset{R}{>}}\!\!=\!\text{Se} \ + \ \underset{R'}{\overset{R'}{>}}\!\!=\!\text{N}_2 \ \longrightarrow \ \underset{R}{\overset{R}{>}}\!\!\overset{\text{N=N}}{\underset{\text{Se}}{}}\!\!\underset{R'}{\overset{R'}{<}}$$

$$R = t\text{-Bu}, \ R' = \text{Ph}$$

$$\text{(15)}$$

$$\Delta \downarrow -\text{N}_2$$

$$\underset{R}{\overset{R}{>}}\!=\!\underset{R'}{\overset{R'}{<}} \ = \quad , \quad , \quad \left[\underset{R}{\overset{R}{>}}\!\!\overset{R'}{\underset{\text{Se}}{}}\!\!\overset{R'}{} \right]$$

$$\downarrow -\text{Se}$$

$$\underset{R}{\overset{R}{>}}\!=\!\underset{R'}{\overset{R'}{<}} \ = \ \underset{R'}{\overset{R'}{>}}\!=\!\underset{R'}{\overset{R'}{<}} \quad , \quad , \quad \underset{R}{\overset{R}{>}}\!=\!\underset{R'}{\overset{R'}{<}}$$

$$(18)$$
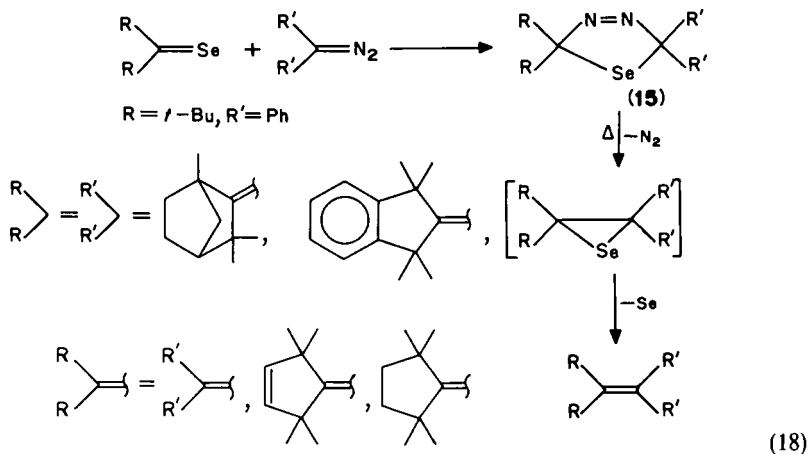
Although a variety of sterically hindered olefins have been prepared using this method, in some extreme cases retrocyclization of the selenadiazoline can compete with the desired extrusion, affording complex mixtures of products (equation 19). Olefin-forming two-fold extrusion reactions using selone.intermediates have been recently summarized[21].

Photolysis of the isolated selenadiazoline intermediates affords symmetrical and unsymmetrical sterically hindered azines **16** (equation 20)[61].

$$(19)$$

$$(20)$$

(16)
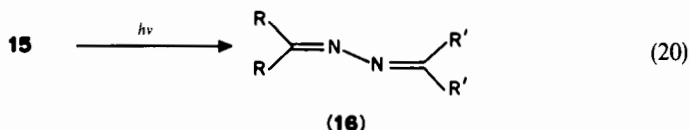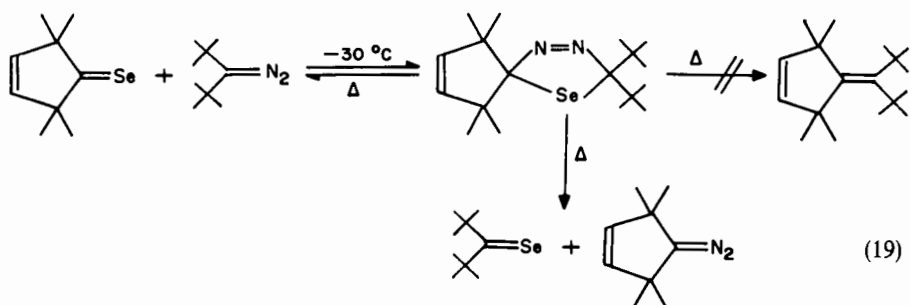
Treatment of selones with azides affords, on pyrolysis, sterically hindered imines (17), presumably through a two-fold extrusion pathway (equation 21)[62]. Although thiones also undergo this transformation, selones are more reactive and afford cleaner products.

$$(21)$$

(17)
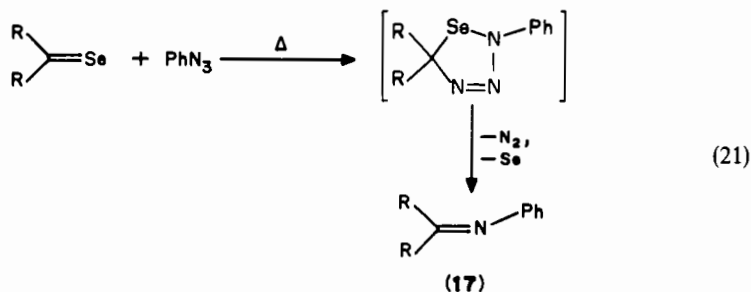
Selones react with organometallic reagents to give addition products (18) from nucleophilic attack at the selenium center—selenophilic addition (equation 22)[63-65]. In most cases with selones no attack at carbon is observed, whereas the corresponding thiones give mixtures of thiophilic and carbophilic addition products. This is consistent with greater α-stabilization of both anions and radicals by selenium than in the corresponding sulfur cases.

$$(22)$$

(18)

$$(23)$$

(19)

$$M = C, Se, O, Si, S, Sn, Ge$$
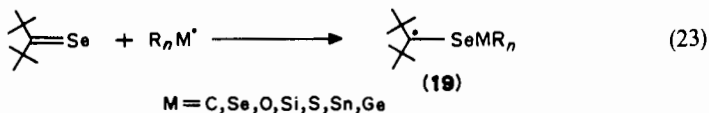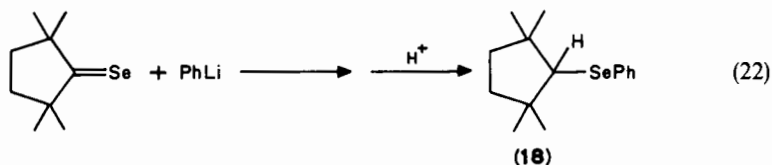
Selones react with a variety of radical species to afford persistent selenoalkyl radicals (19) (equation 23)[66-68]. Low spin density was observed on selenium in these radicals. In these reactions selones are better radical traps than the corresponding thiones[69].

The detailed photochemistry of di-*tert*-butyl selone and selenofenchone has been investigated and compared with that of the corresponding thiones[70,71]. Irradiation of di-*tert*-butyl selone in a variety of solvents leads to the diselenide (equation 24). An intermediate radical (20) has been detected on low-temperature irradiation. This radical was also subsequently detected in the low-temperature radical-induced reaction of this selone (equation 25)[67].

$$ (24) $$

$$ (25) $$
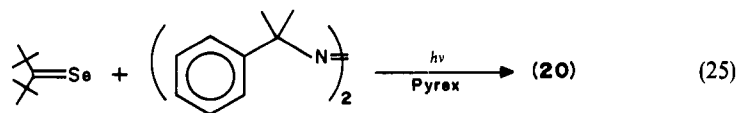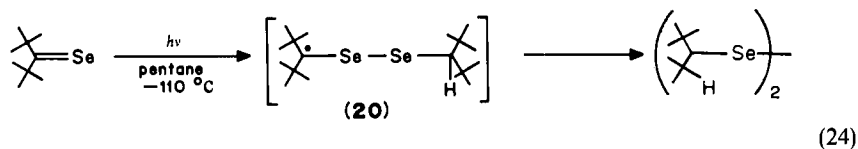
Irradiation of selenofenchone leads to a mixture of diselenides, including some resulting from intermolecular hydrogen transfer (equation 26). No such reaction was noted on irradiation of thiofenchone. No cycloadducts were noted when irradiations of sterically hindered selones were carried out in the presence of olefins.

$$ (26) $$
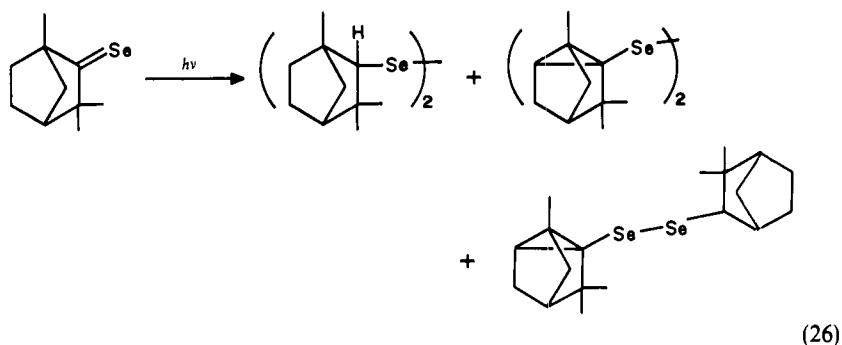
C. Telluroketones

Apart from the previously described early report[43], no well characterized telluroketone has appeared in the literature. No telluroketone is formed on pyrolysis of a phosphoranylidine hydrazone in the presence of tellurium[72].

D. Selenoaldehydes—Preparation and Detection

No monomeric selenoaldehydes unstabilized by metal complexation or resonance interactions had been isolated and characterized up to 1985.

Apart from the previously mentioned attempts at the acid-catalysed preparations of

selenoformaldehyde (Section II.A), reactions of methylene with selenium mirrors afforded a volatile product presumed to be selenoformaldehyde which polymerized on cooling[73,74]. It was subsequently shown that methylene generated by diazomethane thermolysis reacted with a selenium mirror to give, on cooling, the trimeric 'selenoformaldehyde' (equation 27)[75].

$$CH_2 + Se \longrightarrow [SeCH_2] \longrightarrow \qquad\qquad (27)$$

Monomeric selenoaldehydes have been postulated as intermediates in the amine-catalysed hydrogen selenide reductions of aldehydes to diselenides (equation 28)[76-80]. It should be noted that no diselenides are formed in this reaction in the absence of amines.

$$RCHO + HNR_2' \; \underset{}{\overset{H^+}{\rightleftharpoons}} \; \left[\begin{matrix} R \\ H \end{matrix}\!\!>\!\!C=\overset{+}{N}R_2' \right] \; \overset{HSe^-}{\rightleftharpoons} \; \left[\begin{matrix} Se \\ \| \\ RCH \end{matrix} \right]$$

$$\Big\downarrow HSe^-$$

$$(RCH_2-Se)_{\frac{1}{2}} \qquad\qquad (28)$$
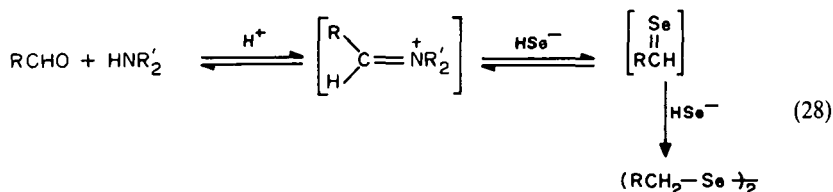
Monomeric selenoformaldehyde has been generated by flash pyrolysis of dimethylselenide at 700 °C (equation 29). Its spectrum in the near-infrared region has been recorded and compared with that of monomeric thioformaldehyde and formaldehyde[79].

$$Me_2Se \xrightarrow{700\,°C} [H_2C=Se] + CH_4 \qquad\qquad (29)$$

The photoelectron spectrum of monomeric selenoformaldehyde has been recorded by application of 'computer spectra stripping' to the spectra of pyrolysis mixtures derived from dimethyl diselenide, methyl selenocyanate, methyl selenyl chloride and trimeric selenoformaldehyde[80]. The resulting spectra compared favourably with that calculated for monomeric selenoformaldehyde. The photoelectron spectra for monomeric selenoacetaldehyde and selenocarbonyl difluoride were also observed in a similar manner.

Irradiation of propadieneselone (21) (Section VI.A) isolated in an argon matrix at 12 K affords propyneselenal (22), which was observed by low-temperature infrared difference spectrometry (equation 30)[81].

$$\xrightarrow{700\,°C} \quad CH_2{=}C{=}C{=}Se \quad \xrightarrow[{[1,3]-shift}]{hv} \quad HC{\equiv}C{-}\overset{Se}{\overset{\|}{C}}\diagdown_H$$

(21)   (22)

(matrix isolation,   (matrix isolation,
12 K)   12 K)

$$(30)$$
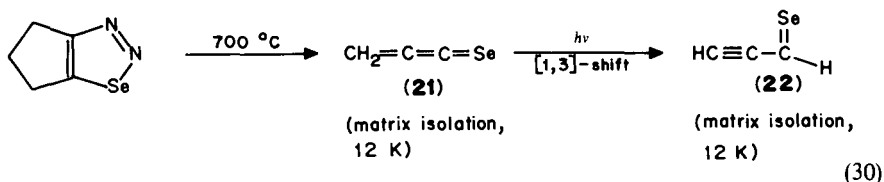
Metal-stabilized selenoformaldehyde and selenobenzaldehyde are discussed later (Section XII).

(See Note, p. 273).

E. Telluroaldehydes—Preparation and Reactions

The reaction of a tellurium mirror with methylene generated by thermal decomposition of diazomethane or methane, or by photolysis of ketene, was claimed to afford telluroformaldehyde as a monomeric gas[73,74]. This material trimerized to tritellurofor-

$$CH_2 + Te \longrightarrow \left[CH_2Te \right] \longrightarrow \text{(ring structure)} \tag{31}$$

(23)
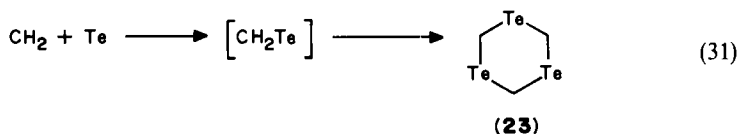
maldehyde **(23)** (equation 31)[75]. Gaseous telluroformaldehyde (or the trimer) reacted with bromine and iodine to afford the corresponding dihalomethanes[74].

III. Se/Te ESTERS

A. Selenoesters

1. Preparation

Selenoesters may be conveniently prepared by the reactions of N,N-dialkyliminium esters with sodium hydrogen selenide[38] or by the reactions of imidate esters with hydrogen selenide[82,83]. The first procedure is probably the most convenient[38]. The iminium esters can be easily prepared by the reaction of a dialkylamide with phosgene. The chloroiminium salt **24** is then treated with an alcohol, and the resulting iminium ester **25** treated with ethanolic sodium hydrogen selenide to afford the selenoester **26** (equation 32). A great variety of O-alkyl and O-aryl selenoesters were obtained in good yields using this procedure. One limitation of this route was noted; in the case of the hindered O-aryl iminium ester ($R = i$-Bu, $R'' = $ Ph) only selenoamide was obtained.

$$\underset{\underset{(24)}{}}{\overset{O}{\underset{\|}{RCNR_2'}}} \xrightarrow{COCl_2} \underset{(24)}{\overset{Cl}{\underset{\|}{RC}}} = \overset{+}{N}R_2' \quad Cl^- \tag{32}$$

$R = H, alkyl, aryl$

$R' = alkyl$ $R''OH$ $R'' = alkyl, Ph$

$$\underset{(26)}{\overset{Se}{\underset{\|}{R}} \overset{C}{\diagdown} OR''} \xleftarrow[EtOH]{NaHSe} \underset{(25)}{\overset{OR''}{\underset{\|}{RC}} = \overset{+}{N}R_2' Cl^-} $$
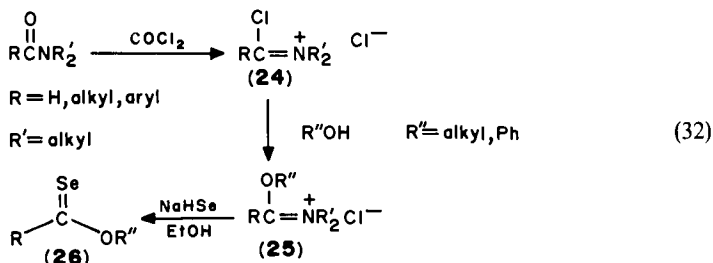
A second route starts with the conversion of a nitrile to the imidate ester **27**, followed by reaction with hydrogen selenide (equation 33). This method is limited to selenoesters of low molecular weight alcohols, and uses a large excess of gaseous hydrogen selenide[82,83].

$$RC{\equiv}N \xrightarrow[(2)NH_3, -15\ ^{\circ}C]{(1)EtOH, HCl} \underset{(27)}{\overset{N^{\diagup H}}{\underset{\|}{RCOEt}}} \xrightarrow{H_2Se} \overset{Se}{\underset{\|}{RCOEt}} \tag{33}$$

$R = alkyl, aryl$
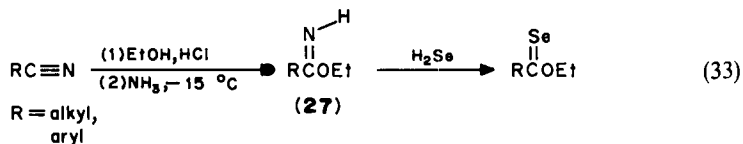
Selenoesters unsubstituted at the 2-position can be prepared by reaction of a selenoketene intermediate **(29)** with an alcohol (equation 34). The selenoketene (Section VI.A) can be prepared by pyrolysis or base-catalysed fragmentation of 4-substituted-1, 2, 3-selenadiazolines **(28)**[84].

Selenoesters can also be prepared in low yield by the reaction of pentacarbonyl-chromium(0) arylalkoxycarbenes **(30)** with selenium (equation 35)[85].

Selenocarbonyl phthalides and derivatives **(31)** can be prepared from the corresponding

imidates (equation 36)[86,87]. Whereas the selone lactone **31a** and the thiol selone lactone **31b** were stable, the diselenolactone **31c** could not be isolated or characterized*.

(34)

(35)

(36)
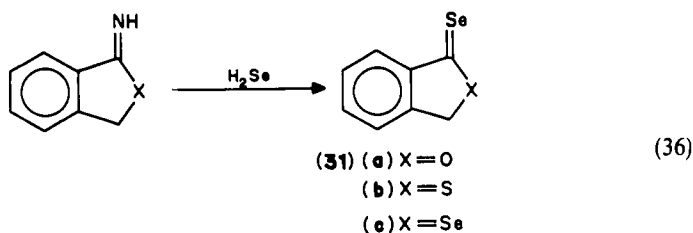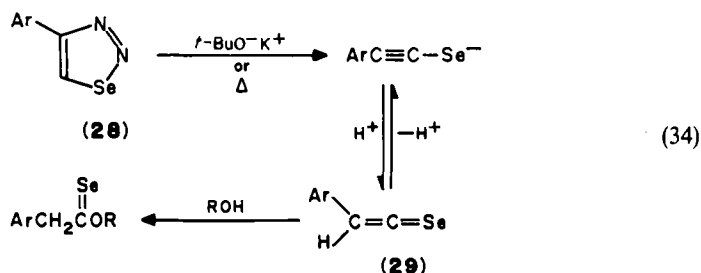
The related diselenoesters (**32**) and selonethiol esters (**33**) can be prepared from tertiary seleno- and thio-amides by alkylation followed by treatment with hydrogen selenide (equations 37 and 38)[88]. Again, the mono-sulfur compounds are more stable than their diselenium analogs.

(37)

(38)

---
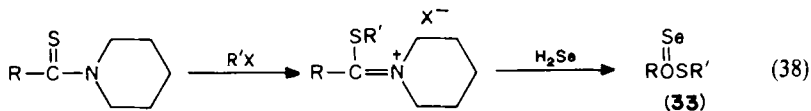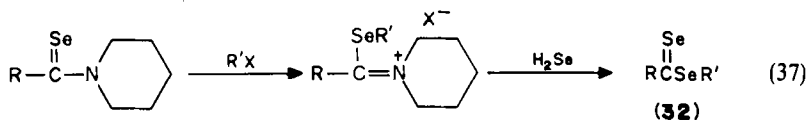
*To avoid ambiguity, in accordance with the proposal on p. 253, these and related selenocarbonyl compounds (Section X.A) are designated as selone derivatives. This nomenclature has not been adopted by IUPAC.

A diselenoformate intermediate (35) generated by reduction of a triselenocarbonate (34) is reported to be unstable, oligomerizing on formation (equation 39)[89].

$$
\begin{array}{c}
\overset{\text{Se}}{\underset{\text{RSeCSeR}}{\|}} \\
\textbf{(34)}
\end{array}
\quad\xrightarrow{\text{RSe}^-\ \text{R}_3^+\text{NH}}\quad
\left[\begin{array}{c}
\overset{\text{Se}}{\underset{\text{RSeCH}}{\|}}
\end{array}\right]
\quad\textbf{(35)}
$$

$$\downarrow$$

$$
\frac{1}{n}\left(\overset{\text{H}}{\underset{\text{SeR}}{\overset{|}{\underset{|}{-\text{C}-\text{Se}-}}}}\right)_n
$$

(39)
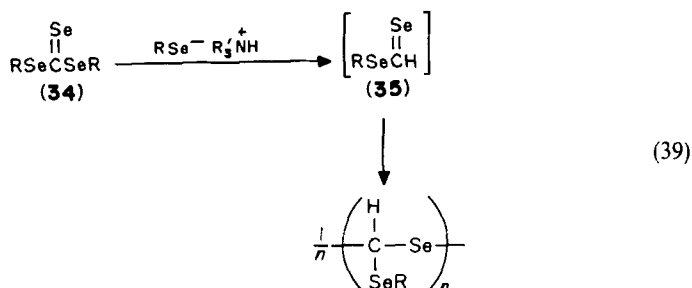
2. Reactions

The reactions of selenoesters have been extensively studied by Barton and coworkers. Selenoesters can be reduced by Raney nickel to the corresponding ethers (equation 40)[90]. The method appears to be useful for the selective formation of ethers in steroids and aminoglycosides.

$$
\overset{\text{Se}}{\underset{\text{PhCOR}}{\|}}\quad\xrightarrow{\text{Raney Ni}}\quad\text{PhCH}_2\text{OR}
$$

(40)
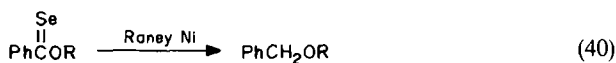
Sodium borohydride reduction of selenoesters under an inert atmosphere led to a remarkably stable tetrahedral intermediate (36), which oxidatively dimerized on workup (equation 41). Treatment of 36 with methyl iodide afforded the alkoxymethyl alkylselenide 37. Treatment of the selone ester with borohydride followed by triethylphosphine addition led to formation of the corresponding ethyl ether (equation 42)[90].

$$
\overset{\text{Se}}{\underset{\text{RCOR'}}{\|}}\quad\xrightarrow{\text{NaBH}_4}\quad
\left[\begin{array}{c}
\overset{\text{Se}^-}{\underset{\text{H}}{\overset{|}{\underset{|}{\text{R}-\text{C}-\text{OR'}}}}}
\end{array}\right]
\quad\textbf{(36)}
$$

R = Ph, H, Me
R' = alkyl

$$
\xrightarrow{\text{O}_2}\quad (\overset{\text{OR'}}{\underset{\text{H}}{\overset{|}{\underset{|}{\text{RC}-\text{Se}}}}}\xrightarrow{\ })_{\!2}
$$

$$
\xrightarrow{\text{MeI}}\quad \overset{\text{OR'}}{\underset{\text{H}}{\overset{|}{\underset{|}{\text{RC}-\text{SeMe}}}}}\quad\textbf{(37)}
$$

(41)

$$
\overset{\text{Se}}{\underset{\text{MeCOR}}{\|}}\quad\xrightarrow{\text{NaBH}_4}\quad\xrightarrow{\text{Et}_3\text{P}}\quad\text{EtOR}
$$

(42)

R = Cholesteryl
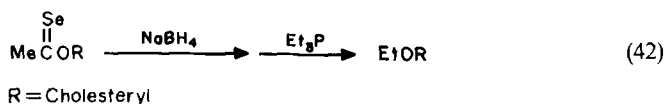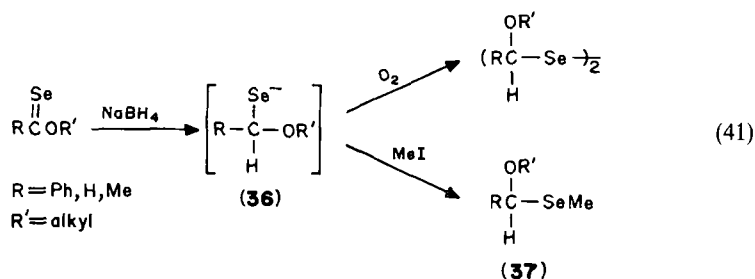
The latter reaction failed in the case of the selenoformate and the selenobenzoate, presumably because of a rapid reaction of these compounds directly with triethylphosphine. Treatment of a selenobenzoate with a trialkylphosphine affords an interesting moderately stable compound (38), which can undergo a variety of reactions, presumably via ylid and carbene intermediates (equation 43)[91].

$$(43)$$
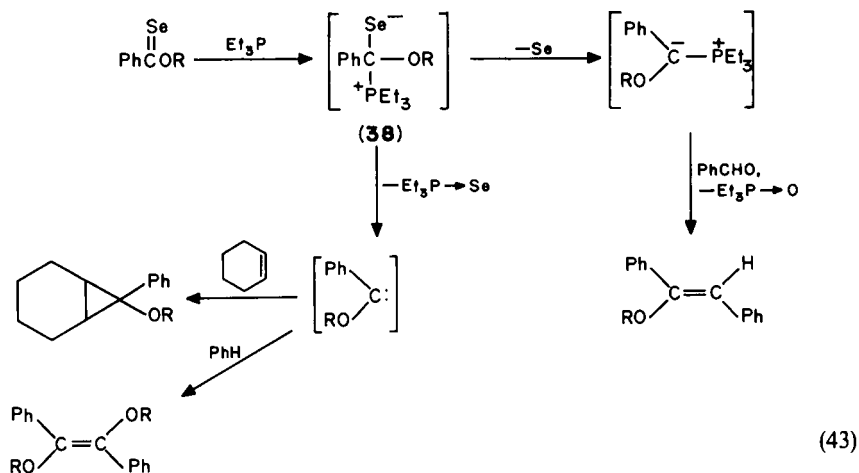
Although selenobenzoates can be used as substrates in the tributylstannane-mediated deoxygenation procedure developed by Barton and McCombie (equation 44), xanthates and thione benzoates appear to be more useful intermediates in this reaction[38].

$$(44)$$

R = Cholesteryl
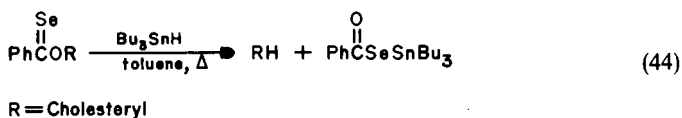
Treatment of selenobenzoates with methylenetriphenylphosphorane affords enol ethers (equation 45)[90].

$$(45)$$

R = alkyl, aryl
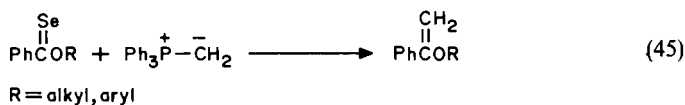
Treatment of an enolizable selenoester with potassium bis(trimethylsilyl)amide affords the intermediate selenolate which can be alkylated affording the ketone monoselenoacetal **39** (equation 46)[90]. When O-cholesteryl selenoacetate was treated with the same hindered base, the alkoxyselenocrotonate **40** was obtained, presumably owing to more favorable explusion of selenium relative to alkoxide (equation 47)[90]. Normal Claisen products are typically obtained from O-alkyl thione esters.

$$(46)$$
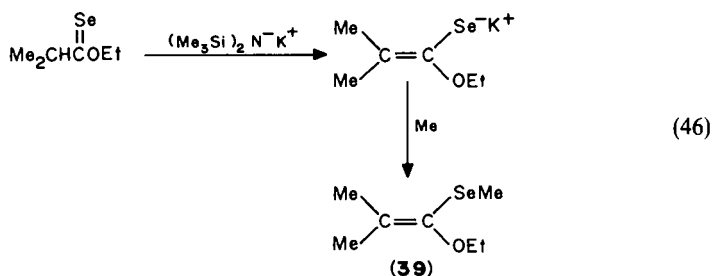
Selenoesters can be used as reagents in the preparation of selenoamides[83]. They also can be converted into thione esters by a thermal reaction with sulfur (equation 48)[59]. The uses of selenoesters in heterocyclic synthesis have also been reported[83].

$$2 \overset{\overset{\text{Se}}{\|}}{\text{MeC}} \text{OR} \xrightarrow{(\text{Me}_3\text{Si})_2 \text{N}^- \text{K}^+} \underset{\underset{\text{OR}}{|}}{\overset{\overset{\text{Se}^-\text{K}^+}{|}}{\text{MeC}}} - \text{CH}_2 \overset{\overset{\text{Se}}{\|}}{\text{C}} \text{OR} \xrightarrow{-\text{KHSe}} \qquad (47)$$

R = cholesterly

(40)

$$\overset{\overset{\text{Se}}{\|}}{\text{PhCOEt}} \xrightarrow[\Delta]{\text{S}} \overset{\overset{\text{S}}{\|}}{\text{PhCOEt}} + \text{Se} \qquad (48)$$
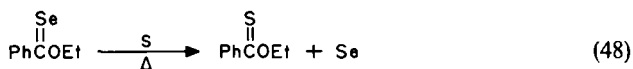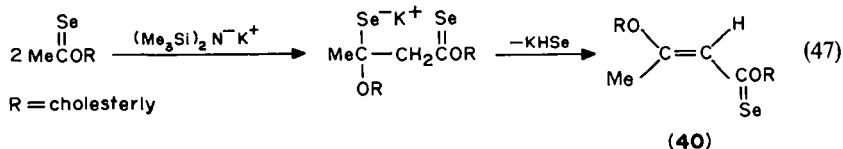
B. Telluroesters—Preparation and Reactions

When the phenyl dimethyliminium salt of cholesterol was treated with excess sodium hydrogen telluride at $-20\,°\text{C}$ under conditions analogous to those used to prepare the selenoester, reduction occurred affording the benzyl ether in good yield[38]. The authors suggested that this reaction proceeded through a tellurobenzoate intermediate (41), which was further reduced by hydrogen telluride to the ether and tellurium (equation 49). The method could be used for the preparation of ether derivatives of complex aminoglycosides[92].

$$\underset{\text{R = cholesteryl}}{\overset{\overset{\overset{+}{\text{NMe}_2} \text{Cl}^-}{\|}}{\text{ROCPh}}} + \text{NaHTe} \xrightarrow{-20\ °\text{C}} \text{ROCH}_2\text{Ph} + \text{Te} \qquad (49)$$

$$\left[\overset{\overset{\text{Te}}{\|}}{\text{ROCPh}} \right]$$

(41)
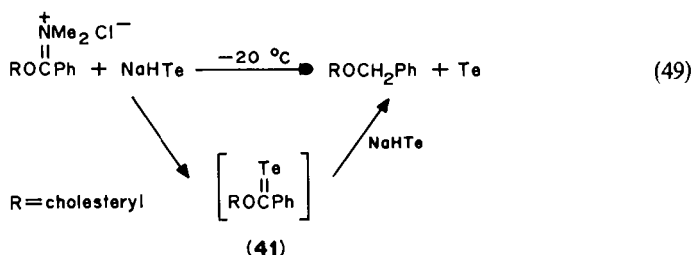
When the analogous reaction was carried out on the unsubstituted iminium compound, a presumed unstable telluroformate and N,N-dimethyltelluroformamide were observed, via partitioning of the tetrahedral intermediate[38].

The use of the more hindered pivaloyl derivative 42 in these reactions led to the first stable characterizable telluroesters (43) (equation 50)[16,93].

$$\text{ROH} + t\text{-Bu}\overset{\overset{\overset{+}{\text{NMe}_2}\text{Cl}^-}{\|}}{\text{CCl}} \xrightarrow{0\ °\text{C}} \underset{(42)}{} \xrightarrow[-78\ °\text{C}]{\text{NaHTe}} t\text{-Bu}\overset{\overset{\text{Te}}{\|}}{\text{COR}}$$

(42)   (43)

R=cholesteryl, t-BuCH$_2$—,

(50)

When pure, the telluroesters were stable to air in the dark or on irradiation (> 500 nm) when oxygen was excluded. Oxidation of the telluroester with diphenylseleninic anhydride afforded the pivalate in excellent yield (equation 51)[93].

$$\textbf{43} + (PhSe)_2O \longrightarrow t\text{-}BuCOR \tag{51}$$

Reduction of the telluroester with buffered sodium hydrogen telluride afforded a mixture of the neopentyl ether **46** and the pinacol ether product **47**. The radicals **44** and **45** have been suggested as intermediates in these hydrogen telluride reductions (equation 52)[93].

$$(52)$$

IV. Se/Te AMIDES

A. Selenoamides

1. Preparation

Primary selenoamides (**48**) can be most conveniently prepared from nitriles. While the earliest procedures involved direct addition of gaseous hydrogen selenide to nitriles (equation 53)[94,95], two more convenient procedures involve *in situ* formation of hydrogen selenide or its salts. The first utilizes aluminum selenide in a mixture of aqueous pyridine and triethylamine, affording a variety of aromatic and heterocyclic aromatic primary selenoamides in good yields (equation 54)[96].

$$ArC \equiv N \xrightarrow{H_2Se} Ar\overset{\overset{\displaystyle Se}{\|}}{C}NH_2 \tag{53}$$
$$\textbf{(48)}$$

$$ArC \equiv N \xrightarrow[H_2O,\ Et_3N]{Al_2Se_3,\ pyridine,} \textbf{48} \tag{54}$$

A recently described procedure utilizes the reducing ability of carbon monoxide to generate hydrogen selenide[97]. Reaction of nitriles with a mixture of selenium, water and triethylamine under 5 atm of carbon monoxide led to formation of both aliphatic and

aromatic selenoamides (equation 55). The aromatic compounds were generally obtained in good yield, with sterically hindered compounds giving lower yields. The aliphatic derivatives were obtained in approximately 35% yield, presumably owing to a decreased stability of these compounds relative to their aromatic analogues.

$$RC{\equiv}N + CO + Se + H_2O \xrightarrow[\text{Et}_3\text{N}]{100\ °C} R\overset{\overset{\displaystyle Se}{\|}}{C}NH_2 \tag{55}$$

R = alkyl or aryl
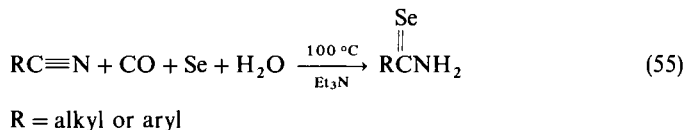
Secondary and tertiary selenoamides can generally be prepared in moderate to good yield by aminolysis of the corresponding selenoesters[77]. While secondary amines react slowly with selenoesters to form tertiary selenoamides without difficulty, the magnesium halide salts of primary amines must be used to avoid imido ester formation (equations 56 and 57). These products were observed when primary amines were used directly in these aminolysis reactions.

$$R\overset{\overset{\displaystyle Se}{\|}}{C}OEt + \underset{R''}{\overset{R'}{{\diagdown}}}NH \longrightarrow R\overset{\overset{\displaystyle Se}{\|}}{C}N\underset{R''}{\overset{R'}{{\diagup}}} \tag{56}$$

$$R\overset{\overset{\displaystyle Se}{\|}}{C}OEt + R''NHMgBr \longrightarrow R\overset{\overset{\displaystyle Se}{\|}}{C}NHR'' \tag{57}$$

R, R′ = alkyl
R″ = alkyl, aryl
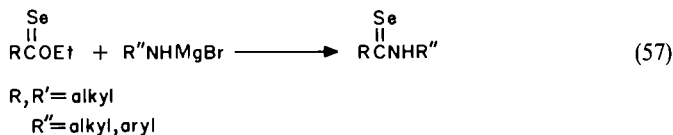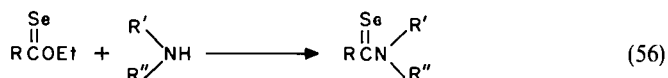
Secondary and tertiary selenoamides unsubstituted at the α-position can be prepared via acetylenic selenol–selenoketene intermediates (49 and 50) analogous to procedures used for the preparation of selenoesters (equations 58 and 59)[98,99] (cf. Section III.A.1).

R = aryl, alkyl, H

R′, R″ = alkyl, H

$$(58)$$
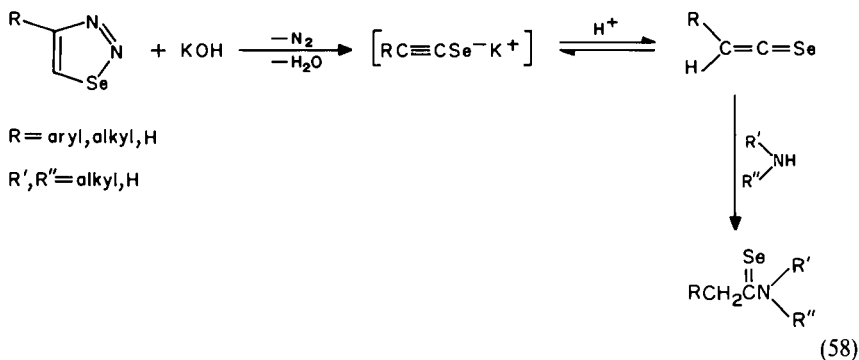
A number of heterocyclic selenoformamides (51) have been prepared from the corresponding aminoheterocycles by treatment with dimethylformamide acetals followed by hydrogen selenide treatment (equation 60)[100]. Heterocyclic vinylogous selenoformamides (52) have been prepared by Vilsmeier–Haack formylation and treatment with hydrogen selenide (equation 61)[101].

$$RC\equiv CLi \xrightarrow{\ Se\ } RC\equiv CSeLi \xrightarrow{\ H^+\ } \underset{(49)}{RC\equiv CSeH} \rightleftharpoons \underset{(50)}{\overset{R}{\underset{H}{>}}C=C=Se} \tag{59}$$

$$\downarrow R'NH_2$$

$$\underset{RCH_2\overset{\overset{Se}{\parallel}}{C}NHR'}{}$$

$$ArNH_2 + Me_2NCH(OR)_2 \longrightarrow ArN=CHNMe_2 \tag{60}$$

$$\downarrow H_2Se$$

$$\underset{(51)}{ArNH\overset{\overset{Se}{\parallel}}{C}H}$$

$$R=alkyl$$
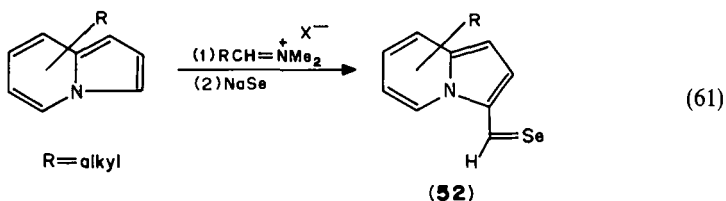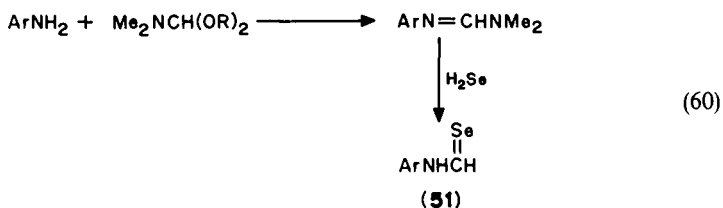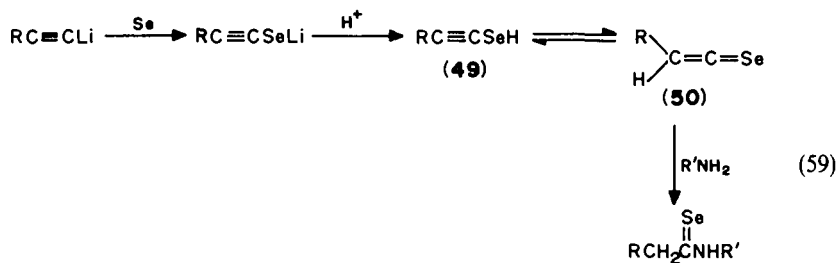
Another interesting procedure for the preparation of selenoformamides utilizes dibenzyltriselenocarbonate (53) as a starting material[89]. Treatment of the triselenocarbonate with benzyl selenol in the presence of triethylamine affords an oligomeric form of benzyl diselenoformamide, which on treatment with secondary or hindered primary amines affords the selenoformamides (equation 62). The less reactive aromatic amines or sterically hindered amines lead to lowered yields of products.

$$\underset{(53)}{(PhCH_2Se)_2\overset{\overset{Se}{\parallel}}{C}} + PhCH_2SeH \xrightarrow{\ Et_3N\ } \frac{1}{n}(PhCH_2SeCHSe)_n \tag{62}$$

$$R = aryl, alkyl, H$$

$$\downarrow \overset{R}{\underset{R'}{>}}NH$$

$$\overset{R}{\underset{R'}{>}}N\overset{\overset{Se}{\parallel}}{C}H + \frac{1}{2}(PhCH_2Se)_2$$
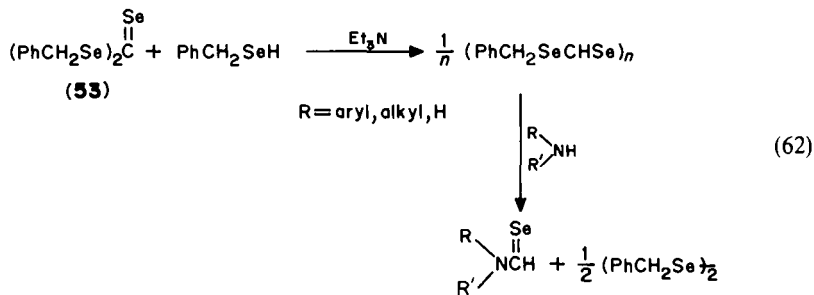
The reactions of chlorimidates (54)[102], S-alkylated thioamides (55)[103] and iminium salts (56)[104] with sodium hydrogen selenide have also been used to prepare selenoamides and vinylogous selenoamides (equations 63–65).

$$
\underset{\textbf{(54)}}{\overset{\overset{\text{Cl}}{|}}{\text{Ph}\overset{}{\text{C}}=\text{NPh}}} \quad\xrightarrow{\ \text{HSe}^-\ }\quad \underset{}{\overset{\overset{\text{Se}}{\|}}{\text{Ph}\text{C}\text{NHPh}}} \tag{63}
$$

$$
\underset{\underset{\textbf{(55)}}{\overset{}{}}}{\overset{\overset{\text{SMe}}{|}}{\underset{\overset{}{\text{X}^-}}{\text{R}\overset{+}{\text{C}}=\text{NR}_2'}}} \quad\xrightarrow{\ \text{HSe}^-\ }\quad \overset{\overset{\text{Se}}{\|}}{\text{R}\text{C}\text{NR}_2'} \tag{64}
$$

$$
\tag{65}
$$
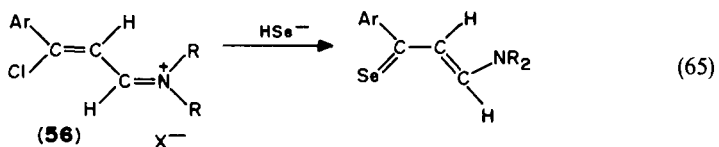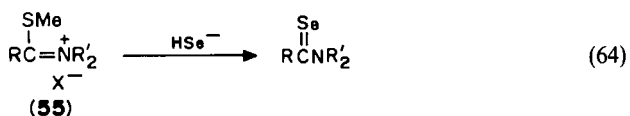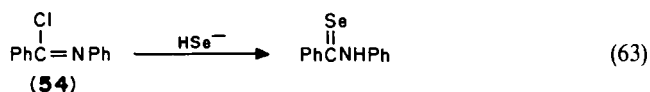
A number of *N*-substituted selenopyridinones (**58**) have been prepared by reaction of the potassium salt of glucondialdehyde (**57**) with isoselenocyanates (equation 66)[105].

$$
\tag{66}
$$
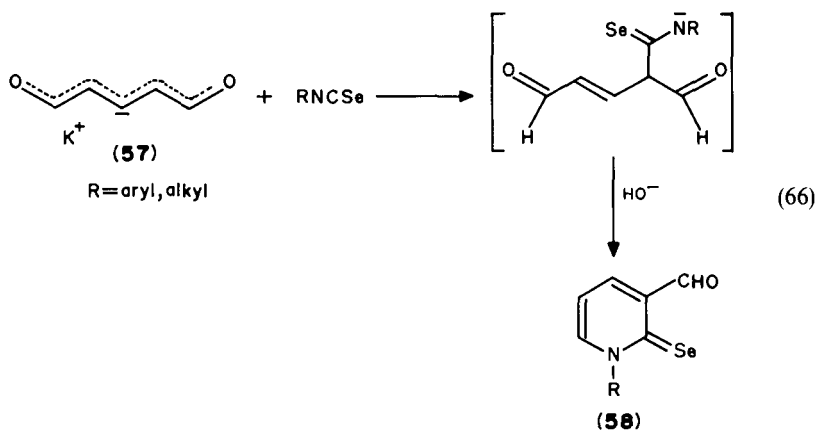
Dimethylselenoformamide has been prepared as a by-product in the synthesis of 1, 3, 4-selenadiazole from dimethylformamide azine (equation 67)[106].

$$
(\text{Me}_2\text{NCH}=\text{N}\tfrac{}{2} \xrightarrow{\ \text{H}_2\text{Se}\ } \underset{}{\overset{}{\text{[selenadiazole ring]}}} + \overset{\overset{\text{Se}}{\|}}{\text{Me}_2\text{NCH}} \tag{67}
$$
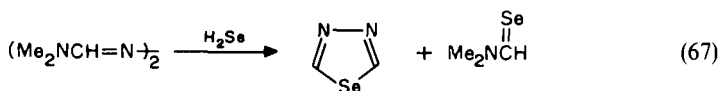
Selenoamides have also been prepared in low yields using phosphorus pentaselenide[107] or by halogen displacement using hydrogen selenide or hydroselenide ion (equation 68)[108].

$$
\tag{68}
$$
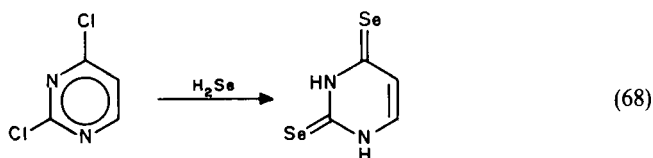
2. Reactions

Selenoamides are reported to be more stable than the corresponding selenoesters[77]. Primary selenoamides are less stable than secondary or tertiary selenoamides owing to slow loss of hydrogen selenide to afford nitriles (equation 69)[97]. The aromatic primary selenoamides are moderately stable at room temperature under nitrogen; in air they are slowly converted into nitriles, water and elemental selenium. Aliphatic primary selenoamides, however, are reported to be thermally unstable and highly sensitive to air[97].

$$
\underset{R=\text{aryl, alkyl}}{\overset{\overset{\displaystyle Se}{\overset{\displaystyle \|}{R\overset{}{C}NH_2}}}{}} \rightleftharpoons RC\equiv N \ + \ H_2Se \tag{69}
$$
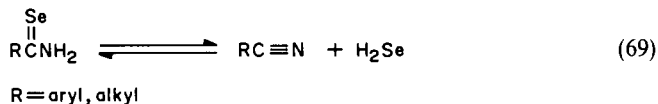
Hydrolysis of a selenoamide affords the corresponding carboxylic acid. (equation 70)[109]. Alkylation and acylation of selenoamides occurs in high yield at selenium[102,104,110-112], providing convenient approaches to selenium-containing heterocycles (**59–61**) (equations 71 and 72)[102,104,112], as do oxidations of selenoamides with iodine (e.g. **62** and **63**, equations 73 and 74)[95,113]. Reactions of selenoamides with hydrazine derivatives also afford interesting heterocyclic systems[83].

$$
\underset{\underset{Se}{\overset{\displaystyle NH_2}{\overset{|}{Me_2C-C-NH_2}}}}{} \xrightarrow{\ H_3O^+\ } \underset{\overset{+}{NH_3}}{Me_2\overset{|}{C}CO_2^-} \ + \ NH_4^+HSe^- \tag{70}
$$

(71)

(**59**)

(72)

(**60**)

(**61**)

$$
\underset{\text{PhCNH}_2}{\overset{\overset{\displaystyle Se}{\|}}{}} \xrightarrow{\text{I}_2} \quad \text{(62)} \tag{73}
$$

$$
\underset{\text{NH}_2\text{CCH}_2\text{CNH}_2}{\overset{\overset{\displaystyle Se \quad Se}{\| \quad \|}}{}} \xrightarrow{\text{I}_2} \quad \text{(63)} \tag{74}
$$
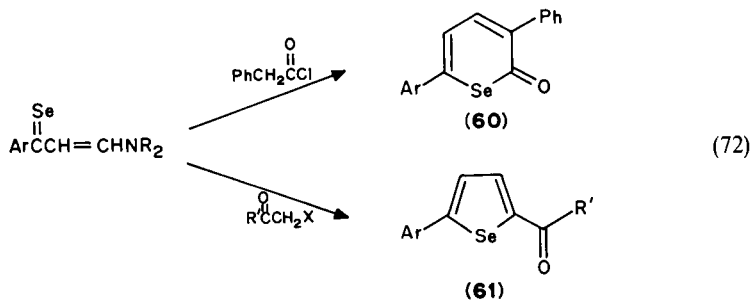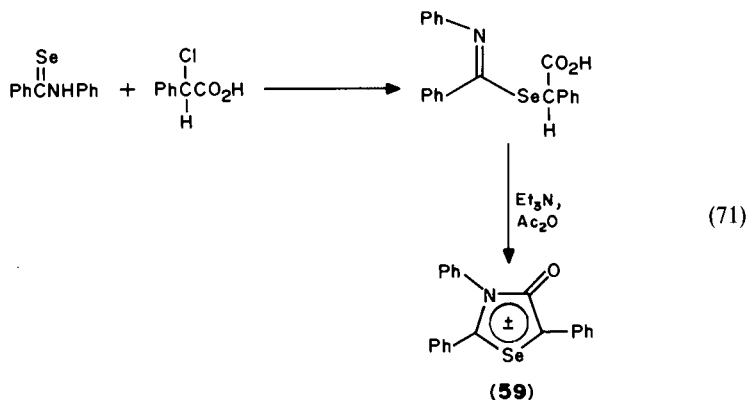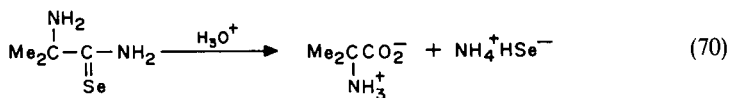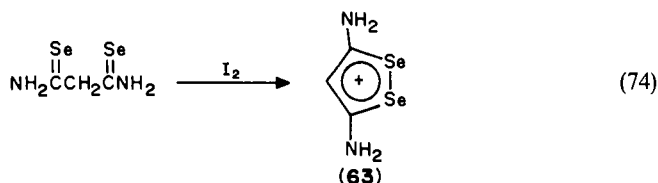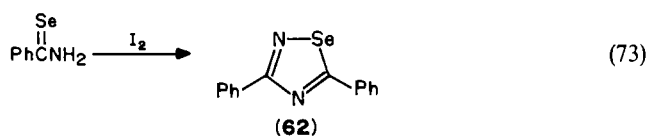
Tertiary selenoamides with α-hydrogens may be conveniently trimethylsilylated at selenium in good yield to afford **64** (equation 75)[114]. Tertiary selenoamides are also used in the preparation of diselenoesters (see Section III.A.1, equation 38)[88].

$$
\underset{\text{R}_2\text{CHCNEt}_2}{\overset{\overset{\displaystyle Se}{\|}}{}} \xrightarrow{\text{LIN}(i\text{-Pr})_2} \quad \text{R}_2\text{C}=\text{C}\underset{\text{NEt}_2}{\overset{\text{SeLi}}{}}
$$

$$
\downarrow \text{Me}_3\text{SiCl} \tag{75}
$$

$$
\text{R}_2\text{C}=\text{C}\underset{\text{NEt}_2}{\overset{\text{SeSiMe}_3}{}}
$$

$$
\text{(64)}
$$
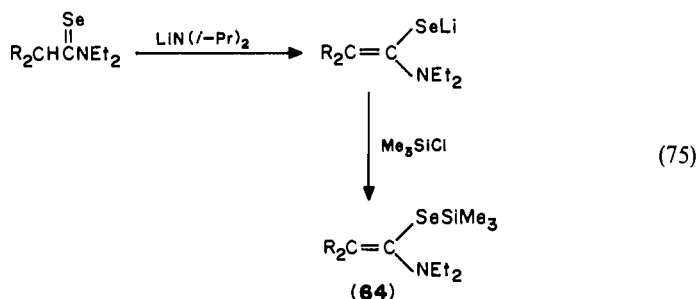
Selenoamides have recently been used as reagents in the stereospecific deoxygenation of epoxides[115]. This reaction is acid catalysed and proceeds with retention, presumably via the cyclic intermediate **65** (equation 76).

(65)

$$
\tag{76}
$$
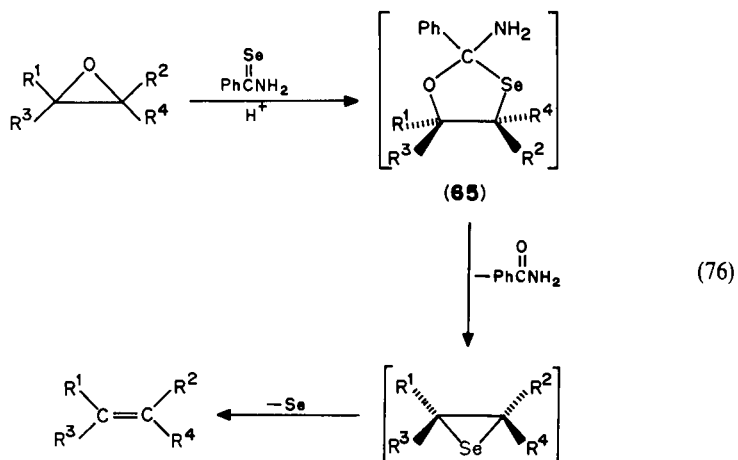
Like selones and selone esters, selenoamides react thermally with sulfur, affording the corresponding thiocarbonyl compounds (equation 77)[59].

$$\underset{\substack{\text{II}\\ \text{PhCNMe}_2}}{\overset{\text{Se}}{}} \xrightarrow[\Delta]{S} \underset{\substack{\text{II}\\ \text{PhCNMe}_2}}{\overset{\text{S}}{}} + \text{Se} \qquad (77)$$
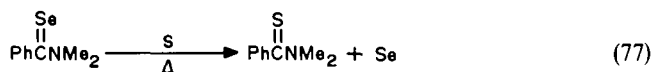
B. Telluroamides—Preparation and Reactions

A compound presumed to be the unstable dimethyltelluroformamide was observed in the attempted preparation of steroidal telluroformates, by treatment of the iminium salt with sodium hydrogen telluride[38]. Subsequently, dimethyltellurobenzamide (66) was prepared at $-40\,^{\circ}$C under argon by addition of hydrogen telluride to a solution of the iminium species and triethylamine in dichloromethane (equation 78)[116]. These conditions must be more rigorously controlled than those required for the preparation of selenoamides.

$$\underset{\substack{\text{II}\\ \text{PhCNMe}_2}}{\overset{\text{S}}{}} \xrightarrow{\text{MeI}} \underset{\substack{\text{II}\\ \text{PhCSMe}}}{\overset{\overset{+}{\text{NMe}_2}\; \text{I}^-}{}} \xrightarrow[\substack{\text{CH}_2\text{Cl}_2\\ <-40\,^{\circ}\text{C}}]{\text{H}_2\text{Te},\text{Et}_3\text{N}} \underset{\substack{\text{II}\\ \text{PhCNMe}_2}}{\overset{\text{Te}}{}} \qquad (78)$$
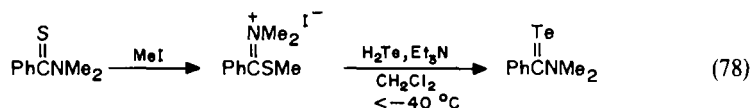
Dimethyltellurobenzamide was stable at room temperature in an inert atmosphere in the absence of moisture but began to decompose in refluxing toluene[116]. It was rapidly attacked by wet solvents or the atmosphere to give dimethylbenzamide and tellurium.

V. Se/Te CARBOXYLIC ACIDS AND SALTS

Relatively little is known about the chemistry of selenium analogs of carboxylic acids[88]. In contrast to thiocarboxylic acids, which can be prepared from acid chlorides and hydrogen sulfide or its salts, attempts to prepare selenocarboxylic acids using an analogous procedure led, in general, to diacyldiselenides. Early descriptions of the preparation and properties of selenobenzoic acid were in error[117,118], the product described being in fact dibenzoyl diselenide[119].

Jensen and coworkers[119] suggested that this product formed either by oxidative dimerization of the initially formed selenobenzoic acid (67), or that loss of hydrogen selenide from the initially formed selenocarboxylic acid occurred, generating dibenzoyl selenide (68) (Equation 79). This compound could further react with selenobenzoic acid via a redox reaction to afford the diselenide 69[119].

$$\underset{\substack{\text{II}\\ \text{PhCCl}}}{\overset{\text{O}}{}} + \text{H}_2\text{Se} \longrightarrow \underset{\substack{\text{II}\\ \text{PhCSeH}\\ \textbf{(67)}}}{\overset{\text{O}}{}} \xrightarrow{\text{O}_2} \underset{\substack{\text{II}\\ (\text{PhCSe})_{\frac{1}{2}}\\ \textbf{(69)}}}{\overset{\text{O}}{}}$$

$$\Big\downarrow -\text{H}_2\text{Se}$$

$$\underset{\substack{\text{II}\\ \text{PhCH(SeCPh)}_2}}{\overset{\text{O}\quad\;\; \text{O}}{}} + \underset{\substack{\text{II}\\ (\text{PhCSe})_{\frac{1}{2}}\\ \textbf{(69)}}}{\overset{\text{O}}{}} \xleftarrow[\text{PhCSeH}]{\overset{\substack{\text{O}\\ \text{II}}}{}} \underset{\substack{\text{II}\;\; \text{II}\\ \text{PhCSeCPh}\\ \textbf{(68)}}}{\overset{\text{O}\;\; \text{O}}{}} \qquad (79)$$
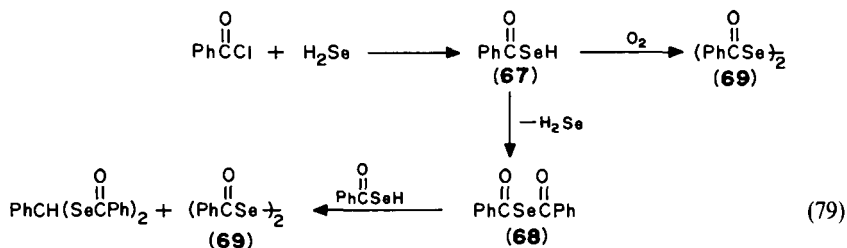
Careful control of the addition of hydrogen selenide to benzoyl chloride led to the formation of the unstable selenobenzoic acid 67[119]. This compound is readily soluble in aqueous sodium hydrogen carbonate without liberation of elemental selenium, and can

be precipitated by addition of sulfuric acid (equation 80). As expected, in the presence of air, dibenzoyl diselenide was formed from the selenoacid. The selenoacid rapidly lost hydrogen selenide with formation of dibenzoyl selenide. The selenoacid reacted with *m*-nitrobenzaldehyde to give the acylselenoacetal **70**. Sodium selenobenzoate could be alkylated to the *Se*-alkyl ester **71**[119].

$$
\underset{\substack{\text{O} \\ \|\\ \text{PhCSeH}}}{} \quad \underset{\text{H}_2\text{SO}_4}{\overset{\text{NaHCO}_3}{\rightleftharpoons}} \quad \underset{\substack{\text{O} \\ \|\\ \text{PhCSe}^-\text{Na}^+}}{}
$$

$$\downarrow m\text{-NO}_2\text{C}_6\text{H}_4\text{CHO} \qquad\qquad \downarrow p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{Br} \tag{80}$$

$$
\underset{(70)}{m\text{-NO}_2\text{C}_6\text{H}_4\overset{\overset{\text{OH}}{|}}{\text{CH}}\overset{\overset{\text{O}}{\|}}{\text{Se}}\text{CPh}} \qquad \underset{(71)}{p\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2\text{Se}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{Ph}}
$$
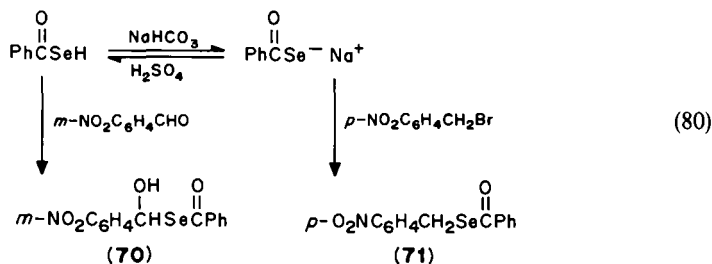
Attempts to prepare aliphatic selenoacids similarly were unsuccessful, leading to low yields of diacyl selenides[119]. Dipropionyl selenide (**72**) reacts with two equivalents of aniline affording two moles of the anilide and hydrogen selenide (equation 81), indicating that selenoacids, like thioacids, can act as acylating agents.

$$
\underset{(72)}{\overset{\substack{\text{O} \quad \text{O} \\ \| \quad \|}}{\text{EtCSeCEt}}} \quad \xrightarrow{\text{PhNH}_2} \quad \left[\overset{\substack{\text{O} \\ \|}}{\text{EtCSeH}}\right] + \overset{\substack{\text{O} \\ \|}}{\text{EtCNHPh}}
$$

$$
\underset{\overset{\substack{\text{O} \\ \|}}{\text{EtCNHPh}}}{} \quad \nwarrow^{\text{PhNH}_2}_{-\text{H}_2\text{Se}} \tag{81}
$$
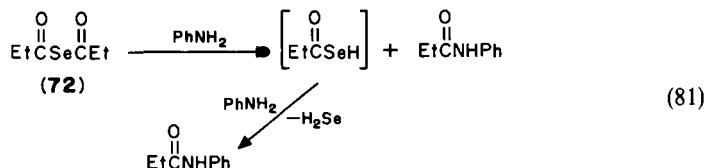
Salts of selenocarboxylic acids may be prepared by treatment of the relatively unstable diacyl selenides (**73**) with potassium hydroxide or piperidine (equation 82)[120,121]. A more convenient procedure utilizes aminolysis of the more stable diacyl diselenides (**74**) (equation 83)[122]. The diacyl selenides and diacyl diselenides can be prepared from the corresponding acid chlorides[120-122].

$$
\underset{(73)}{\overset{\substack{\text{O} \quad \text{O} \\ \| \quad \|}}{\text{RCSeCR}}} + \text{KOH} \quad \longrightarrow \quad \text{RCOSe}^-\text{K}^+ + \text{RCO}_2^-\text{K}^+ \tag{82}
$$

$$
\underset{(74)}{\overset{\substack{\text{O} \quad \text{O} \\ \| \quad \|}}{\text{RCSeSeCR}}} + 2 \underset{\substack{\text{N} \\ \text{H}}}{\bigcirc} \quad \xrightarrow{-\text{Se}} \quad \overset{\substack{\text{O} \\ \|}}{\text{RC}}\cdots\text{Se} \quad \underset{\substack{+ \\ \text{N} \\ \text{H}_2}}{\bigcirc} + \overset{\substack{\text{O} \\ \|}}{\text{RC}}\text{N}\bigcirc \tag{83}
$$
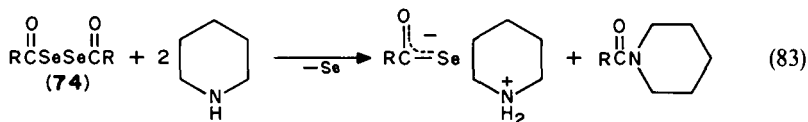
Selenocarboxylate salts can be alkylated on selenium or oxidized to diacyl diselenides. Two equivalents of selenostearate react with dichloromethane to afford bis(selenostearoyl)methane (**75**) (equation 84)[120].

$$
2\ \text{Me}(\text{CH}_2)_{16}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{Se}^-\text{K}^+ + \text{CH}_2\text{Cl}_2 \quad \longrightarrow \quad \left[\text{Me}(\text{CH}_2)_{16}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{Se}\right]_2\text{CH}_2 \tag{84}
$$

$$\underset{(75)}{}$$

Potassium selenobenzoate reacts with trimethylsilyl chloride at the oxygen center to afford the very water-sensitive *O*-trimethylsilyl ester **76** (equation 85)[123]. Presumably the strength of the oxygen—silicon bond overrides the more nucleophilic nature of selenium. The corresponding reactions with trimethyltin chloride and trimethylgermanium chloride afford the Se-metallated derivatives **77**. This behavior of the selenocarboxylate parallels that of the corresponding thiocarboxylate.

$$
\begin{array}{c}
\underset{\text{Se}}{\overset{\parallel}{\text{PhCOSiMe}_3}} \\
\textbf{(76)}
\end{array}
$$

$$
\tag{85}
$$

$$
\begin{array}{c}
\underset{\text{O}}{\overset{\parallel}{\text{PhCSeMMe}_3}} \\
\textbf{(77)}
\end{array}
$$

M = Sn, Ge
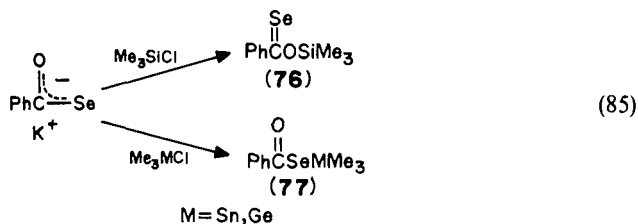
Free diselenocarboxylic acids have not been described. In attempts to prepare these compounds by the reaction of organometallic compounds with carbon diselenide, only the dialkylzinc reagents gave diselenocarboxylate salts[124]. It is likely that these insoluble zinc salts are polymeric[125].

Reactions of carbon diselenide with less basic nucleophilic carbon species with pK_a 8–20 (malonic ester, ethyl cyanoacetate, malononitrile, ethyl acetoacetate, fluorene, aceto-phenone, phenylacetonitrile) afforded the diselenolates **78**, which could be readily dialkylated (equation 86)[126].

$$
\tag{86}
$$
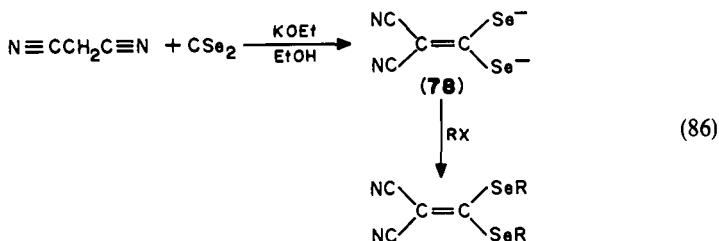
Dipotassium diselenooxalate (**79**) has been prepared by the reaction of potassium selenide with diphenyl oxalate (equation 87), and its structure has been determined by X-ray diffraction[127].

$$
\tag{87}
$$
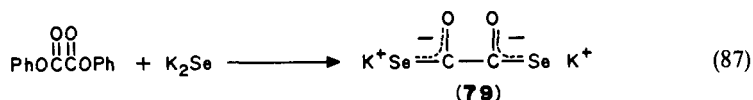
Neither tellurocarboxylic acids nor the corresponding salts have been reported.

VI. Se/Te KETENES

A. Selenoketenes—Preparation and Reactions

Selenoketenes have been postulated as intermediates in the photolysis and base-catalysed fragmentation of 4-substituted-1, 2, 3-selenadiazoles. They have proved to be

valuable intermediates in the preparation of α-unsubstituted selenoesters and selenoamides (Section III.A.1, equation 34; Section IV.A.1, equations 58 and 59).

Vapor-phase pyrolysis of selenadiazoles (**80**) at 500–600 °C and trapping of the intermediates at − 190 °C afforded selenoketenes (**81**) (equation 88)[128–130]. The parent unsubstituted selenoketene polymerized at − 80°C, but could be converted into the selenoamide by reaction at low temperature with dimethylamine vapor. The substituted compounds dimerized thermally to the diselenetanes (**82**)[130].

(88)

(**80**)   (**81**)   (**82**)

R = H, Me, *t*-Bu   R = Me, *t*-Bu
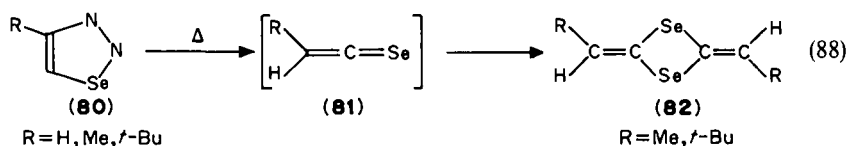
A similar dimer (**83**) has been obtained by the base-catalysed reaction of dimethyl malonate with carbon diselenide, presumably through an intermediate selenoketene (equation 89)[126].

(89)

(**83**)
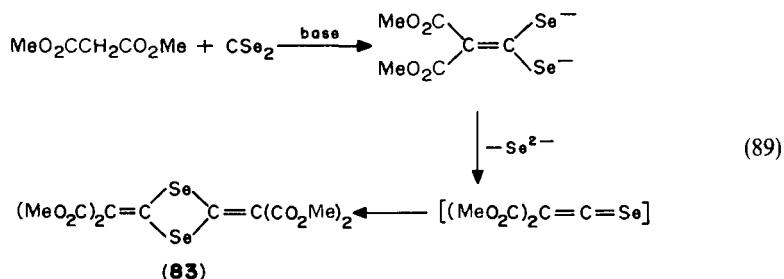
Alkaline or photochemical generation of selenoketenes in concentrated solution affords isomeric mixtures of dimeric 2, 6-disubstituted-1, 4-diselenadihydrofulvenes (**84**) (equation 90)[131–134].

(90)

(**84**)
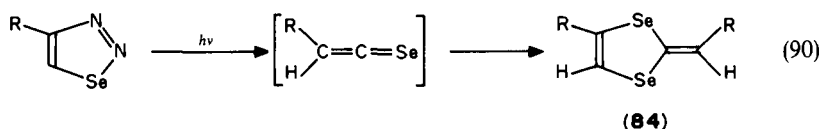
Treatment of lithium acetylides with selenium affords acetylenic selenolates (**85**), which on protonation isomerize to selenoketenes (equation 91)[99]. This provides an alternative to selenadiazole pyrolyses in the preparation of selenoamides (see Section IV.A, equation 59).

$$RC\equiv CLi + Se \longrightarrow RC\equiv C-Se^-Li^+$$

(**85**)

(91)
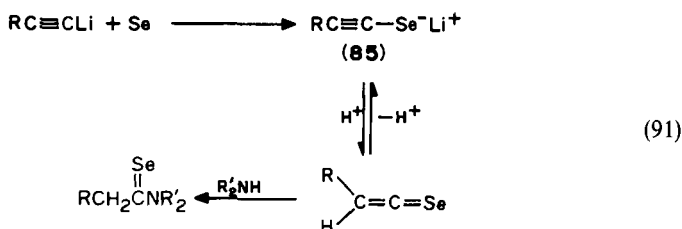
Bistrimethylsilyl selenoketene (**86**) is remarkably stable, and could be distilled at 90 °C[135]. It could be readily prepared by trimethylsilylation of the acetylenic selenolate (equation 92). Reaction of this selenoketene with diethylamine led to selenoamides **87** and **88**.

$$\text{Me}_3\text{SiC}\equiv\text{CSeLi} \xrightarrow[-30\ °\text{C}]{\text{Me}_3\text{SiCl}} (\text{Me}_3\text{Si})_2\text{C}=\text{C}=\text{Se}$$
$$(\textbf{86})$$

$$\downarrow \text{Et}_2\text{NH} \qquad\qquad (92)$$

$$\underset{(\textbf{87})}{\text{Me}_3\text{SiCH}_2\overset{\overset{\text{Se}}{\|}}{\text{C}}\text{NEt}_2} + \underset{(\textbf{88})}{\text{Me}\overset{\overset{\text{Se}}{\|}}{\text{C}}\text{NEt}_2}$$
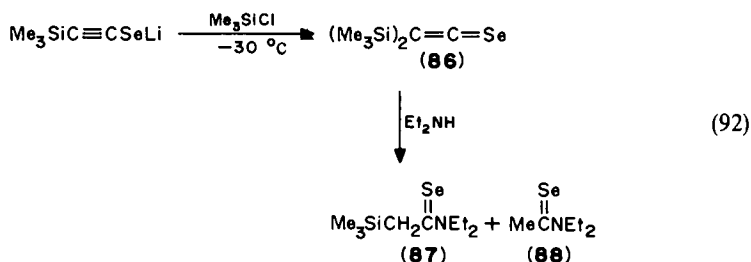
Other thermally stable, sterically hindered selenoketenes (**89**) could also be prepared starting from the acetylenic selenolate through a selena-Cope reaction of the allylic acetylenic selenide (equation 93)[136]. In addition to selenoamide formation, these compounds underwent cycloadditions with 3,4-dihydroisoquinoline to afford the seleno-β-lactam 1:1 adduct **90** and the selenoamide 1:2 adduct **91** (equation 94).

$$\text{RC}\equiv\text{CSeLi} + \text{BrCH}_2\text{CH}=\text{CR}_2' \longrightarrow \text{RC}\equiv\text{CSe}\diagdown_{\diagdown\text{CH}_2}^{}$$

$$R = t\text{-Bu}, \text{Me}_3\text{Si} \qquad\qquad R_2'\text{C}=\text{CH}\diagup$$
$$R' = H, \text{Me}$$

$$\underset{(\textbf{89})}{\overset{R\diagdown}{\underset{R_2'\text{C}\diagdown}{C}}=\text{C}=\text{Se}} \qquad \xleftarrow{\Delta} \qquad\qquad (93)$$

$$\text{CH}=\text{CH}_2$$

$$(94)$$
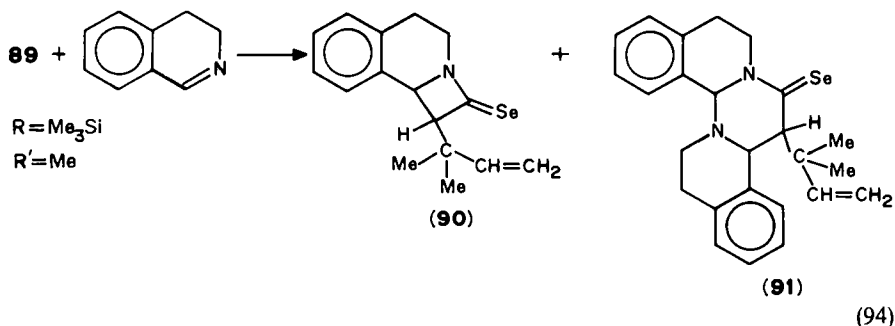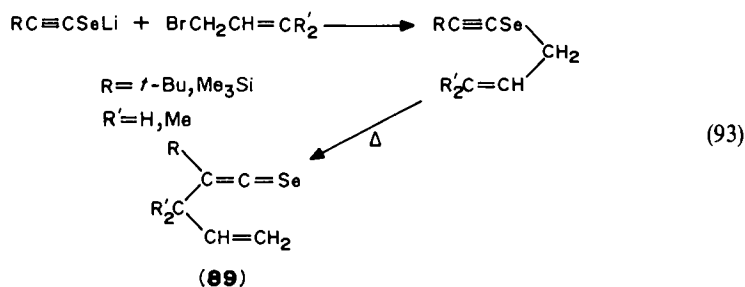
Flash vacuum thermolysis of the selenadiazole **92** at 500 °C and matrix trapping at 12 K afforded the selenoketene **93**[81]. At 700 °C the cumulated selenoketene **94** was observed, presumably by cleavage of **93** (equation 95). Irradiation of matrix-isolated **94** at 12 K gave the acetylenic selenal **95**.

$$\text{(92)} \xrightarrow[\text{500 °C}]{} \square\!\!=\!\!C\!=\!\!Se \quad \begin{array}{l}\text{(argon matrix}\\\text{isolated at 12 K)}\end{array}$$

(93)

$$\downarrow \Delta$$

$$H_2C\!=\!C\!=\!C\!=\!Se \quad \begin{array}{l}\text{(argon matrix}\\\text{isolated at 12 K)}\end{array} \tag{95}$$

(94)

$$\downarrow h\nu$$

$$HC\!\equiv\!C-CHSe \quad \begin{array}{l}\text{(argon matrix}\\\text{isolated at 12 K)}\end{array}$$

(95)

(92) $\xrightarrow{700\ °C}$
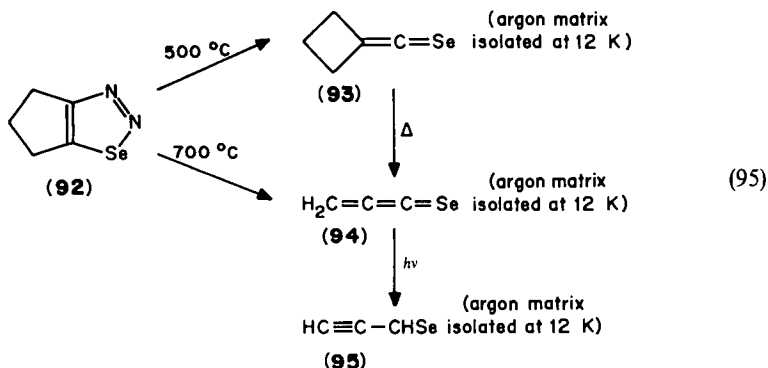
B. Telluroketenes—Preparation and Reactions

The reaction of the sodium salt of phenylacetylene with tellurium, followed by acidification, leads to a mixture of products in which the amounts vary, depending on the reaction conditions[137–140]. The reactions are presumed to go through acetylenic tellurolate and telluroketene intermediates **96** and **97** (equation 96). The telluroketene **97** can dimerize directly to **98** or ditellurodihydrofulvene (**99**), or react with ditellurate to afford **100**. The most recent reference describes this complex reaction most clearly[140].

$$\text{PhC}\!\equiv\!\text{C}^-\text{Na}^+ + \text{Te} \longrightarrow \text{PhC}\!\equiv\!\text{CTe}^-\text{Na}^+$$

(96)

$$\downarrow \text{H}^+$$

$$\left[\begin{array}{c}\text{Ph}\\\text{H}\end{array}\!\!>\!\!C\!=\!\text{Te}\right]$$

(97)

$$\tag{96}$$

(98) $\xleftarrow{}$ PhC≡CTeTe⁻

(100)   **(99)**
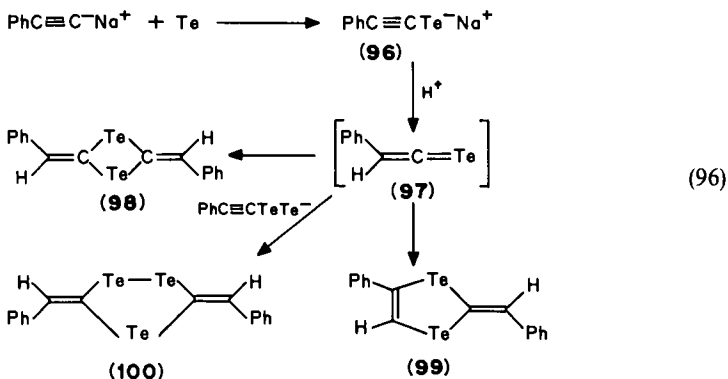
VII. ISOSELENOCYANATES

A. Preparation

The isoselenocyanates **101** may be prepared by reaction of an isonitrile with selenium (equation 97)[141,142]. The sterically hindered isoselenocyanate **102** was best prepared by reaction of the isonitrile anion with selenium at low temperature (equation 98)[52].

$$\overset{+}{R}\overset{-}{N}\!\equiv\!\overset{-}{C} \xrightarrow{\text{Se}} RN\!=\!C\!=\!Se \tag{97}$$

(101)

$$\underset{H}{\overset{+}{\times}}\!\!-\!N\!\equiv\!\bar{C} \xrightarrow[\text{(2) Se}]{\text{(1)}n\text{-BuLi}} \underset{H}{\times}\!\!-\!N\!=\!C\!=\!Se \qquad (98)$$
$$\textbf{(102)}$$
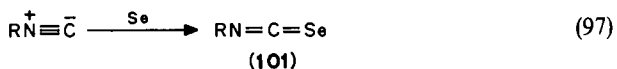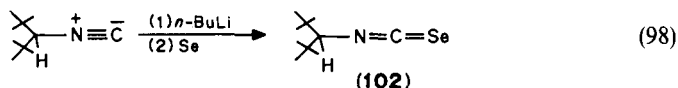
Nucleophilic displacement by selenocyanate on activated halides affords mixtures of isoselenocyanates and selenocyanates (103) owing to the ambidentate nature of the ion (equation 99)[142-144]. Photochemical conversion of benzylic selenocyanates to the corresponding isoselenocyanates has been described (equation 100)[145]. Silyl-, germanyl- and phosphorus-substituted isoselenocyanates have also been prepared[146-149].

$$RX + SeCN^- \longrightarrow RSeCN + RNCSe \qquad (99)$$
$$\textbf{(103)}$$

$$ArCH_2Cl \xrightarrow[\text{DMF}]{\text{KSeCN}} ArCH_2SeCN \xrightarrow{hv} ArCH_2NCSe \qquad (100)$$

$$RNH_2 + CSe_2 + 2Et_3N + HgCl_2 \longrightarrow RNCSe + HgSe + 2Et_3N\cdot HCl \qquad (101)$$
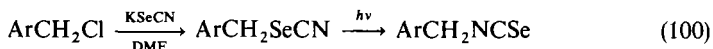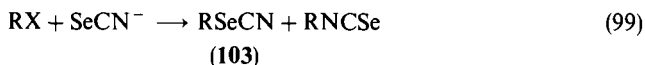
Treatment of a primary amine with carbon diselenide in the presence of a tertiary amine and mercury(II) acetate affords isoselenocyanates in moderate to good yields (equation 101)[150]. Isoselenocyanates have been postulated as intermediates in the reaction of carbon diselenide or triselenocarbonates with primary amines to form selenoureas (see Section XI, equation 152).

Other methods of preparation of isoselenocyanates include the reaction of an isocyanate with phosphorus pentaselenide and the reaction of dichloroisocyanate with sodium selenide[151].

B. Reactions

Isoselenocyanates are useful starting materials for the preparation of selenosemicarbazides and selenoureas (see Section VIII.A and XI.A). Reduction of isoselenocyanates with lithium aluminium hydride or with zinc–hydrochloric acid affords the corresponding amines (equation 102)[152,153].

$$RNCSe \xrightarrow{\text{reduction}} RNH_2 \qquad (102)$$
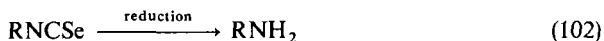
Heating trityl isoselenocyanate (104) leads to extrusion of selenium and formation of triphenylacetonitrile (equation 103)[152].

$$Ph_3CNCSe \xrightarrow[-Se]{\Delta} Ph_3CCN \qquad (103)$$
$$\textbf{(104)}$$
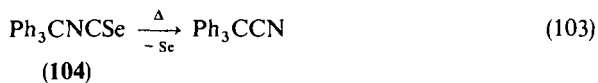
Isoselenocyanates are useful synthetic intermediates in a recently described deamination procedure[154]. Treatment of the steroidal isoselenocyanate 105 with tri-n-butylstannane affords the product 106 in moderate yield (equation 104). Isothiocyanates and isocyanides can also act as substrates in this reduction.

$$(104)$$
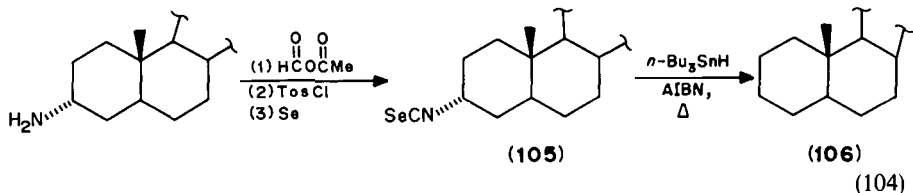
A cycloaddition of phenyl isoselenocyanate to the enamine **107** in the presence of sulfur affords the cyclic selone thiocarbamate **108** (equation 105)[155].

$$\text{(107)} \qquad\qquad\qquad\qquad\qquad \text{(108)} \qquad (105)$$
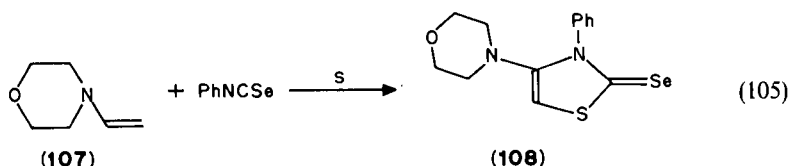
VIII. SELENOSEMICARBAZIDES

A. Preparation

Selenosemicarbazides (**109**) can be prepared by the reaction of a isoselenocyanate with a hydrazine (equation 106)[156–162]. They can also be prepared from isonitriles and hydrazines in the presence of selenium (equation 107)[163]. The highly substituted selenosemicarbazide **111** could be prepared by reaction of bis(N, N, N'-trimethylselenocarbazoyl) diselenide (**110**) (see Section X.A) with dimethylamine (equation 108)[164].

$$
\begin{array}{c}
\text{Se} \\
\parallel \\
\text{RNCSe} + \text{R'NHNH}_2 \longrightarrow \text{RNCNNHR'} \\
\quad\quad\quad\quad\quad\quad\quad\quad | \ \ | \\
\quad\quad\quad\quad\quad\quad\quad\quad \text{H H} \\
\text{(109)}
\end{array}
\qquad (106)
$$

$$\text{RNC} + \text{Se} + \text{R'NHNH}_2 \longrightarrow \textbf{109} \qquad (107)$$

$$\text{(110)} \qquad\qquad\qquad\qquad\qquad \text{(111)} \qquad (108)$$
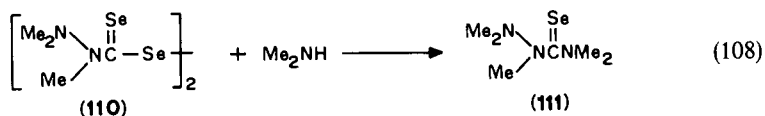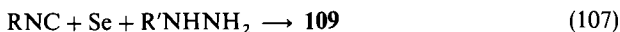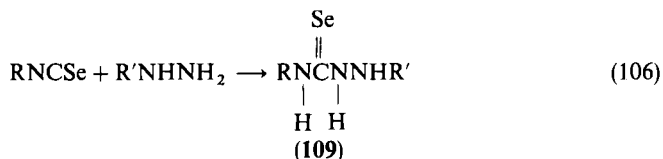
Selenosemicarbazides can also be prepared by addition of hydrogen selenide to cyanohydrazines or aromatic diazonium cyanides[158,165].

While selenosemicarbazones (**112**) could be isolated from the reaction of hydrazine selenocyanate with aldehydes or ketones (equation 109) the parent selenosemicarbazide could not be directly isolated by rearrangement of hydrazine selenocyanate[157].

$$\text{(112)} \qquad (109)$$
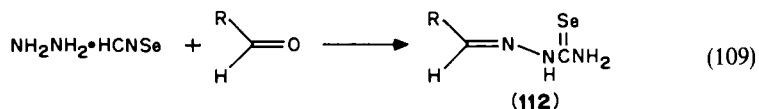
B. Reactions

Selenosemicarbazones can be prepared from aldehydes or ketones and selenosemicarbazides under acid catalysis (equation 110)[158,159,162,165]. Aldehyde derivatives can be prepared by exchange with acetone selenosemicarbazone[157].

$$ (110)$$
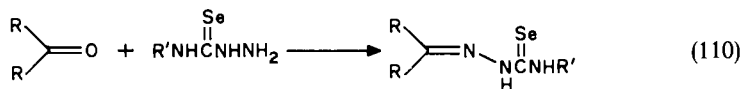
Selenosemicarbazides and selenosemicarbazones are also widely used in the prepar-
ation of a variety of complex selenium-containing heterocycles[5,12,166] (e.g. **113** and **114**,
equations 111 and 112)[159,167].

$$
\underset{\text{H}}{\text{PhN}}\overset{\text{Se}}{\underset{\|}{\text{C}}}\text{NHNH}_2 \; + \; \text{PhCCH}_2\text{Br} \longrightarrow \qquad\qquad\qquad\qquad (111)
$$

(113)

$$
\text{H}_2\text{N}\overset{\text{Se}}{\underset{\|}{\text{C}}}\text{NHN}=\text{CHR} \; + \; \text{R}'\overset{\text{X}}{\underset{|}{\text{CH}}}\text{CO}_2\text{H} \longrightarrow \qquad\qquad\qquad (112)
$$

(114) R'
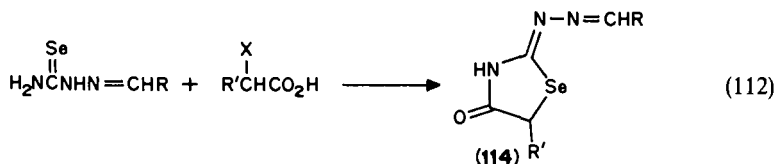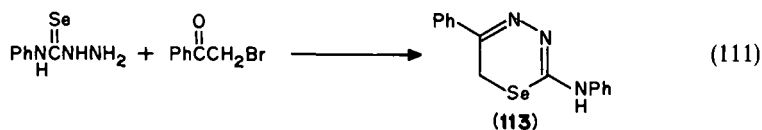
Alkylation of a selenosemicarbazide or a selenosemicarbazone occurs at selenium
(equations 111–113)[158,159,167]. Reaction of a selenocyanate with a selenosemicarbazide
leads to the *N*-acylated product **115** (equation 114)[162].

$$
\text{C}_4\text{H}_9\text{NH}\overset{\text{Se}}{\underset{\|}{\text{C}}}\underset{\text{Me}}{\underset{|}{\text{N}}}\text{NMe}_2 \; + \; (\text{MeO})_2\text{SO}_2 \longrightarrow \text{C}_4\text{H}_9\overset{+}{\text{NH}}=\overset{\text{SeMe}}{\underset{|}{\text{C}}}\underset{\text{Me}}{\underset{|}{\text{N}}}\text{NMe}_2-\text{MeOSO}_3^- \qquad (113)
$$

$$
p\text{-Tol-NH}\overset{\text{Se}}{\underset{\|}{\text{C}}}\text{NHNH}_2 \; + \; p\text{-Tol-N}=\text{C}=\text{Se} \longrightarrow (\,p\text{-Tol-NH}\overset{\text{Se}}{\underset{\|}{\text{C}}}\text{NH}\,)_{\overline{2}} \qquad (114)
$$

(115)
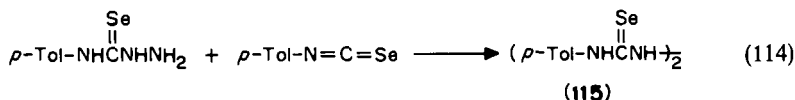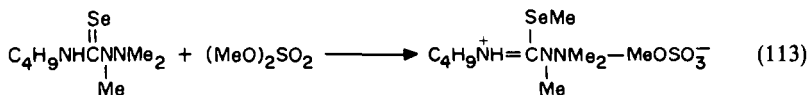
Selenosemicarbazides and derivatives form complexes with a variety of metal
ions[168–170].

IX. SELENOCARBONATES

A. Preparation

Selenium derivatives of carbonic acids are not well characterized and decompose with
liberation of hydrogen selenide. The chemistry of these acids has been reviewed[169]. A
variety of selenocarbonate derivatives have been prepared by alkylation reactions. Diethyl
triselenocarbonate (**116**) can be prepared in low yield by alkylation of barium triselenocar-
bonate (equation 115)[170].

Other dialkyl triselenocarbonates can be prepared by reaction of an alkyl halide, carbon
diselenide and base in DMSO (equation 116)[171].

$$
\text{BaCSe}_3 \; + \; 2\,\text{EtI} \longrightarrow \text{EtSe}\overset{\text{Se}}{\underset{\|}{\text{C}}}\text{SeEt} \qquad\qquad (115)
$$

(116)

$$
\text{CSe}_2 + \text{RX} + \text{KOH} \xrightarrow[\text{H}_2\text{O}]{\text{DMSO}} \text{RSe}\overset{\text{Se}}{\underset{\|}{\text{C}}}\text{SeR} \qquad (116)
$$
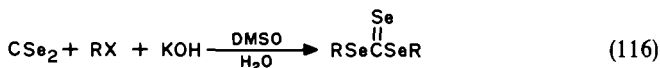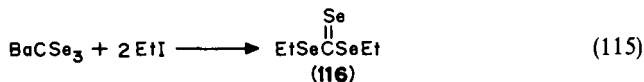
While the reaction of a selenolate with carbon diselenide followed by alkylation does not afford triselenocarbonates[171], the O- and S-alkyl derivatives can be satisfactorily prepared starting from the alkoxide or thiolate (equations 117–119)[172,173].

$$\text{RSe}^- + \text{CSe}_2 \xrightarrow{\quad\not\quad} \text{RSe}\overset{\displaystyle\text{Se}}{\overset{\|}{\text{C}}}\text{Se}^- \tag{117}$$

$$\text{RS}^- + \text{CSe}_2 \longrightarrow \text{RS}\overset{\displaystyle\text{Se}}{\overset{\|}{\text{C}}}\text{Se}^- \xrightarrow{\text{ClCH}_2\text{CO}_2^-} \text{RS}\overset{\displaystyle\text{Se}}{\overset{\|}{\text{C}}}\text{SeCH}_2\text{CO}_2^- \tag{118}$$

$$\text{RO}^- + \text{CSe}_2 \longrightarrow \text{RO}\overset{\displaystyle\text{Se}}{\overset{\|}{\text{C}}}\text{Se}^- \xrightarrow{\text{ClCH}_2\text{CO}_2^-} \text{RO}\overset{\displaystyle\text{Se}}{\overset{\|}{\text{C}}}\text{SeCH}_2\text{CO}_2^- \tag{119}$$
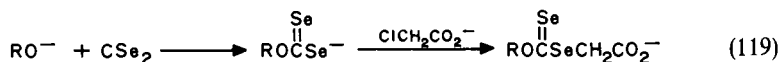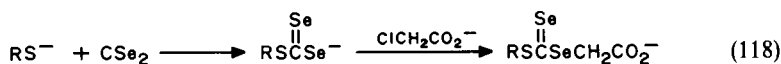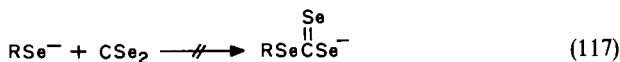
Cyclic selenocarbonates have been extensively studied as starting materials in the preparation of organic semiconductors[174]. Alkylation of dithio- or diseleno-carbamate anions (see Section X.A) followed by acid-catalysed cyclization and hydrogen selenide treatment provides a convenient route to disubstituted triselenocarbonates[175] and selonedithiocarbonates (117) (equation 120)[176].

$$\text{Y} = \text{S, Se}$$
$$\text{X} = \text{halogen}$$

(117)

(120)
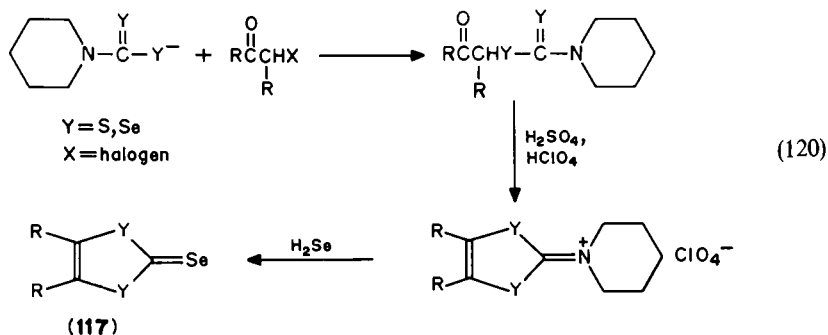
The unsubstituted triselenocarbonate 118 can be prepared by reaction of sodium acetylide with carbon diselenide and selenium, followed by acidification (equation 121)[177].

(121)

(118)
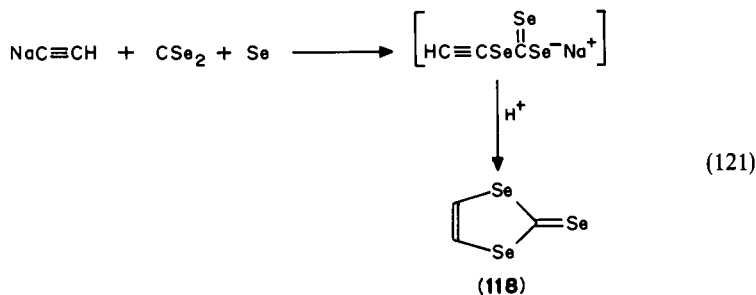
This compound can also be prepared via the reaction of bis(N,N-dialkylselenocarbamoyl) selenide (119) (see Section X.A) with the diselenide 120 (equation 122)[178].

$$\left(\left(\underset{N-C}{\overset{\overset{Se}{\|}}{\bigcirc}} \right)_2 \hspace{-0.5em} Se \right) + (H\overset{O}{\overset{\|}{C}}CH_2Se)_2 \xrightarrow{H^+} \bigcirc N-\overset{\overset{Se}{\|}}{C}SeCH_2CHO$$

(119)   **(120)**   (122)

$$\Big\downarrow \begin{array}{l}(1)\,H_2SO_4,\,0\ ^\circ C\\(2)\,H_2Se\end{array}$$

118

Two more recent routes to triselenocarbonates avoid the use of the noxious carbon diselenide as a selenium source. The first utilizes alkylation of tetramethylselenourea followed by hydrogen selenide treatment to afford the diselenourethane intermediate **121** (equation 123)[179].

$$R\overset{O}{\overset{\|}{C}}\overset{}{\underset{\underset{Br}{|}}{C}}HR + Me_2N\overset{\overset{Se}{\|}}{C}NMe_2 \longrightarrow \underset{R}{\overset{R}{\diagdown}}\hspace{-0.3em}\underset{Se}{\overset{O}{=}}\hspace{-0.3em}\underset{NMe_2}{\overset{Me\diagup N^+\diagdown Me}{}}$$

$$\Big\downarrow H_2Se$$ (123)

$$\underset{R}{\overset{R}{\diagdown}}\hspace{-0.3em}\underset{Se\overset{\overset{Se}{\|}}{C}NMe_2}{\overset{O}{=}}$$

(121)

A related procedure involves the *in situ* preparation of the dialkyl diselenocarbamate anion **123** from dichloromethylenedimethylammonium chloride **(122)** (equation 124)[180,181].

$$Me_2\overset{+}{N}=CCl_2Cl^- \xrightarrow{H_2Se,\,Et_3N} Me_2N\overset{\overset{Se}{\|}}{C}Se^-Et_3\overset{+}{N}H$$

(122)   **(123)**

$$\Big\downarrow RCOCHRBr$$

$$Se=\hspace{-0.3em}\underset{\diagdown Se\diagdown}{\overset{\diagup Se\diagup R}{}}\hspace{-0.3em}\underset{R}{} \xleftarrow{H_2Se} Me_2\overset{+}{N}=\hspace{-0.3em}\underset{\diagdown Se\diagdown}{\overset{\diagup Se\diagup R}{}}\hspace{-0.3em}\underset{R}{} \xleftarrow[H_2SO_4]{CF_3CO_2H} Me_2N\overset{\overset{Se}{\|}}{C}Se\overset{\overset{R}{|}}{C}H\overset{\overset{O}{\|}}{C}R$$

(124)

Thiocarbonyl–selenocarbonyl exchange in carbonate derivatives can be carried out by S-alkylation followed by hydrogen selenide treatment (equation 125)[182].

$$\bigcirc\hspace{-0.3em}\underset{\diagdown Se\diagdown}{\overset{\diagup Se\diagup}{}}\hspace{-0.3em}C=S \xrightarrow{(MeO)_2\overset{+}{C}HBF_4^-} \bigcirc\hspace{-0.3em}\underset{\diagdown Se\diagdown}{\overset{\diagup Se\diagup}{}}\hspace{-0.3em}C\overset{+}{\underset{\diagdown Me}{S}}$$

$$\Big\downarrow H_2Se$$ (125)

$$\bigcirc\hspace{-0.3em}\underset{\diagdown Se\diagdown}{\overset{\diagup Se\diagup}{}}\hspace{-0.3em}C=Se$$

Thermolysis of 1,2,3-benzoselenadiazole (124) in the presence of excess of carbon diselenide provides an alternative route to benzotriselenocarbonate (125) (equation 126)[183].

$$\text{(124)} \quad \xrightarrow[\text{CSe}_2]{\Delta} \quad \text{(125)} \tag{126}$$
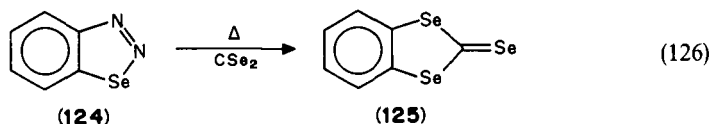
Electrochemical reduction of carbon diselenide affords the diselenolate 126, which can be alkylated to the cyclic triselenocarbonate 127 (equation 127)[184].

$$\text{CSe}_2 \quad \xrightarrow{e^-} \quad \text{(126)} \quad \xrightarrow{\text{BrCH}_2\text{CH}_2\text{Br}} \quad \text{(127)} \tag{127}$$
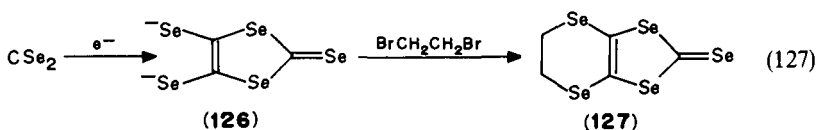
The selenocarbonate derivative 128 can be prepared by selenation of the corresponding carbonyl compound using bistricyclohexyltin selenide–boron trichloride (equation 128)[176].

$$\xrightarrow[\text{BCl}_3]{\left[\left(\bigcirc \right)_3 \text{Sn} \right]_2 \text{Se}} \quad \text{(128)} \tag{128}$$
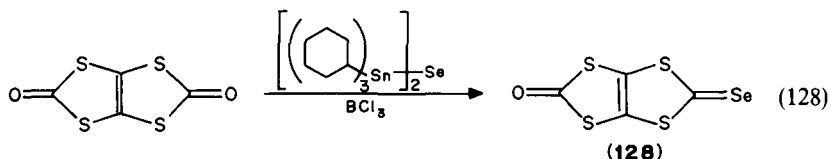
Selenopyrones 130 and 132 can be prepared from the corresponding carbonyl and thiocarbonyl compounds 129 and 131 (equations 129 and 130)[185,186].

$$\text{(129)} \quad \xrightarrow[\text{DMF}]{\text{POCl}_3} \quad \xrightarrow{\text{K}_2\text{SeO}_3} \quad \text{(130)} \tag{129}$$

$$\text{(131)} \quad \xrightarrow{\text{MeI}} \quad \xrightarrow{\text{NaHSe}} \quad \text{(132)} \tag{130}$$

$$X = O, S$$
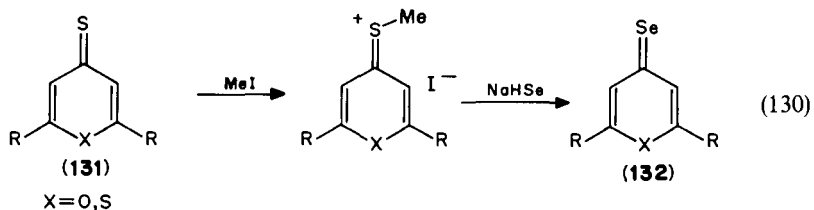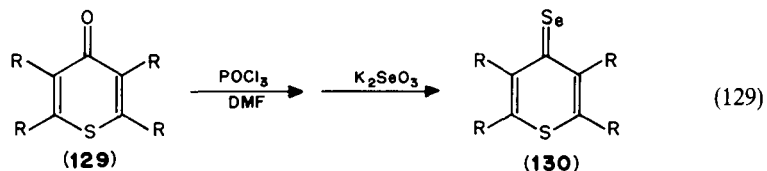
B. Reactions

Treatment of a selenocarbonate with a tertiary phosphine or phosphite affords the dihydrofulvalene derivatives 134[177,182,183]. This coupling reaction is typically much more successful for selenocarbonyl derivatives than the corresponding thiocarbonyl compounds, although an exception has been noted[184]. It is likely that the desired coupling

occurs through a 1, 3-dipolar intermediate **133** formed by nucleophilic attack on the thio- or seleno-carbonyl derivative (equation 131)[176,187]. Such 'heterophilic attacks' would be more facile in the case of the selenocarbonyl compounds (see Section II.B.2). No reaction was observed in the carbonyl case.

$$(131)$$
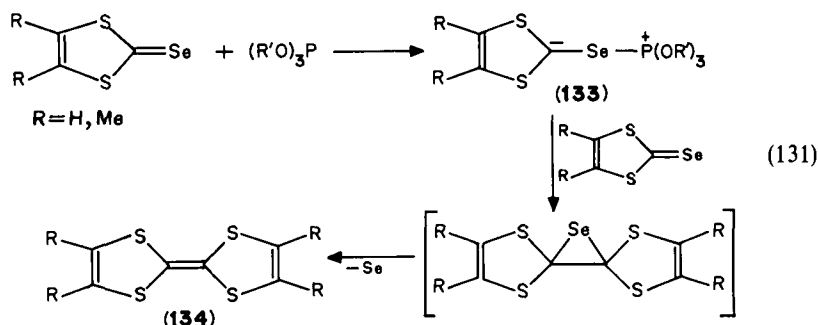
The selenocarbonyl group of selenocarbonates can be readily alkylated and the alkylated product reduced with borohydride (equation 132)[188,189]. Treatment of the resulting dithiole **135** with acid affords the stabilized carbocation **136**; only in the case of the dithiolium salt ($X = Y = S$) was coupling possible to the fulvalene.

$$(132)$$

Pyrolysis of selenopyrones **137** and **139** afforded olefins **138** and **140** (equations 133 and 134)[186,190].

$$(133)$$

$$(134)$$

Dialkyl triselenocarbonates react with amines in a variety of ways. Reaction of dialkyl triselenocarbonates with secondary amines afford diselenocarbamates (see Section X.A). Reaction of the triselenocarbonate with primary amines presumably affords a selenocarbamate intermediate. This intermediate further reacts generating the selenoisocyanate and ultimately the selenourea. As previously described, dialkyl triselenocarbonates react with amines in the presence of a selenolate to afford selenoformamides (see Section IV.A.1, equation 62)[88]. These differences in reactivity have been explained by differences in the electrophilic nature of the triselenocarbonate depending on whether the nucleophile is 'hard' (reaction at the selenocarbonyl carbon) or 'soft' (reaction at the selenium of the Se alkyl group) (equation 135)[191].

$$\text{RSeCSeR} \tag{135}$$

X. Se/Te CARBAMATES AND HYDRAZIDES

A. Selenocarbamates and Selenohydrazides—Preparation and Reactions

The reactions of secondary amines[192–196] or hydrazines[197,198] with carbon diselenide afford salts of diselenocarbamic acid (141, 142) (equations 136 and 137). These can be readily alkylated to selenocarbamates, which have been previously described as important intermediates in the preparation of cyclic selenocarbonates (Section IX.A, equation 120).

$$2R_2NH + CSe_2 \longrightarrow R_2NCSe_2^- \; R_2NH_2^+ \tag{136}$$
$$\textbf{(141)}$$

$$R_2NNH_2 + CSe_2 \longrightarrow R_2\overset{+}{N}NHCSe_2^- \tag{137}$$
$$\textbf{(142)}$$

On mild oxidation, dialkyl selenocarbamate salts afford equimolar mixtures of the bisselenocarbamoyl selenide and the triselenide[192,198,199]. The reaction has been shown to go through a diselenide intermediate 143, which is in equilibrium with the selenide 144 and triselenide 145 (equation 138)[199]. Treatment of 143 or 145 with triethyl phosphite affords 144; treatment of 144 with selenium affords 145 (equation 139).

$$R_2NCSe_2^- \; R_2\overset{+}{N}H_2 \xrightarrow{\;[o]\;} R_2N\overset{Se}{\overset{\|}{C}}-SeSe-\overset{Se}{\overset{\|}{C}}NR_2 \tag{}$$
$$\textbf{(143)}$$

$$2\,\textbf{143} \rightleftharpoons R_2N\overset{Se}{\overset{\|}{C}}Se\overset{Se}{\overset{\|}{C}}NR_2 + R_2NC \tag{138}$$
$$\textbf{(144)} \qquad\qquad \textbf{(145)}$$

$$\textbf{144} \underset{P(OEt)_3}{\overset{Se_8}{\rightleftharpoons}} \textbf{145} \tag{139}$$

Selenourethane derivatives can be prepared by ammonolysis or hydrazinolysis of selenocarbonates (equation 140)[191,200,201] or by reaction of an alcohol with a selenoisocyanate (equation 141)[202]. Unsubstituted monoselenourethanes can be obtained by addition of hydrogen selenide to alkyl cyanates (146) (equation 142)[203].

$$
\begin{array}{c}
\overset{\text{Se}}{\underset{\|}{\text{ROCSeR}'}} \quad
\begin{array}{c}
\xrightarrow{\text{NH}_3} \quad \overset{\text{Se}}{\underset{\|}{\text{ROCNH}_2}} \\[2em]
\xrightarrow{\text{NH}_2\text{NH}_2} \quad \overset{\text{Se}}{\underset{\|}{\text{ROCNHNH}_2}}
\end{array}
\end{array}
\qquad (140)
$$

$$
\text{RNCSe} + \text{R}'\text{OH} \longrightarrow \overset{\text{Se}}{\underset{\|}{\text{RNHCOR}'}} \qquad (141)
$$

$$
\underset{\textbf{(146)}}{\text{ROCN}} + \text{H}_2\text{Se} \longrightarrow \overset{\text{Se}}{\underset{\|}{\text{ROCNH}_2}} \qquad (142)
$$
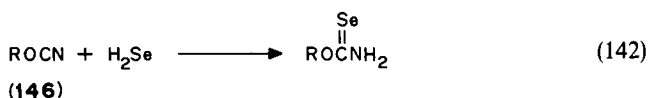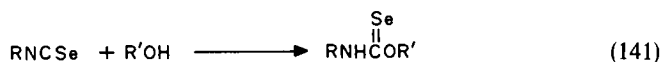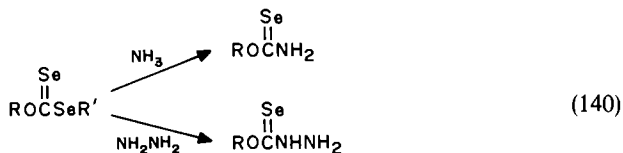
Selenothiocarbamates can be prepared from thioureas by alkylation, followed by reaction with hydrogen selenide at pH 5–6 (equation 143)[204] (cf. reaction at alkaline pH, Section XI.A.1, equation 147).

$$
\overset{\text{S}}{\underset{\|}{\text{R}_2\text{NCNR}_2}} \xrightarrow{\text{MeI}} \overset{\text{SMe}}{\underset{|}{\text{R}_2\text{NC}}}\overset{+}{=}\text{NR}_2 \xrightarrow[\text{pH 5-6}]{\text{HSe}^-} \overset{\text{Se}}{\underset{\|}{\text{R}_2\text{NCSMe}}} \qquad (143)
$$

$$
\text{R}_2\text{NNCS} + \text{H}_2\text{Se} \longrightarrow \text{R}_2\overset{+}{\text{N}}\text{HNH}\overset{\text{S}}{\underset{\|}{\text{C}}}\text{Se}^- \qquad (144)
$$
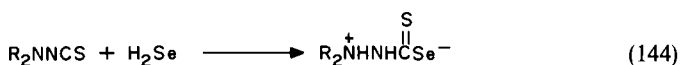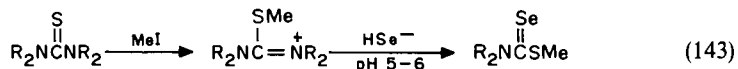
Addition of hydrogen selenide to an N-isothiocyanatoamine affords the seleno-thiocarbazate salt (equation 144)[205].

B. Tellurohydrazides and Tellurocarbazates

Tellurohydrazides (147) have been prepared from the corresponding thiohydrazides by alkylation and careful treatment of the S-alkylated product with triethylamine–hydrogen telluride in dichloromethane at −40 °C under an inert atmosphere (equation 145)[116]. These compounds are much more sensitive than their selenium analogues. Although they are stable at room temperature in an inert atmosphere, they are rapidly attacked by moisture or the atmosphere to afford the corresponding hydrazides and elemental tellurium.

$$
\overset{\text{S}}{\underset{\|}{\text{RCNR}'\text{NR}'_2}} \xrightarrow{\text{MeI}} \overset{\text{SMe}}{\underset{|}{\text{RC}}}\overset{+}{=}\text{NR}'\text{NR}'_2
$$

$$
\xrightarrow[\text{CH}_2\text{Cl}_2]{\substack{\text{H}_2\text{Te, Et}_3\text{N, Ar,} \\ <-40\,°\text{C}}}
$$

$$
\underset{\textbf{(147)}}{\overset{\text{Te}}{\underset{\|}{\text{RCNNR}'_2}}\underset{|}{\text{R}'}} \qquad (145)
$$
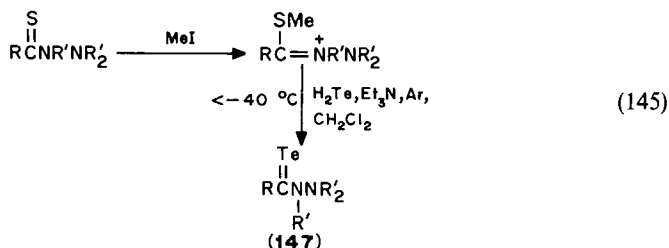
Treatment of the *N*-isothiocyanatoamine **148** with hydrogen telluride afforded the ditelluride **150**, presumably through an unstable tellurothiocarbazic acid **(149)** (equation 146)[205].

$$
R_2NNCS + H_2Te \longrightarrow \left[\underset{\substack{| \\ H}}{R_2NN} \overset{\overset{S}{\|}}{C} TeH \right]
$$

$$\text{(148)} \qquad\qquad \text{(149)}$$

$$\downarrow O_2 \qquad\qquad (146)$$

$$(R_2NNH \overset{\overset{S}{\|}}{C} - Te)_{\frac{1}{2}}$$

$$\text{(150)}$$
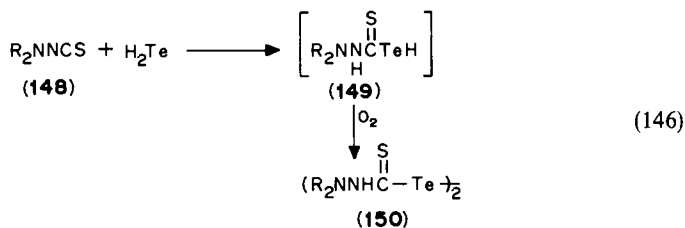
XI. Se/Te UREAS

A. Selenoureas

1. Preparation

A variety of methods are available for the preparation of selenoureas **(151)**. They may be prepared from thioureas via alkylation followed by treatment with hydroselenide ion at pH 8–9 (equation 147)[204]. Reaction of the salt at more acidic pH affords the selenocarbamate (see Section X.A.1, equation 143). This method provides a convenient route for the preparation of tetrasubstituted selenoureas. Trisubstituted selenoureas could be prepared via a similar procedure[206].

$$
\underset{\substack{\| \\ }}{\overset{\overset{S}{\|}}{Me_2NCNMe_2}} \xrightarrow{MeI} \underset{\substack{| \\ }}{\overset{\overset{SMeI^-}{|}}{Me_2NC}} {=} \overset{+}{N}Me_2 \xrightarrow[pH8-9]{NaHSe} \overset{\overset{Se}{\|}}{Me_2NCNMe_2} \qquad (147)
$$

$$\text{(151)}$$
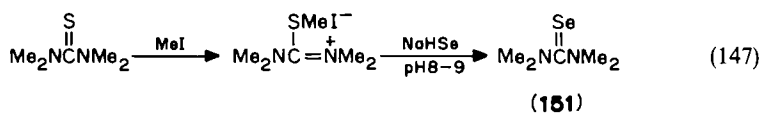
Mono-, di- and tri-substituted selenoureas can be prepared by the reaction of an isoselenocyanate with ammonia, primary or secondary amines (equation 148)[156,159,162,207]. Reaction of selenocyanate ion with amines also yields selenoureas (equation 149)[208].

$$
RNCSe + R'_2NH \longrightarrow RNH\overset{\overset{Se}{\|}}{C}NR'_2 \qquad (148)
$$

$$R' = H, alkyl,$$
$$aryl$$

$$
PhCH_2\overset{+}{N}H_3Cl^- + KSeCN \longrightarrow PhCH_2NH\overset{\overset{Se}{\|}}{C}NH_2 \qquad (149)
$$
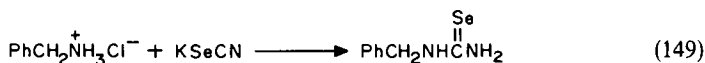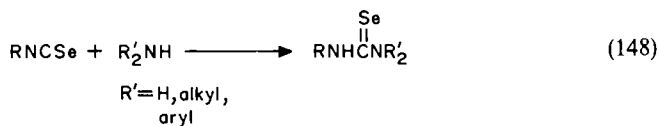
Reaction of cyanamide with hydrogen selenide provides a convenient route to the unsubstituted selenourea (equation 150)[209]. Substituted cyanamides afford mono- or 1,1-di-substituted selenoureas[210–212]. Carbodiimides also react with hydrogen selenide to afford 1,3-disubstituted selenoureas (equation 151)[210].

$$
NH_2C{\equiv}N + H_2Se \longrightarrow H_2N\overset{\overset{Se}{\|}}{C}NH_2 \qquad (150)
$$

$$RN=C=NR + H_2Se \longrightarrow RNH\overset{\overset{\displaystyle Se}{\|}}{C}NHR \tag{151}$$
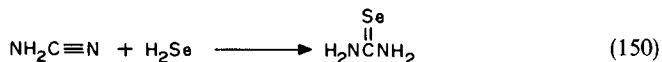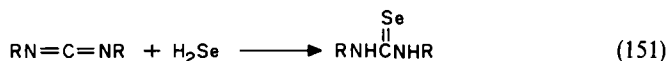
The reactions of dialkyl triselenocarbonates or carbon diselenide with excess of primary amines both afford symmetrical 1,3-disubstituted selenoureas (equation 152)[191,213]. These reactions presumably involve an isoselenocyanate intermediate.

$$(PhCH_2Se)_2C=Se + RNH_2 \longrightarrow \left[PhCH_2Se\overset{\overset{\displaystyle Se}{\|}}{C}NHR \right]$$

$$\downarrow -PhCH_2SeH$$

$$RNH_2 + CSe_2 \longrightarrow \overset{\overset{\displaystyle Se}{\|}}{RNHC}-Se^{-} \overset{-RNH_3\bar{S}eH}{\longrightarrow} [RN=C=Se] \tag{152}$$
$$\overset{+}{RNH_3}$$

$$\downarrow RNH_2$$

$$RNHCNHR$$
$$\overset{\|}{Se}$$
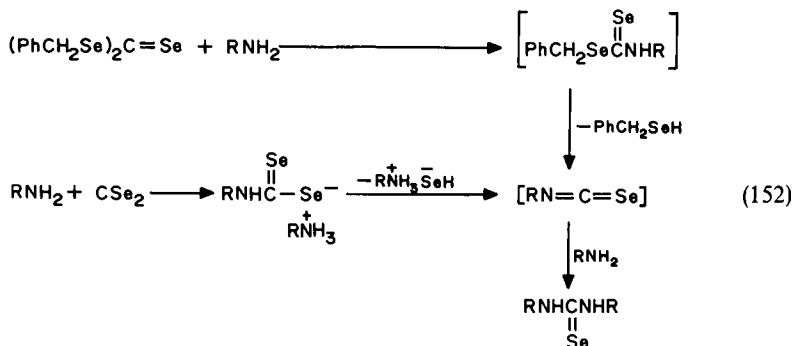
Phosphorus pentaselenide converts urea into selenourea in poor yield[214]. Selenobiurets (152) could be prepared from thiobiurets by the previously described alkylation–sodium hydrogen selenide procedure (equation 153)[204,215].

$$\overset{\overset{\displaystyle S}{\|}}{H_2NC}\overset{\overset{\displaystyle X}{\|}}{NHC}NH_2 \overset{(1)\ MeI}{\underset{(2)NaHSe}{\longrightarrow}} \overset{\overset{\displaystyle Se}{\|}}{H_2NC}\overset{\overset{\displaystyle X}{\|}}{NHC}NH_2 \tag{153}$$
$$(152)$$
$$X=O,S,Se$$
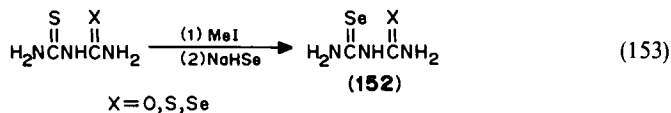
Sterically hindered tetrasubstituted selenoureas can be prepared using diselenocarbamoyl selenides or triselenides (153) (equation 154)[199]. This selenide mixture may also be generated *in situ*.

$$\left[R_2N\overset{\overset{\displaystyle Se}{\|}}{C} \right]_2 Se_n + 2\ R_2'NH \overset{O_2}{\underset{70\ ^\circ C}{\longrightarrow}} R_2N\overset{\overset{\displaystyle Se}{\|}}{C}NR_2 \tag{154}$$
$$(153)$$

$$\tag{155}$$

$$R=i\text{-Pr}$$
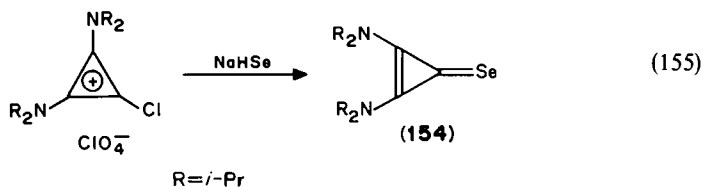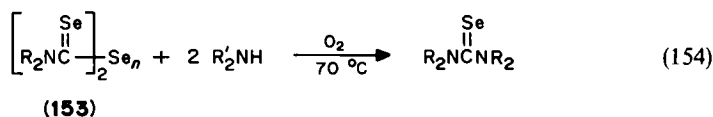
The 'quasi-selenourea' 154 was prepared in quantitative yield from the cyclopropenium salt and sodium hydrogen selenide (equation 155)[126]. The spectral properties of this molecule resemble those of a selenourea rather than those of a selone because of the strong conjugation through the cyclopropene ring.

$$(156)$$

$$(157)$$
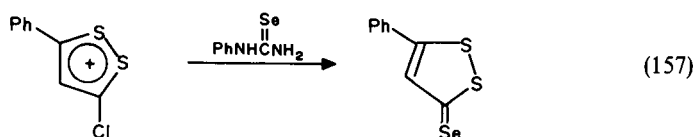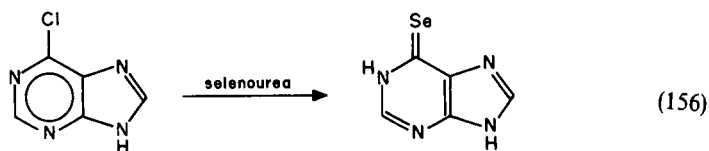
2. Reactions

Selenoureas are widely used for introducing selenium into organic molecules (equation 156 and 157). As expected, the selenium center is especially nucleophilic. Selenoureas are very useful as reagents in the synthesis of selenium-containing heterocycles[5,12,166] (e.g. **155–158**, equations 158–161).

$$(158)$$

(155)

$$(159)$$

(156)

$$(160)$$

(157)

$$(161)$$

(158)
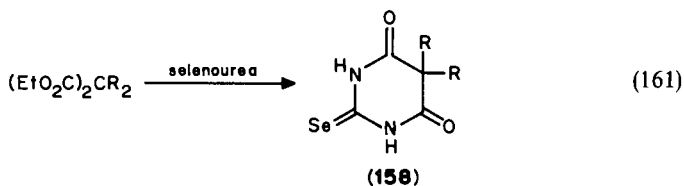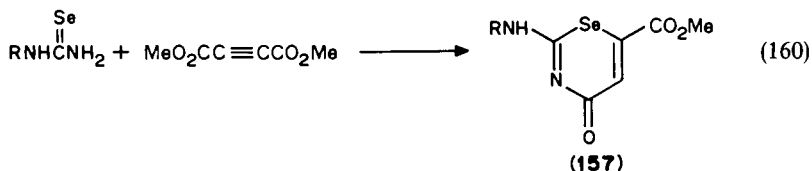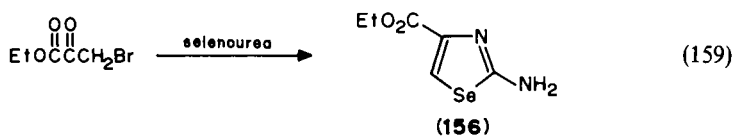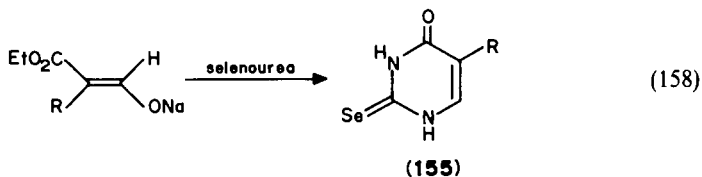
Selenourea adds to α,β-unsaturated systems in a conjugative sense (equations 162 and 163)[221,222].

$$\underset{\substack{\| \\ O}}{PhCC\equiv CPh} \quad\xrightarrow{\text{selenourea}}\quad \underset{\substack{\| \\ O}}{PhCCH=C}\diagdown\overset{Ph}{\underset{Se\diagdown\underset{\substack{\| \\ NH}}{C}\diagup NH_2}{}} \qquad (162)$$

$$H_2C=CHCO_2H \quad\xrightarrow{\text{selenourea + HX}}\quad \underset{}{H_2N\overset{SeCH_2CH_2CO_2H}{\overset{|}{C}}=NH_2^+ \ X^-} \qquad (163)$$
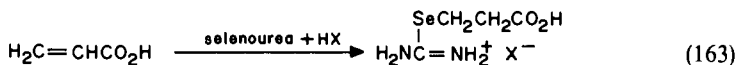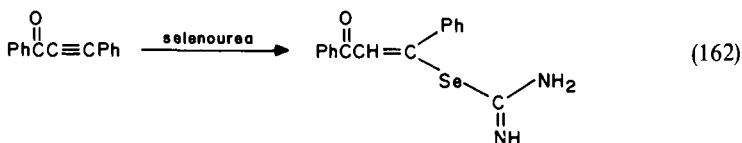
Selenourea is easily oxidized to the α,α-diselenobisformamidium cation **159** using hydrogen peroxide, hexacyanoferrate(III), p-benzoquinone or by electrochemical oxidation (equation 164)[223,224].

$$\underset{\substack{\| \\ H_2NCNH_2}}{\overset{Se}{}} \quad\xrightarrow{[o]}\quad \underset{\substack{\| \\ (H_2NCSe)_2}}{\overset{\overset{+}{N}H_2}{}} \qquad (164)$$

(159)
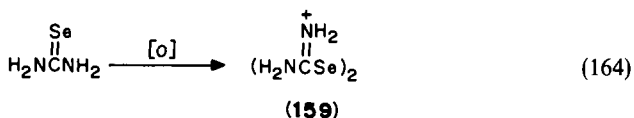
Treatment of dicyclohexylselenourea with DMSO in the presence of acid leads to an oxidative deselenation (equation 165)[225].

$$\underset{\substack{\| \\ RNHCNHR}}{\overset{Se}{}} \quad\xrightarrow[H^+]{DMSO}\quad \underset{\substack{\| \\ RNHCNHR}}{\overset{O}{}} + Se + Me_2S \qquad (165)$$
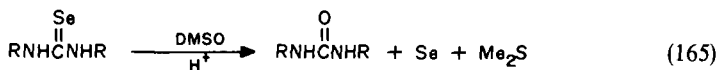
B. Telluroureas—Preparation and Reactions

Treatment of 1,3-dimethylbenzimidazoline with 2 mol of tellurium at elevated temperature is reported to give the cyclic tellurourea **160** (equation 166)[226].

$$(166)$$

(160)
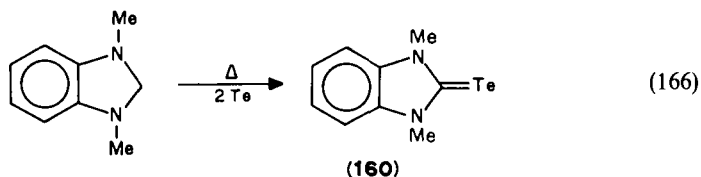
The first well documented telluroureas (**162**) were prepared by heating the electron-rich olefins **161** with tellurium (equation 167)[227]. The resulting crystalline materials were air sensitive both in solution and in the solid state. They extruded tellurium thermally and photochemically, regenerating the starting olefin.

$$(167)$$

(161)   **(162)**

R = Me, Et
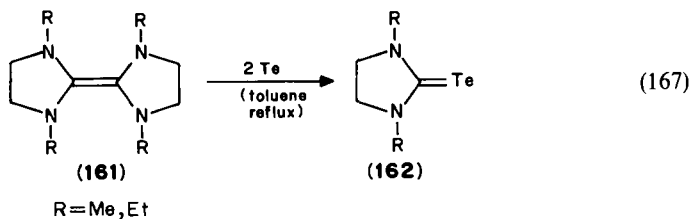
Metal complexes of these telluroureas have been prepared (Section XII, equation 175)[227]. The authors suggest that the facile detelluration of these telluroureas and their metal complexes may lead to their use in synthesis as 'masked' nucleophilic carbenes, amines and acylcarbanions.

XII. METAL AND RESONANCE STABILIZED Se/Te DERIVATIVES

Many otherwise unstable seleno- and telluro-carbonyl compounds can be isolated as metal complexes. Complexes of both seleno- and telluro-formaldehyde have recently been isolated using a variety of methods. These include reactions of sodium hydrogen selenide or telluride with diiodo-rhodium and -osmium complexes (equation 168)[228,229], and carbon diselenide addition to the osmium–formaldehyde complex, followed by extrusion of carbonyl selenide (equations 169 and 170)[230].

$$CpCORh\underset{CH_2I}{\overset{I}{<}} \quad \xrightarrow{\text{NaHY}} \quad CpCORh\underset{CH_2}{\overset{Y}{<}} \quad (168)$$
$$Y = Se, Te$$

$$L_2(CO)_2Os\underset{O}{\overset{CH_2}{<}} \quad \xrightarrow{\text{CSe}_2} \quad L_2(CO)_2Os\overset{CH_2-O}{\underset{Se-C\diagdown_{Se}}{<}} \quad (169)$$

$$\Big\downarrow \text{HI} \qquad\qquad\qquad \Big\downarrow \Delta, -\text{COSe}$$

$$L_2(CO)_2Os\underset{I}{\overset{CH_2I}{<}} \quad \xrightarrow{\text{NaHSe}} \quad L_2(CO)_2Os\underset{Se}{\overset{CH_2}{<}} \quad (170)$$
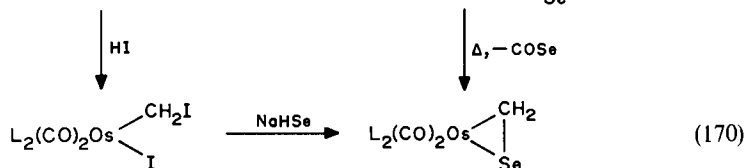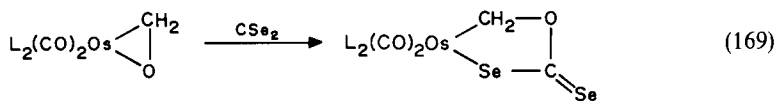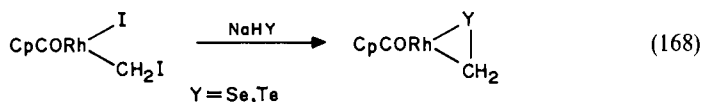
Alternatively, addition of diazomethane to organometallic manganese complexes of selenium and tellurium affords the seleno- and telluro-formaldehyde derivatives (equations 171 and 172)[231].

$$M_3Te \quad \xrightarrow[-N_2, -M]{CH_2N_2} \quad M\diagdown\underset{M}{\overset{}{Te=CH_2}} \quad (171)$$
$$M = CpMn(CO)_2$$

$$\begin{array}{c} M'\overset{Se}{\diagup\diagdown}M' \\ \text{or} \\ M'\diagdown_{Se}\diagdown\diagup^{M'}_{Se} \end{array} \quad \xrightarrow[-N_2]{CH_2N_2} \quad M'\diagdown\underset{M'}{\overset{}{Se=CH_2}} \quad (172)$$
$$M' = Me_5CpMn(CO)_2$$
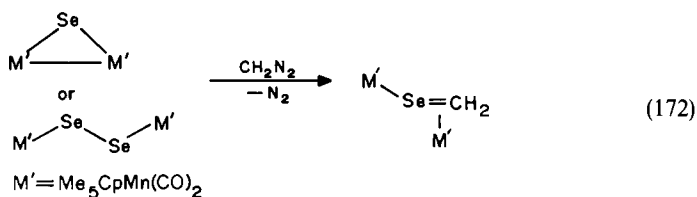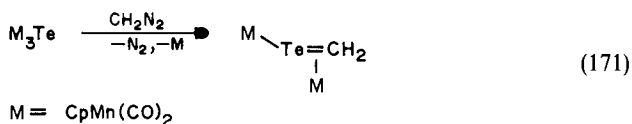
Chromium and tungsten complexes of selenobenzaldehyde[232], selenobenzophenone[233] and tellurobenzophenone[234] have been prepared by carbenoid abstraction of selenium or tellurium from seleno- and telluro-cyanates (equations 173 and 174). The complex

bonding in the selenobenzaldehyde case has been studied[232]. A number of stable metal complexes of the telluroureas **163** have been prepared (equation 175)[227].

$$(CO)_5M{=}C{\underset{Ar}{\overset{H}{<}}} + Et_4\overset{+}{N}\ NCS\overset{-}{e} \longrightarrow (CO)_5M{-}Se{=}C{\underset{Ar}{\overset{H}{<}}} \qquad (173)$$

M = W, Cr

$$(CO)_5M{=}CPh_2 + Y{=}C{=}N^- \longrightarrow (CO)_5M{-}Y{=}CPh_2 \qquad (174)$$

Y = Se, Te

$$(175)$$

M = Cr, Mo, W

(163)
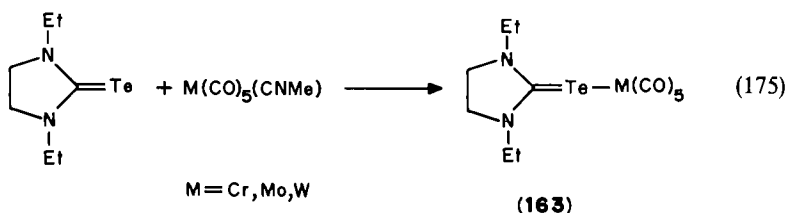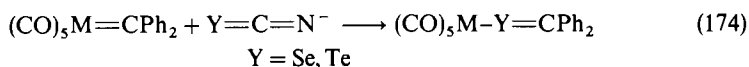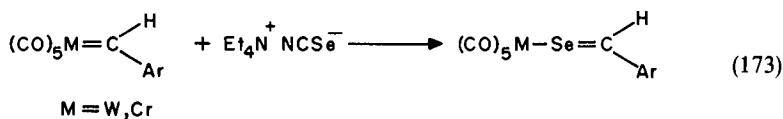
A number of selenium analogues of diketones, stabilized by metals or intramolecular hydrogen bonding, have been prepared (equation 176–178)[235–237].

M = Zn, Cd, Hg

$$(176)$$

$$(177)$$

M = Mo, Ni, W   n = 2, 3

$$(178)$$
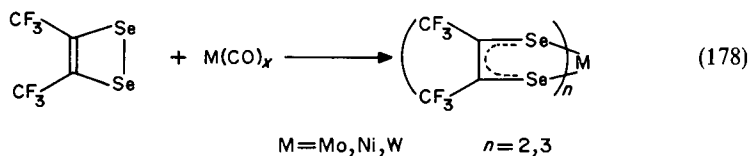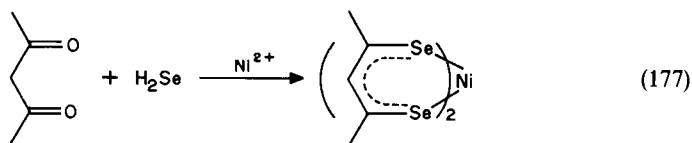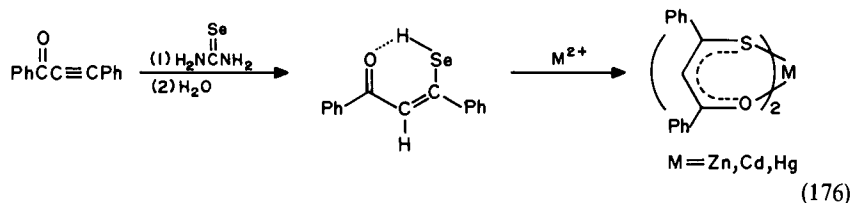
The especially well stabilized selenolate **164** can be prepared by hydrogen selenide addition to a bromocyclobutenedione[238]. Alkylation and protonation occur at selenium while aniline addition occurs at a carbonyl center (equation 179).

(179)
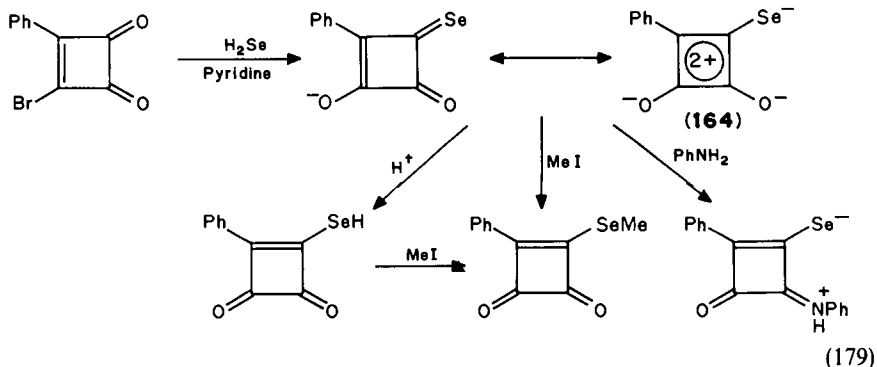
A number of selenium compounds have been obtained which formally contain selenocarbonyl groups stabilized by 'no-bond resonance'. Treatment of the selenopyrone **165** with sodium selenide affords a mixture of the dieneselenol **166** and its oxidation product **167**. Treatment of this material with phosphorus pentasulfide afforded a mixture of selenothiophthenes **168** and **169** (equation 180)[239-241].

(180)
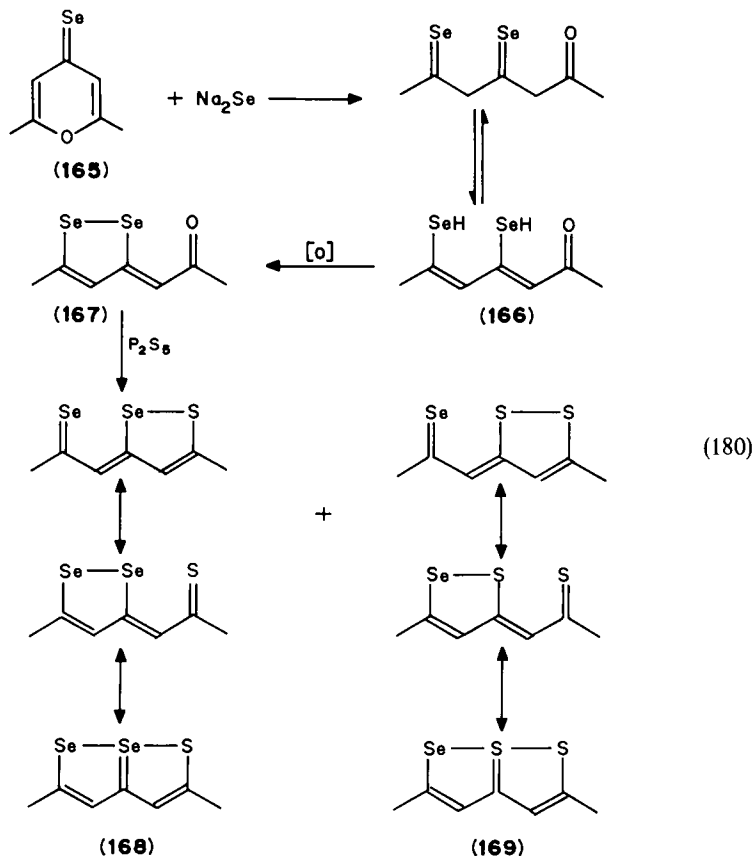
Treatment of aldehyde **170** with phosphorus pentaselenide afforded the selenodithioph-
thene **171** (equation 181)[242]. X-ray analysis of **171** showed that the S—S bond was longer
than the S—Se bond, suggesting relatively little selenocarbonyl character in this molecule.

$$\text{(181)}$$
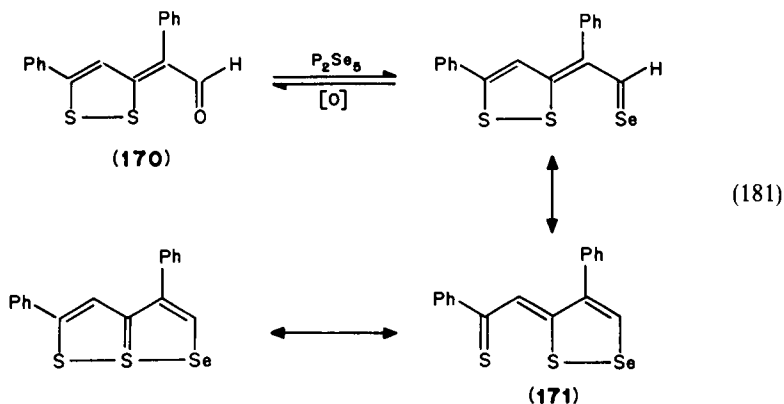
Related compounds **172** and **173** have been prepared by oxidation of dianions
(equation 182)[185]. Compounds **168, 172** and **173** are perhaps best considered as hyperva-
lent selenium species. Analogous tellurium compounds have also been reported[243].

$$\text{(182)}$$
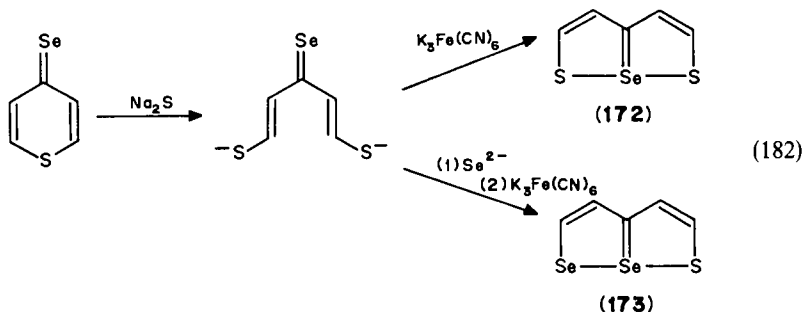
Other molecules containing formal selenocarbonyl groups stabilized by metals (**174**)
have been produced photochemically and thermally (equation 183)[244-246].

$$\text{(183)}$$
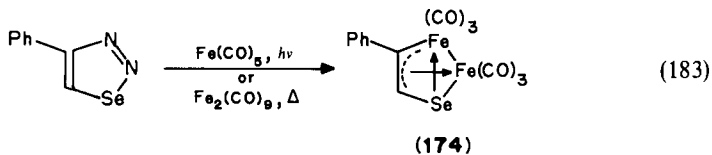
XIII. SELENOCARBONYL COMPOUNDS OF BIOLOGICAL INTEREST

A selenocarbonyl-containing nucleoside, 5-methylaminomethyl-2-selenouridine (**175**) has
been isolated from t-RNAs of a number of bacteria grown in low levels of selenite[247]. This
compound was synthesized and compared spectroscopically with other selenonucleosides.
Another selenonucleoside related to 2-selenouridine was also present in these bacterial

t-RNAs but could not be identified. There is also some evidence for naturally occurring 4-selenouridine[248,249].

Other selenocarbonyl analogues of compounds of biochemical and medicinal interest have also been prepared. A number of selone nucleoside derivatives have been prepared and evaluated as antineoplastic agents. Treatment of 2-aminoadenosine with hydrogen selenide in aqueous pyridine led to displacement of a heterocyclic amine group affording 6-selenoguanosine (**176**)[250–252]. Other 6-selenopurine nucleoside derivatives could be similarly prepared. A number of other selenocarbonyl-containing purine and pyridine derivatives, including selenocytosine, 5-methylselenocytosine, diselenothymine, 6-seleno-purine, 2-selenouracil and 2-selenothymine, have also been prepared and evaluated as purine and pyrimidine antagonists[108,253–256]. Selenosemicarbazones have also been evaluated as antineoplastic agents[257]. A number of selenocarbonyl derivatives have been evaluated as antifungal and antimicrobial agents[255,258,259]. Selenobarbituric acid derivatives have also been prepared[220].

(175)   (176)
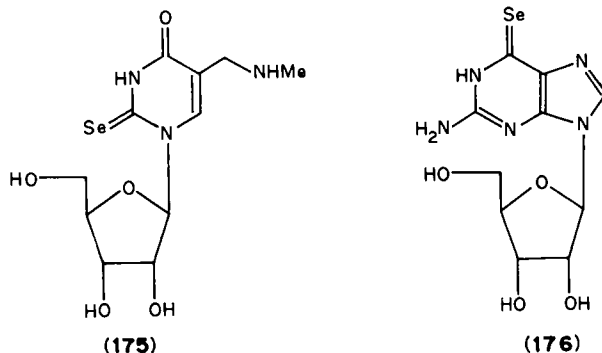
XIV. SPECTROSCOPIC AND ELECTROCHEMICAL STUDIES OF Se/Te CARBONYL COMPOUNDS

A. NMR Spectra

^{13}C NMR studies of selenocarbonyl compounds show that the selenocarbonyl carbon is shifted significantly downfield relative to the corresponding thiocarbonyl and carbonyl compounds[260]. The selenocarbonyl carbons of selones are reported to be the most deshielded carbons observed in neutral molecules (287–295 ppm)[59,260]. ^{77}Se NMR studies of selenocarbonyl compounds show that the δ ^{77}Se shifts of the selenocarbonyl group are also shifted significantly downfield (ca. 100 ppm relative to dimethyl selenide)[18]. The ^{77}Se shift closely parallels the λ_{max} of the n → π* transition of the selenocarbonyl group, and is very sensitive to changes in electronic structure.

The ^{77}Se–^{13}C coupling constants of selenocarbonyl compounds have been determined and found to be much larger than previously observed (209–221 Hz)[18,261]. The ^{13}C isotope effect on ^{77}Se shielding has been determined and correlated with C—Se bond distances for a number of selenocarbonyl compounds[262]. A comparison of the ^{77}Se and ^{77}O chemical shifts of selenocarbonyl and carbonyl compounds has also been made[17]. Deshielding of $\delta(^{77}$Se) is always accompanied by shielding of $\delta(^{13}$C=Se), paralleling the change of $\delta(^{77}$O) versus $\delta(^{13}$C=O). Both ^{77}Se and ^{17}O shifts are dominated by the local paramagnetic screening term. Based on these observations, the bond order term of the C=Se bond of selones was shown to closely resemble the bond order term of the

$C=O$ bond of ketones, indicating the true double bond nature of the selenocarbonyl group[17].

^{1}H NMR studies of amide analogues show an increased barrier to rotation about the $C-N$ bond on going from amide to thioamide to selenoamide[263,264]. This indicates an increased contribution of the dipolar resonance form **177b** in the order $O < S < Se$. This result is consistent with ^{14}N and ^{13}C NMR studies of these compounds[260,265]. Similar results were observed in the case of selenosemicarbazides[264].

$$
\begin{array}{ccc}
\overset{\displaystyle X}{\underset{\displaystyle R\,C\,NR_2'}{\|}} & \longleftrightarrow & \overset{\displaystyle X^-}{\underset{\displaystyle R\,C=\overset{+}{N}R_2'}{|}} \\
(177a) & & (177b)
\end{array}
$$

$$X = O, S, Se$$
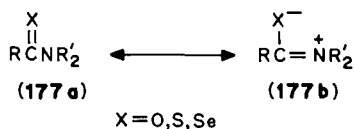
Studies of tetramethylselenourea indicate that there is free rotation about the $C-N$ bond in this compound even at $-120\,°C$[263]. This has been explained by the increased steric effect of selenium in the ground state effectively lowering the barrier to rotation. ^{14}N decoupled NMR studies showed that the rotational barrier of selenourea was the same as that of thiourea[266].

In the case of tellurocarbonyl compounds, ^{13}C NMR spectra have been reported only for telluroesters, the $C=Te$ carbon resonance being at ca. 229 ppm[16]. The N-methyl groups of telluroamides are reported to be shifted significantly downfield (δ 3.6–3.75)[116] in the ^{1}H NMR.

B. Infrared Spectra

Infrared spectroscopy has not been especially useful as a technique for characterizing seleno- and telluro-carbonyl compounds. Comparison of the infrared spectra of telluroamides and tellurohydrazides with those of the corresponding selenium compounds showed them to be almost superimposable[16]. Relatively little change had previously been reported in a comparison of the infrared spectra of thiolactams and selenolactams. Reasons for the difficulties in determining the $C=Se$ (and hence $C=Te$) frequencies have been discussed in detail[267]. Suffice it to say that the $C=Se$ and $C=Te$ absorption bands would be expected to be much weaker than $C=O$ bands. Owing to significant resonance interactions in the compounds studied (amides, hydrazides and semicarbazide derivatives), the main absorptions due to the seleno- and telluro-carbonyl groups would be in the $C-Se$ and $C-Te$ single-bonded regions. In addition, coupling of these bonds with other vibrations would be expected, and would complicate detailed interpretations.

C. Ultraviolet and Visible Spectra

The ultraviolet and visible spectra of a number of selenocarbonyl and tellurocarbonyl compounds have been reported. Selones are typically deep blue compounds which exhibit an $n \rightarrow \pi^*$ transition in the visible region ($\lambda_{max} \approx 600$–$700$ nm, $\varepsilon \approx 20$–40 $1\,mol^{-1}\,cm^{-1}$)[18,268]. An intense $\pi \rightarrow \pi^*$ transition ($\lambda_{max} \approx 270$ nm, $\varepsilon \approx 10^4$ $1\,mol^{-1}\,cm^{-1}$) as well as a presumed $n \rightarrow \sigma^*$ transition ($\lambda_{max} \approx 230$ nm, $\varepsilon \approx 10^3$ $1\,mol^{-1}\,cm^{-1}$) occur in the ultraviolet region. The long-wavelength band is dominated by a singlet-triplet component[269]. The UV–visible data for selenofenchone, thiofenchone and fenchone have been compared[268,269].

The ultraviolet spectra of methyl phenylacetate and its thione and selone analogs have been compared, with a red shift observed on going from the ester ($\lambda_{max} = 214$ nm, $\varepsilon = 6.0 \times 10^3$ $1\,mol^{-1}\,cm^{-1}$) to the thione ester $\lambda_{max} = 240$ nm, $\varepsilon = 7.1 \times 10^3$ $1\,mol^{-1}\,cm^{-1}$) to the selone ester ($\lambda_{max} = 275$ nm, $\varepsilon = 6.7 \times 10^3$ $1\,mol^{-1}\,cm^{-1}$)[84]. Similar shifts have been

observed for the amide, semicarbazide and urea derivatives[270]. This trend has been explained by a decrease in the energy difference between ground and excited states, due to an enhanced contribution of the dipolar resonance species **177b**[108,165,220] (cf. NMR Spectra, Section XIV.A, and Dipole Moment Studies, Section XIV.E).

Telluro-amides and -hydrazides, although much less well studied than their selenium analogs, also show red shifts of both the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ bonds relative to the selenium analogues [For X = Te ($\lambda_{max} = 375$ nm, $\varepsilon = 10^4$ mol^{-1} cm^{-1}; $\lambda_{max} = 540$ nm, $\varepsilon = 10^3$ l mol^{-1} cm^{-1}), X = Se ($\lambda_{max} = 316$ nm, $\varepsilon = 10^4$ l mol^{-1} cm^{-1}; $\lambda_{max} = 442$ nm, $\varepsilon = 4 \times 10^2$ l mol^{-1} cm^{-1})][116]. Telluroesters exhibit maxima at ca. 240 nm ($\varepsilon \approx 4 \times 10^3$ l mol^{-1} cm^{-1}), ca. 265 nm(sh) ($\varepsilon = 10^3$ l mol^{-1} cm^{-1}), 345 nm ($\varepsilon \approx 7.5 \times 10^3$ l mol^{-1} cm^{-1}) and ca. 590 nm ($\varepsilon \approx 3 \times 10^2$ l mol^{-1} cm^{-1}).

D. Mass Spectra

Comparisons of the mass spectral behavior of selenoureas[271] and selones[272] with their sulfur analogs have been made. Data allowing a similar comparison for selenoamides and thioamides have also been published[96]. The molecular ion abundance was less for selenocarbonyl compounds than for their thiocarbonyl analogs, yet in general, thiocarbonyl compounds give more intense molecular ions than their oxygen analogs. Fragments containing multiply bonded selenium were absent, or of much lower intensity than the corresponding sulfur fragments. It is likely that the greater ability of selenium to stabilize a positive charge is more than counterbalanced by the lowered stability of multiply bonded selenium in cationic species, accounting for the differences observed in the oxygen, sulfur and selenium spectra[272]. Similar conclusions resulted from mass spectral studies of furan, thiophene, selenophene and tellurophene[273].

E. Dipole Moment Studies

A comparison of dipole moments of fenchone derivatives (**178**) has been carried out[21]. The carbonyl moieties of these molecules are not stabilized by resonance and may be considered as 'pure' carbon—chalcogen double bonds. The results are consistent with a decreased, but not reversed, polarity of the chalcogen—carbon bond in the order O > S > Se. In contrast, in the resonance-stabilized pyridone and phthalide series, dipole moments increased in the order O < S < Se, presumably owing to increased dipolar resonance contributions in the thione and selone cases[274].
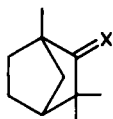
(178)

X=O,S,Se

F. Chiroptical Properties

The CD and ORD spectra of chiral selenofenchone have been reported[268,269]. The chiroptical properties of (−)-fenchone and the thione and selone derived from this ketone are parallel, showing long-wavelength negative Cotton effects. The long-wavelength CD and UV bonds in selenofenchone are well separated. The magnetic circular dichroism spectrum of racemic selenofenchone has also been reported and discussed in terms of a dominant singlet–triplet component in the $n \rightarrow \pi^*$ transition[269].

G. Electrochemical Studies

In a comparison of the reductions of O-methyl selenobenzoate and the corresponding thione benzoate using zinc and hydrochloric acid, the selenium compound was more easily reduced[275]. Polarographic studies of the reduction of these esters and the corresponding imidate indicate that the order of ease of reduction is $C=Se > C=NH > C=S > C=O$. A comparison of the reductions of selenobenzamide and thiobenzamide was consistent with this series.

The electrochemical reductions of di-t-butyl selone and 1,1,3,3-tetramethylindane-2-selone to the corresponding radical anions have been carried out, and the half-wave potentials for these reactions have been determined[276,277]. The reduction to the radical anion of the indaneselone is electrochemically reversible. The reduction product was isolated as the corresponding diselenide.

H. Photoelectron Spectra

A comparison of the photoelectron spectra of pyridone derivatives (179) has been reported[278]. Replacement of oxygen by sulfur or selenium affects both the HOMO energy and electron distribution. In the latter cases the HOMO is concentrated on the chalcogen atom, paralleling the increased nucleophilicity of the chalcogen. These results were consistent with ^{13}C NMR studies of these compounds, and also with calculations describing similar compounds[279,280].

R=H,CHO
X=O,S,Se

(179)
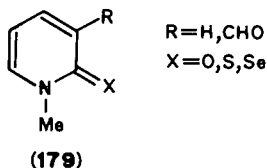
The photoelectron spectra of the unstable selenoformaldehyde, selenoactaldehyde and selenocarbonyl difluoride have been obtained by 'computer spectra stripping'[80]. The photoelectron spectrum of selenoformaldehyde compared favorably with its calculated spectrum.

I. X-Ray and Microwave Studies

A limited number of structural studies on selenocarbonyl compounds have been reported[281,282]. As yet, no data on an unstabilized selenocarbonyl moiety (e.g. in a selone) have appeared. The selenium—carbon bond length in resonance-stabilized selenoureas is typically in the range 1.82–1.89 Å[283–285]. The selenocarboxylate of dipotassium diselenooxalate has a C—Se bond distance of 1.87 Å[127]. These bonds are probably intermediate between carbon—selenium single and double bonds. In diselenouracil (180) two widely differing C—Se bond lengths were observed[286]. In addition to the usual selenourea-like C—Se bond at the 2-position of uracil there is a very long C—Se bond at the 4-position. This lengthening has been explained by an enhanced single bond character due to resonance.

Hydrogen bonding in selenocarbonyl compounds has been reported for selenourea (Se···HN bond distance of 3.51 Å)[285], 1-benzoyl-3-phenyl-2-selenourea (3.83 Å)[283] and diselenouracil (3.47 and 3.75 Å)[286]. No hydrogen bonds were observed in 1-acetyl-3-phenyl-2-selenourea[284].

Structural studies of metal complexes of selenocarbonyl compounds have also

(180)
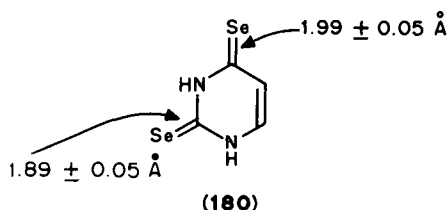
appeared. Nickel bisdiethylaminodiselenocarbonate exhibits two unequal carbon—selenium bond lengths (1.84 and 1.97 Å)[287].

A bisisoselenocyanato nickel complex (181) has a carbon—selenium bond length of 1.71 Å[288], in line with that expected for a C—Se double bond ca. 1.74 Å, see Table 3). Microwave studies of selenoketene indicate a carbon—selenium double bond length of about 1.70 Å[128].

(181)   **(182)**
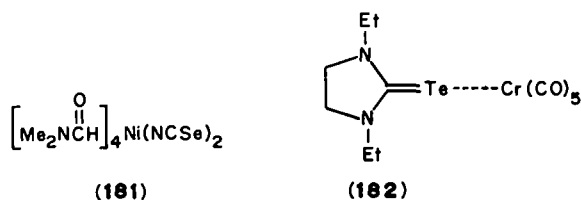
An X-ray structure of a tellurourea derivative (182) with the tellurocarbonyl tellurium complexed to chromium exhibits a carbon—tellurium bond length, 2.12 Å, typical of a carbon—tellurium single bond[227]. This is consistent with stabilization of the tellurocarbonyl moiety due to a lowering of the carbon—tellurium bond order by resonance and interaction with the metal.

XV. ACKNOWLEDGEMENTS

XVI. REFERENCES

1. D. L. Klayman and W. H. H. Gunther (Eds.), *Organic Selenium Compounds: Their Chemistry and Biology*, Wiley–Interscience, New York, 1973.
2. R. A. Zingaro and W. C. Cooper (Eds.), *Selenium*, Van Nostrand Reinhold, New York, 1974.
3. R. B. Silverman, in Ref., 1 p. 245.
4. K. A. Jensen, in Ref. 1, p. 263.
5. R. J. Shine, in Ref.1, p. 273.
6. H. G. Mautner, in Ref. 1, p. 497.
7. K. J. Irgolic and M. V. Kuchadker, in Ref. 2, p. 408.
8. K. J. Irgolic, *The Organic Chemistry of Tellurium*, Gordon and Breach, New York, 1974, pp. 52–55, 242–243.
9. W. Cooper, *Tellurium*, Van Nostrand, New York, 1971, p. 255.
10. D. Reid, *Organic Chemistry of Sulphur, Selenium and Tellurium*, Vols. 1–6, Royal Society of Chemistry, London, 1970–81.
11. P. D. Magnus, in *Comprehensive Organic Chemistry* (Eds. D. H. R. Barton and W. D. Ollis), Vol. 3 (Ed. D. N. Jones), Pergamon Press, Oxford, 1979, p. 489.

12. M. Renson, in *Organic Chemistry of Se and Te Containing Functional Groups* (Eds. S. Patai and Z. Rappaport), Vol. 1, (Eds.), Wiley, New York, 1985, p. 399.
13. International Union of Pure and Applied Chemistry, *Nomenclature of Organic Chemistry*, Pergamon Press, New York, 1979, pp. 247, 299.
14. A. Ohno, *Organic Chemistry of Sulfur* (Ed. S. Oae), Plenum Press, New York, 1977, p. 189.
15. T. G. Back, D. H. R. Barton, M. R. Britten-Kelly and F. S. Guziec, Jr., *J. Chem. Soc., Chem. Commun.*, 539 (1975).
16. A. G. Barrett, D. H. R. Barton and R. W. Read, *J. Chem. Soc., Chem. Commun.*, 645 (1979).
17. T. C. Wong, F. S. Guziec, Jr., and C. A. Moustakis, *J. Chem. Soc., Perkin Trans. 2*, 1471 (1983).
18. E. R. Cullen, F. S. Guziec, Jr., C. J. Murphy, T. C. Wong and K. K. Andersen, *J. Am. Chem. Soc.*, **103**, 7055 (1981).
19. L. Pauling, *The Nature of the Chemical Bond*, 3rd ed., Cornell University Press, Ithaca, N.Y., 1960, p. 224.
20. J. Hinze and H. H. Jaffe, *J. Am. Chem. Soc.*, **84**, 540 (1962); *J. Phys. Chem.*, **67**, 1501 (1963).
21. F. S. Guziec, Jr., L. J. SanFilippo, C. J. Murphy, C. A. Moustakis and E. R. Cullen, *Tetrahedron*, **41**, 4843 (1985).
22. W. H. Günther, in Ref. 1, p. 35.
23. K. W. Bagnall, *The Chemistry of Selenium, Tellurium and Polonium*, Elsevier, Amsterdam, 1966, pp. 10, 45.
24. F. Fehler, *Handbook of Preparative Inorganic Chemistry*, Vol. I, Academic Press, New York, 1963, p. 418.
25. N. Sonoda, K. Kondo, K. Nagano, N. Kambe and F. Morimoto, *Angew. Chem., Int. Ed. Engl.*, **19**, 308 (1980).
26. D. L. Klayman and T. S. Griffin, *J. Am. Chem. Soc.*, **95**, 197 (1973).
27. F. Fehler, in Ref. 24, p. 421.
28. J. E. Drake and B. M. Glavincevski, *Inorg. Synth.*, **20**, 171 (1980).
29. J. A. Gladysz, J. L. Hornby and J. E. Garbe, *J. Org. Chem.*, **43**, 1205 (1978).
30. J. S. Warner, *J. Org. Chem.*, **28**, 1642 (1963).
31. L. Henriksen and E. S. Kristiansen, *Int. J. Sulfur Chem. Part A*, **2**, 133 (1972).
32. W. -H. Pan, J. P. Fackler and H. W. Chen, *Inorg. Chem.*, **20**, 856 (1981).
33. W. H. Gunther, in Ref. 1, p. 44.
34. F. S. Guziec, Jr., and C. A. Moustakis, *J. Org. Chem.*, **49**, 189 (1984).
35. K. Steliou and M. Mrani, *J. Am. Chem. Soc.*, **104**, 3104 (1982).
36. N. Kambe, K. Kondo, S. Morita, S. Murai and N. Sonoda, *Angew. Chem., Int. Ed. Engl.*, **19**, 1009 (1980).
37. M. R. Detty and M. D. Seidler, *J. Org. Chem.*, **47**, 1354 (1982).
38. D. H. R. Barton and S. W. McCombie, *J. Chem. Soc., Perkin Trans. 1*, 1574 (1975).
39. A. Schröder, *Chem. Ber.*, **4**, 400 (1871).
40. G. Cole, *Chem. Ber.*, **8**, 1165 (1875).
41. L. Vanino and A. Schinner, *J. Prakt. Chem.*, **91**, 116 (1915).
42. R. E. Lyons and W. E. Brandt, *Chem. Ber.*, **60**, 824 (1927).
43. R. E. Lyons and E. D. Scudder, *Chem. Ber.*, **64**, 530 (1931).
44. R. Kuhn, *J. Chem. Soc.*, 605 (1938).
45. D. S. Margolis and R. W. Pittman, *J. Chem. Soc.*, 799 (1957).
46. H. J. Bridger and R. W. Pittman, *J. Chem. Soc.*, 1371 (1950).
47. L. Mortillaro, L. Credali, M. Mammi, and G. Valle, *J. Chem. Soc.*, 807 (1965).
48. L. Credali, M. Russo, L. Mortillaro, C. De Checchi, G. Valle and M. Mammi, *J. Chem. Soc. B*, 117 (1967).
49. L. Mortillaro, L. Credali, M. Russo and C. De Checchi, *J. Polym. Sci., Part B*, **3**, 581 (1965).
50. M. Russo, L. Mortillaro, L. Credali and C. De Checchi, *J. Polym. Sci., Part A1*, **4**, 248 (1966).
51. L. Szperl and W. Wiorogorski, *Rocz. Chem.*, **12**, 270 (1932).
52. T. G. Back, D. H. R. Barton, M. R. Britten-Kelly and F. S. Guziec, Jr., *J. Chem. Soc., Perkin Trans. 1*, 2079 (1976).
53. F. S. Guziec, Jr., and C. J. Murphy, *J. Org. Chem.*, **45**, 2890 (1980).
54. E. R. Cullen, F. S. Guziec, Jr., M. I. Hollander and C. J. Murphy, *Tetrahedron Lett.*, 4563 (1981).
55. E. R. Cullen, F. S. Guziec, Jr., and C. J. Murphy, *J. Org. Chem.*, **47**, 3563 (1982).
56. P. de Mayo, G. L. R. Petrasiunas and A. C. Weedon, *Tetrahedron Lett.*, 4621 (1978).
57. N. Y. M. Fung, *MSc Thesis*, University of Western Ontario, 1979.

58. R. Okazaki, A. Ishii, N. Fukuda, H. Oyama, and N. Inamoto, *J. Chem. Soc., Chem. Commun.*, 1187 (1982).
59. C.-P. Klages and J. Voss, *Angew. Chem., Int. Ed. Engl.*, **16**, 725 (1977).
60. G. A. Olah, T. Nakajima and G. K. Surya Prakash, *Angew. Chem., Int. Ed. Engl.*, **19**, 811 (1980).
61. F. S. Guziec, Jr., C. J. Murphy and E. R. Cullen, *J. Chem. Soc., Perkin Trans. 1*, 107 (1985).
62. F. S. Guziec, Jr., and C. A. Moustakis, *J. Chem. Soc., Chem. Commun.*, 63 (1984).
63. C. A. Moustakis and F. S. Guziec, Jr., American Chemical Society 187th National Meeting, St. Louis, Mo, April 1984, Abstract 135.
64. R. Okazaki, A. Ishii and N. Inamoto, *Tetrahedron Lett.*, **25**, 5147 (1984).
65. F. S. Guziec, Jr., C. A. Moustakis and L. J. SanFilippo, submitted for publication.
66. J. C. Scaiano and K. U. Ingold, *J. Chem. Soc., Chem. Commun.*, 205 (1976).
67. J. C. Scaiano and K. U. Ingold, *J. Phys. Chem.*, **80**, 1901 (1976).
68. J. C. Scaiano and K. U. Ingold, *J. Am. Chem. Soc.*, **99**, 2079 (1977).
69. J. C. Scaiano, *J. Am. Chem. Soc.*, **99**, 1494 (1977).
70. B. J. McKinnon, P. de Mayo, N. C. Payne and B. Ruge, *Nouv. J. Chim.*, **2**, 91 (1978).
71. N. Y. M. Fung, P. de Mayo, B. Ruge, A. C. Weedon and S. K. Wong, *Can, J. Chem.*, **58**, 6 (1980).
72. D. H. R. Barton and F. S. Guziec, Jr., unpublished work.
73. F. O. Rice and A. L. Glasebrook, *J. Am. Chem. Soc.*, **56**, 2381 (1934).
74. T. G. Pearson, R. H. Purcell and G. S. Saigh, *J. Chem. Soc.*, 409 (1938).
75. F. D. Williams and F. X. Dunbar, *J. Chem. Soc., Chem. Commun.*, 459 (1968).
76. W. H. Gunther, *J. Org. Chem.*, **32**, 3929 (1967).
77. V. I. Cohen, *J. Org. Chem.*, **42**, 2510 (1977).
78. J. W. Lewicki, W. H. Gunther and J. Y. Chu, *J. Org. Chem.*, **43**, 2672 (1978).
79. R. H. Judge and D. C. Moule, *J. Am. Chem. Soc.*, **106**, 5406 (1984).
80. H. Bock, S. Aygen, P. Rosmus, B. Solouki and E. Weissflog, *Chem. Ber.*, **117**, 187 (1984).
81. W. W. Sander and O. L. Chapman, *J. Org. Chem.*, **50**, 543 (1985).
82. C. Collard-Charon and M. Renson, *Bull. Soc. Chim. Belg.*, **71**, 563 (1962).
83. V. I. Cohen, *J. Org. Chem.*, **42**, 2645 (1977); *J. Heterocycl. Chem.*, **15**, 237 (1978); **15**, 1113 (1978); **16**, 365 (1979).
84. F. Malek-Yazdi and M. Yalpani, *J. Org. Chem.*, **41**, 729 (1976).
85. E. O. Fisher and S. Riedmüller, *Chem. Ber.*, **107**, 915 (1974).
86. M. Renson and R. Collienne, *Bull. Soc. Chim. Belg.*, **73**, 491 (1964).
87. I. Wallmark, M. H. Krackov, S.-H. Chu and H. G. Mautner, *J. Am. Chem. Soc.*, **92**, 4447 (1970).
88. K. A. Jensen, *Q. Rep. Sulfur Chem.*, **5**, 45 (1970).
89. L. Henriksen, *Synthesis*, 501 (1974).
90. D. H. R. Barton, P. E. Hansen and K. Picker, *J. Chem. Soc., Perkin Trans. 1*, 1723 (1977).
91. P.-E. Hansen, *J. Chem. Soc., Perkin Trans. 1*, 1627 (1980).
92. A. G. Barrett, R. W. Read and D. H. R. Barton, *J. Chem. Soc., Perkin Trans. 1*, 2184 (1980).
93. A. G. Barrett, R. W. Read and D. H. R. Barton, *J. Chem. Soc., Perkin Trans. 1*, 2191 (1980).
94. F. von Dechend, *Chem. Ber.*, **7**, 1273 (1874).
95. W. Becker and J. Meyer, *Chem. Ber.*, **37**, 2550 (1904); V. I. Cohen, *Synthesis*, 768 (1978).
96. V. I. Cohen, *Synthesis*, 668 (1978).
97. A. Ogawa, J.-I. Miyake, Y. Karasaki, S. Murai and N. Sonada, *J. Org. Chem.*, **50**, 384 (1985).
98. F. Malek-Yazdi and M. Yalpani, *Synthesis*, 328 (1977).
99. R. S. Sukhai, R. DeJong and L. Brandsma, *Synthesis*, 888 (1977).
100. M. Tisler, B. S. Tanovnik, Z. Zrimsek and C. Stropnik, *Synthesis*, 299 (1981).
101. D. H. Reid, R. G. Webster and S. McKenzie, *J. Chem. Soc., Perkin Trans. 1*, 2334 (1979).
102. M. P. Cava and L. E. Saris, *J. Chem. Soc., Chem. Commun.*, 617 (1975).
103. H. Hartmann, *Z. Chem.*, **11**, 60 (1971).
104. J. Liebscher and H. Hartmann, *Synthesis*, 521 (1976).
105. J. Becher, E. G. Frandsen, C. Dreier and L. Henriksen, *Acta Chem. Scand., Ser. B*, **31**, 843 (1977).
106. R. V. Kendall and R. A. Olofson, *J. Org. Chem.*, **35**, 806 (1970).
107. *Ger. Pat.*, 910, 199 (1954); *Chem. Abstr.*, **53**, 936h (1959).
108. H. G. Mautner, *J. Am. Chem. Soc.*, **78**, 5293 (1956).
109. F. Asinger, H. Berding and H. Offermanns, *Monatsh. Chem.*, **99**, 2072 (1968).
110. K. A. Jensen and P. H. Nielsen, *Acta Chem. Scand.*, **20**, 597 (1966).
111. C. O. Maese, W. Walter, H. Mrotzek and H. Mirzai, *Chem. Ber.*, **109**, 956 (1976).
112. J. Liebscher and H. Hartmann, *Tetrahedron*, **33**, 731 (1977).

113. K. A. Jensen and L. Henriksen, *Acta Chem. Scand.*, **21**, 1991 (1967).
114. R. S. Sukhai and L. Brandsma, *Synthesis*, 455 (1979).
115. A. Ogawa, J. -I. Miyake, S. Murai and N. Sonada, *Tetrahedron Lett.*, **26**, 669 (1985).
116. K. A. Lerstrup and L. Henriksen, *J. Chem. Soc., Chem. Commun.*, 1102 (1979).
117. Q. Mingoia, *Gazz. Chim. Ital.*, **56**, 835 (1926).
118. D. T. Lewis, *J. Chem. Soc.*, 831 (1940).
119. K. A. Jensen, L. Boje and L. Henriksen, *Acta Chem. Scand.*, **26**, 1465 (1972).
120. H. Ishihara and Y. Hirabayashi, *Chem. Lett.*, 203 (1976).
121. H. Ishihara, S. Sato and Y. Hirabayashi, *Bull. Chem. Soc. Jpn.*, **50**, 3007 (1977).
122. H. Ishihara, S. Muto and S. Kato, *Synthesis*, 128 (1986).
123. H. Ishihara and S. Kato, *Tetrahedron Lett.*, 3751 (1972).
124. K. A. Jensen, J. B. Carlsen, A. Holm and P. H. Nielsen, *Acta Chem. Scand.*, **17**, 550 (1963).
125. K. A. Jensen, in Ref. 1, p. 268.
126. K. A. Jensen and L. Henriksen, *Acta Chem. Scand.*, **24**, 3213 (1970).
127. C. Matz and R. Mattes, *Z. Naturforsch., Teil B*, **33**, 461 (1978).
128. B. Bak, O. J. Nielsen, H. Svanholt and A. Holm, *Chem. Phys. Lett.*, **55**, 36 (1978).
129. B. Bak, O. J. Nielsen, H. Svanholt and A. Holm, *Chem. Phys. Lett.*, **53**, 374 (1978).
130. A. Holm, C. Berg, C. Bjerre, B. Bak and H. Svanholt, *J. Chem. Soc., Chem. Commun.*, 99 (1979).
131. I. Lalezari, A. Shafiee and M. Yalpani, *Tetrahedron Lett.*, 5105 (1969).
132. H. Meier and I. Menzel, *Tetrahedron Lett.*, 445 (1972).
133. I. Lalezari, A. Shafiee and M. Yalpani, *J. Org. Chem.*, **38**, 338 (1973).
134. M. H. Ghandehari, D. Davalion, M. Yalpani and M. H. Partovi, *J. Org. Chem.*, **39**, 3906 (1974).
135. R. S. Sukhai and L. Brandsma, *Recl. Trav. Chim. Pays-Bas*, **98**, 55 (1979).
136. E. Schaumann and F. F. Grabley, *Tetrahedron Lett.*, **21**, 4251 (1980).
137. M. L. Petrov, V. Z. Laishev and A. A. Petrov, *Zh. Org. Khim.*, **15**, 2596 (1979).
138. S. L. Bender, N. F. Haley and H. R. Luss, *Tetrahedron Lett.*, **22**, 1495 (1981).
139. M. V. Lakshmikanthan, M. P. Cava, M. Albeck, L. Engman, F. Wudl and E. Ahran-Shalom, *J. Chem. Soc., Chem. Commun.*, 829 (1981).
140. M. V. Lakshmikanthan, M. P. Cava, M. Albeck, L. Engman, P. Carroll, J. Bergman and F. Wudl, *Tetrahedron Lett.*, **22**, 4199 (1981).
141. E. Bulka and K. -D. Ahlers, *Z. Chem.*, **3**, 348 (1963).
142. C. Collard-Charon and M. Renson, *Bull. Soc. Chim. Belg.*, **71**, 531 (1962).
143. I. B. Douglass, *J. Am. Chem. Soc.*, **59**, 740 (1937).
144. C. T. Pedersen, *Acta Chem. Scand.*, **17**, 1459 (1963).
145. H. Suzuki, M. Usuki and T. Hanafusa, *Synthesis*, 705 (1979).
146. E. A. Ebsworth and M. J. Mays, *J. Chem. Soc.*, 3893 (1963).
147. J. S. Thayer, *J. Organomet. Chem.*, **9**, 30 (1967).
148. H. Burger and U. Goetze, *J. Organomet. Chem.*, **10**, 380 (1967).
149. T. Gabrio and G. Barnikov, *Z. Chem.*, **9**, 183 (1969).
150. L. Hendriksen and J. Ehrbor, *Synthesis*, 519 (1976).
151. C. Collard-Charon and M. Renson, *Bull. Soc. Chim. Belg.*, **71**, 531 (1962).
152. T. Tarantelli and C. Pecile, *Ann. Chim. (Rome)*, **52**, 75 (1962).
153. W. J. Franklin and R. L. Werner, *Tetrahedron Lett.*, 3003 (1965).
154. D. H. R. Barton, G. Bringmann, G. Lamotte, W. B. Motherwell, R. S. Motherwell and A. E. Porter, *J. Chem. Soc., Perkin Trans. 1*, 2657 (1980).
155. H. Spies, K. Gewald and R. Mayer, *J. Prakt. Chem.*, **314**, 646 (1972).
156. K. A. Jensen and E. Fredericksen, *Z. Anorg. Allg. Chem.*, **230**, 31 (1936).
157. R. Huls and M. R. Renson, *Bull. Soc. Chim. Belg.*, **65**, 684 (1956); **66**, 265 (1957).
158. C. Collard-Charon, R. Huls and M. Renson, *Bull. Soc. Chim. Belg.*, **71**, 541 (1962).
159. E. Bulka and K. -D. Ahlers, *Z. Chem.*, **3**, 348 (1963).
160. C. T. Pedersen, *Acta Chem. Scand.*, **17**, 1459 (1963).
161. K. A. Jensen, G. Felbert, C. T. Pedersen and U. Svanholm, *Acta Chem. Scand*, **20**, 278 (1966).
162. E. Bulka, K. -D. Ahlers and E. Tucek, *Chem. Ber.*, **100**, 1373 (1967).
163. M. Lipp, F. Dallacker, I. Meir zu Köchen, *Monatsh. Chem.*, **90**, 41 (1959).
164. L. Henriksen, *J. Chem. Soc., Chem. Commun.*, 773 (1982).
165. H. G. Mautner and W. D. Kumler, *J. Am. Chem. Soc.*, **78**, 97 (1956).
166. E. Bulka, in Ref. 1, p. 459.
167. A. M. Comrie, D. Dingwall and J. B. Stenlake, *J. Pharm. Pharmacol.*, **16**, 268 (1964).

168. K. A. Jensen and C. K. Jorgensen, in Ref. 1, p. 1017; V. Krishnan and R. A. Zingaro, in Ref. 2, p. 337; H. J. Gysling, in *The Chemistry of Organic Se/Te Compounds* (Eds. S. Patai and Z. Rappaport).
169. M. Dräger and G. Gattow, *Angew. Chem., Int. Ed. Engl.*, **11**, 868 (1968).
170. M. Dräger and G. Gattow, *Chem. Ber.*, **104**, 1429 (1971).
171. L. Henriksen, *Acta Chem. Scand.*, **21**, 1981 (1967).
172. K. A. Jensen and U. Anthoni, *Acta Chem. Scand.*, **24**, 2055 (1970).
173. K. A. Jensen, P. A. Fredericksen and L. Henriksen, *Acta. Chem. Scand.*, **24**, 2061 (1970).
174. M. Narita and C. U. Pittman, Jr., *Synthesis*, 489 (1976).
175. K. Bechgaard, D. O. Cowan, A. N. Bloch and L. Henriksen, *J. Org. Chem.*, **40**, 746 (1975).
176. F. S. Guziec, Jr., G. C. Long and J. M. Russo, unpublished work.
177. E. M. Engler, B. A. Scott, S. Etemad, T. Penney and V. V. Patel, *J. Am. Chem. Soc.*, **99**, 5909 (1977).
178. I. Johannsen, K. Lerstrup, L. Henriksen and K. Bechgaard, *J. Chem. Soc., Chem. Commun.*, 89 (1984).
179. P. Shu, A. N. Block, T. F. Carruthers and D. O. Cowan, *J. Chem. Soc., Chem. Commun.*, 505 (1977).
180. F. Wudl and D. Nalewajek, *J. Chem. Soc., Chem. Commun.*, 866 (1980).
181. L. -Y. Chiang, T. O. Poehler, A. N. Block and D. O. Cowan, *J. Chem. Soc., Chem. Commun.*, 866 (1980).
182. K. Lerstrup, M. Lee, F. M. Wiygul, T. J. Kistenmacher and D. O. Cowan, *J. Chem. Soc., Chem. Commun.*, 294 (1983).
183. I. Johannsen, K. Bechgaard, K. Mortensen and C. Jacobsen, *J. Chem. Soc., Chem. Commun.*, 295 (1983).
184. V. Y. Lee, E. M. Engler, R. R. Schumaker and S. S. Parkin, *J. Chem. Soc., Chem. Commun.*, 235 (1983).
185. D. H. Reid, *J. Chem. Soc. C*, 3187 (1971).
186. D. J. Sandman, A. J. Epstein, T. J. Holmes and A. P. Fisher, III, *J. Chem. Soc., Chem. Commun.*, 177 (1977).
187. G. Scherowsky and J. Weiland, *Chem. Ber.*, 107, 3155 (1974).
188. E. M. Engler and V. V. Patel, *J. Chem. Soc., Chem. Commun.*, 671 (1975).
189. E. M. Engler and V. V. Patel, *Tetrahedron Lett.*, 1259 (1975).
190. G. Traverso, *Ann. Chim. (Rome)*, **47**, 1244 (1957).
191. L. Henriksen and E. S. Kristiansen, *Ann. N. Y. Acad. Sci.*, 101 (1972).
192. D. Barnard and D. T. Woodbridge, *J. Chem. Soc.*, 2922 (1961).
193. G. M. Larin, P. M. Solozhenkin, N. I. Kopitsya and H. Kirspuu, *Dokl. Akad. Nauk. Tadzh. SSR*, **12**, 32 (1969); *Chem. Abstr.*, **72**, 84787j (1970).
194. K. A. Jensen and V. Krishnan, *Acta Chem. Scand.*, **21**, 2904 (1967).
195. B. Lorenz and E. Hoyer, *Z. Chem.*, **8**, 230 (1968).
196. M. L. Shankaranarayana, *Acta Chem. Scand.*, **24**, 251 (1970).
197. U. Anthoni, *Acta Chem. Scand.*, **20**, 2742 (1966).
198. U. Anthoni, B. M. Dahl, C. Larsen and P. H. Nielsen, *Acta Chem. Scand.*, **24**, 959 (1970).
199. L. Henriksen, *Synthesis*, 771 (1982).
200. K. A. Jensen and A. Holm, *Acta Chem. Scand.*, **18**, 2417 (1964).
201. K. A. Jensen, P. A. Fredericksen and L. Henriksen, *Acta Chem. Scand.*, **24**, 2061 (1970).
202. N. Sonoda, G. Yamamoto and S. Tsutsumi, *Bull. Soc. Chem. Jpn.*, **45**, 2937 (1972).
203. K. A. Jensen, M. Due, A. Holm and C. Wentrup, *Acta Chem. Scand.*, **20**, 2091 (1966).
204. D. L. Klayman and R. J. Shine, *J. Org. Chem.*, **34**, 3549 (1969).
205. U. Anthoni, C. Larsen and P. H. Nielsen, *Acta Chem. Scand.*, **21**, 2571 (1967).
206. C. Collard-Charon and M. Renson, *Bull. Soc. Chim. Belg.*, **72**, 149 (1963).
207. V. I. Cohen, *Synthesis*, 60 (1980).
208. M. Giua and R. Bianco, *Gazz. Chim. Ital.*, **89**, 693 (1959).
209. H. Hope, *Acta Chem. Scand.*, **18**, 1800 (1964).
210. R. A. Zingaro, F. C. Bennett, Jr., and G. W. Hammar, *J. Org. Chem.*, **18**, 292 (1953).
211. F. C. Bennett, Jr., and R. A. Zingaro, *Org. Synth.*, Coll. Vol. **4**, 359 (1963).
212. L. C. King and R. J. Hlavacek, *J. Am. Chem. Soc.*, **73**, 1864 (1951).
213. H. G. Grimm and H. Metzger, *Chem. Ber.*, **69**, 1356 (1936).
214. K. A. Jensen, G. Felbert and B. Kägi, *Acta Chem. Scand.*, **20**, 281 (1966).

215. T. S. Griffin and D. L. Klayman, *J. Org. Chem.*, **39**, 3161 (1974).
216. Z. I. Yoshida, H. Konishi and H. Ogoshi, *J. Chem. Soc., Chem. Commun.*, 359 (1975).
217. H. Spies, K. Gewald and R. Mayer, *J. Prakt. Chem.*, **313**, 804 (1971).
218. A. Shafiee and I. Lalezari, *J. Heterocycl. Chem.*, **12**, 675 (1975).
219. A. Shafiee, F. Assadi and V. I. Cohen, *J. Heterocycl. Chem.*, **15**, 39 (1978).
220. H. Mautner and E. M. Clayton, *J. Am. Chem. Soc.*, **81**, 6270 (1959).
221. G. Wilke and E. Uhlemann, *Z. Chem.*, **14**, 288 (1974); **15**, 66 (1975).
222. Ref. 11, p. 523.
223. P. W. Preisler and T. N. Scortia, *J. Am. Chem. Soc.*, **80**, 2309 (1958).
224. A. Chiesi Villa, G. Grossoni, M. Nardelli and M. E. Vidoni Toni, *J. Chem. Soc., Chem. Commun.*, 404 (1969).
225. M. Mikolajczyk and J. Luczak, *Chem. Ind. (London)*, 76 (1972).
226. M. Z. Girshovich and V. El'tsov, *Zh. Obshch. Khim.*, **39**, 941 (1969).
227. M. F. Lappert, T. R. Martin and G. M. McLaughlin, *J. Chem. Soc., Chem. Commun.*, 635 (1980).
228. W. Paul and H. Werner, *Angew Chem., Int. Ed. Engl.*, **22**, 316 (1983).
229. H. Werner and W. Paul, *Angew. Chem., Int. Ed. Engl.*, **23**, 58 (1984).
230. C. E. Headford and W. A. Roper, *J. Organomet. Chem.*, **244**, C53 (1983).
231. W. A. Hermann, J. Weichmann, R. Serrano, K. Blechschmitt, H. Pfisterer and M. L. Ziegler, *Angew. Chem., Int. Ed. Engl.*, **22**, 314 (1983).
232. H. Fischer, S. Zeuner and J. Riede, *Angew. Chem., Int. Ed. Engl.*, **23**, 726 (1984).
233. H. Fischer and S. Zeuner, *Z. Naturforsch., Teil B*, **38**, 1365 (1983).
234. H. Fischer and S. Zeuner, *J. Organomet. Chem.*, **252**, C63 (1983).
235. C. G. Barraclough, R. L. Martin and I. M. Stewart, *Aust. J. Chem.*, **22**, 891 (1969); A. Davison and E. T. Shawl, *J. Chem. Soc., Chem. Commun.*, 670 (1967); *Inorg. Chem.*, **9**, 1820 (1970).
236. V. A. Alekseevskii, O. A. Ramazanova and L. A. Deryabina, *Zh. Neorg Khim.*, **23**, 545 (1978); *Chem. Abstr.*, **88**, 142408 (1978).
237. E. Uhlemann, *Int. Symp. Specific Interact. Mol. Ions, Proc., 3rd*, **2**, 539 (1976); *Chem. Abstr.*, **88**, 79947 (1978).
238. A. H. Schmidt, W. Ried and P. Pustoslemsek, *Angew. Chem., Int. Ed. Engl.*, **15**, 704 (1976).
239. G. Traverso, *Ann. Chim. (Rome)*, **47**, 3 (1957).
240. S. Bezzi, *Gazz Chim. Ital.*, **92**, 859 (1962).
241. S. Pietra, C. Garbuglio and M. Mammi, *Gazz. Chim. Ital.*, **94**, 48 (1964).
242. J. H. van den Hende and E. Klingberg, *J. Am. Chem. Soc.*, **88**, 5045 (1966).
243. M. R. Detty and H. R. Luss, *J. Org. Chem.*, **48**, 5149 (1983).
244. T. L. Gilchrist, P. G. Mente and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, 2165 (1972).
245. G. N. Schrauzer and H. J. Kisch, *J. Am. Chem. Soc.*, **95**, 2501 (1973).
246. K. H. Pannell, A. J. Mayr, R. Hoggard and R. C. Pettersen, *Angew. Chem., Int. Ed. Engl.*, **19**, 632 (1980).
247. A. J. Wittwer, L. Tsai, W. -M. Ching and T. Stadtman, *Biochemistry*, **23**, 4650 (1984).
248. J. W. Hoffman and K. P. McConnell, *Biochim. Biophys. Acta*, **366**, 109 (1974).
249. Y. S. Prasado Rao and J. D. Cherayil, *Life Sci.*, **14**, 2051 (1974).
250. C. -Y. Shiue and S. -H. Chu, *J. Chem. Soc., Chem. Commun.*, 319 (1975).
251. L. B. Townsend and G. H. Milne, *J. Heterocycl. Chem.*, **7**, 753 (1970).
252. S. -W. Chu, *J. Med. Chem.*, **14**, 254 (1971); **15**, 1088 (1972).
253. F. Bergmann and M. Rashi, *Isr. J. Chem.*, **7**, 63 (1969).
254. H. G. Mautner and J. J. Jaffe, *Cancer Res.*, **18**, 294 (1958).
255. H. G. Mautner, *Biochem. Pharmacol.*, **1**, 169 (1959).
256. S. -H. Chu, C. -Y. Shiue and M. Y. Chu., *J. Med. Chem.*, **18**, 559 (1975); *J. Pharm. Sci.*, **64**, 1343 (1975).
257. K. C. Agrawal, B. A. Booth, R. L. Michand, E. C. Moore and A. C. Santorelli, *Biochem. Pharmacol.*, **23**, 2421 (1976).
258. H. G. Mautner, W. D. Kumler, Y. Okono and R. Pratt, *Antibiot. Chemother.*, **6**, 51 (1956).
259. K. Bednarz, *Diss. Pharm.*, **9**, 249 (1957); *Chem. Abstr.*, **52**, 8083f (1958).
260. E. R. Cullen, F. S. Guziec, Jr., C. J. Murphy and T. C. Wong, *J. Chem. Soc., Perkin Trans. 1*, 473 (1982).
261. W. Gombler, *Z. Naturforsch., Teil B*, 1561 (1981).
262. W. Gombler, *J. Am. Chem. Soc.*, **104**, 6616 (1982).
263. K. A. Jensen and J. Sandstrom, *Acta Chem. Scand.*, **23**, 1911 (1969).

264. U. Svanholm, *Ann. N. Y. Acad. Sci.*, **192**, 124 (1972).
265. P. Hampson and A. Mathias, *Mol. Phys.*, **13**, 361 (1967).
266. W. Walter, E. Schaumann and H. Rose, *Tetrahedron*, **28**, 3233 (1972).
267. K. A. Jensen, L. Henriksen and P. H. Nielsen, in Ref. 1, pp. 843–851.
268. K. K. Andersen, D. M. Gash, J. D. Robertson and F. S. Guziec, Jr., *Tetrahedron Lett.*, **23**, 911 (1982).
269. W. M. Wijekoon, E. Bunnenberg, R. Records and D. A. Lightner, *J. Phys. Chem.*, **87**, 3034 (1983).
270. J. E. Kuder, in Ref. 1, pp. 872–874.
271. A. M. Kirkien, R. J. Shine and J. R. Plimmer, *Org. Mass Spectrom.* **7**, 233 (1973).
272. F. S. Guziec, Jr., and C. A. Moustakis, *Phosphorus Sulfur*, **21**, 189 (1984).
273. F. Fringuelli and A. Taticchi, *J. Heterocycl. Chem.*, **15**, 137 (1978).
274. Ref. 6, p. 500.
275. R. Mayer, S. Scheithauer and D. Kunz, *Chem. Ber.*, **99**, 1393 (1966).
276. C. -P. Klages and J. Voss, *Chem. Ber.*, **113**, 2255 (1980).
277. W. E. Britton, E. Alaydros, R. Kashyap, J. Blair and F. S. Guziec, Jr., unpublished work.
278. C. Dreier, J. Becher, E. G. Frandsen and L. Henriksen, *Tetrahedron*, **37**, 2663 (1981).
279. H. G. Mautner and G. Bergson, *Acta Chem. Scand.*, **17**, 1694 (1963).
280. A. Azman, M. Drofenik, D. Hadzi and B. Lukman, *J. Mol. Struct.*, **1**, 181 (1968).
281. I. J. Karle and J. Karle, in Ref. 1, p. 989.
282. A. W. Cordes, in Ref. 2, p. 298.
283. H. Hope, *Acta Crystallogr.*, **18**, 259 (1965).
284. M. Perez-Rodriguez and A. Lopez-Castro, *Acta Crystallogr., Sect. B*, **25**, 532 (1969).
285. J. S. Rutherford and C. Calvo, *Z. Kristallogr.*, **128**, 229 (1969).
286. E. Shefter, M. N. James and H. G. Mautner, *J. Pharm. Sci.*, **55**, 643 (1966).
287. M. Bonamico and G. Dessy, *J. Chem. Soc., Chem. Commun.*, 1114 (1967).
288. G. U. Tsintsadze, M. A. Porai-Koshits and A. S. Antsyshkina, *J. Struct. Chem.*, **8**, 253 (1967).

NOTE ADDED IN PROOF

Recently three papers have appeared dealing with the preparation and trapping of intermediate monomeric selenoaldehydes:

R. Okazaki, A. Ishii and N. Inamoto, *J. Chem. Soc., Chem. Commun.*, 71 (1986).
G. W. Kirby and A. N. Trethewey, *J. Chem. Soc., Chem. Commun.*, 1152 (1986).
G. A. Krafft and P. T. Meinke, *J. Am. Chem. Soc.*, **108**, 1314 (1986).

CHAPTER **5**

Photochemistry of organic compounds of selenium and tellurium

ZEEV GOLDSCHMIDT

Department of Chemistry, Bar Ilan University, Ramat-Gen, Israel

I. INTRODUCTION

The photochemistry of organic selenium and tellurium compounds has attracted much less attention than the light-induced reactions of the early organochalcogen derivatives of oxygen[1,2] and sulfur[3,4]. Although the sensitivity to sunlight of dibenzyl diselenide (1), one of the most common selenium compounds, has been known since 1875[5], the mechanistic details of this photofragmentation lay dormant for nearly a century[6]. It seems that the frequently observed deposition of elemental selenium and tellurium during photolyses, although a very useful process in photography, deterred chemists from exploring the fate of the organic residue. Accordingly, it is perhaps not surprising that photoreactions of the heavier organochalcogens are hardly mentioned in comprehensive treatises on the chemistry of these compounds[7,8], and that the single photochemical review appeared only in 1980[9].

$$PhCh_2SeSeCH_2Ph$$

$$(1)$$

The last decade has witnessed substantial progress in the understanding of the physical and chemical consequences of the electronic excitation of organoselenium and tellurium compounds. In general, it is found that whereas in organic oxygen compounds carbonyl excited states play the major role in the photochemical transformations, selenium and tellurium derivatives, like their sulfur counterparts, react mainly via homolytic cleavage of sigma bonds.

This chapter intends to provide a comprehensive review of the synthetic and mechanistic aspects of the photochemistry of the heavier organochalcogen compounds. It is organized according to reaction types, that is, dissociative and associative processes, rearrangements and isomerizations, oxidations and reductions. Because of the relatively few photoreactions of tellurium compounds, and their resemblance to those of selenium derivatives, both groups will be discussed together. It is hoped that this chapter will provide the reader with a framework for identifying unexploited areas of the organic photochemistry of selenium and tellurium compounds, and help stimulate further progress in this growing field of research.

II. PHOTODISSOCIATIVE PROCESSES

A. Photofragmentation

The homolylic cleavage of a sigma bond between a chalcogen and another atom, to form radicals, is the most common primary process in the photochemistry of organo-selenium and tellurium compounds. In the absence of ground-state molecules to react with these radicals, they may recombine to form the starting material, or dispropor-tionate by a variety of routes. The chemistry of these disproportionation reactions will be examined in this section.

1. Cleavage of Se—C and Te—C bonds

A unique cleavage of an aliphatic selenide bond is observed when selenide **2** is irradiated in benzene solutions in the presence of p-toluenesulfonic acid, yielding acetylacetone (**3**) and PhSeOTs (**4**) (equation 1)[10].

$$\text{MeCOCH(SePh)COMe} \xrightarrow[\text{PhH},p\text{-TsOH}]{h\nu} \text{MeCOCH}_2\text{COMe} + \text{PhSeOTs} \qquad (1)$$

$$\qquad\quad(2)\qquad\qquad\qquad\qquad (3)\qquad\qquad (4)$$

The photochemistry of aromatic selenol esters has been studied extensively. These esters usually undergo photo-Fries type rearrangements (Section IV.A). However, in some cases the main products are formed only by cleavage. Irradiation of the diselenol ester **5** gave high yields of anthraquinone (**6**) and bis(p-tolyl selenide) (**7**) (equation 2)[11].

$$+\ (p\text{-Tol})_2\text{Se}_2 \qquad (2)$$

(5)   (6)   (7)

When the selenoester **8** was photolysed, the major products observed were methyl sulfinyl acid (**9**) (41% yield) and **7** (49%) (equation 3)[12]. Photolysis of selenoester **10** gave, among other substitution products (Section III.A.1.c), a 22% yield of **11** in a presumably photo-Friedel–Crafts reaction[13] (equation 4). No cyclization products were obtained when aliphatic sulfides were irradiated. In a similar photo-Friedel–Crafts reaction of the nicotinic ester **12**, selenoxanthone (**13**) was obtained in 15% yield[14] (equation 5).

$$+\ 7 \qquad (3)$$

(8)   (9)

$$+\ 7 \qquad (4)$$

(10)   (11)

$$+\ 7 \qquad (5)$$

(12)   (13)

Telluroester (14) undergo homolysis on irradiation in dry benzene solutions[15] to give aldehydes (17) and bis(p-tolyl telluride) (18) (equation 6). The mechanism is believed to involve α-cleavage to radicals 15 and 16, followed by hydrogen abstraction by 15 and dimerization of 16, to give the observed products. Although the origin of the hydrogen atom abstracted was not determined, it may be derived from the solvent. As with the selenium analogs, small amounts of photo-Fries rearrangement products are obtained (Section IV.A) together with some elemental tellurium. In the case of the photolysis of 19[16], an intramolecular substitution occurred giving 20 (Section III.A.1) (equation 7).

(6)

(7)
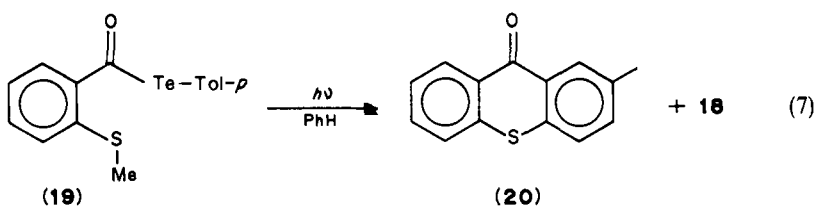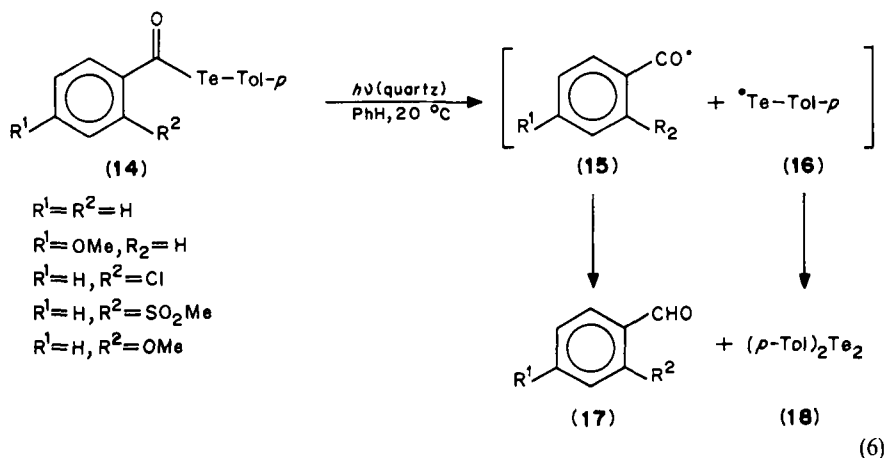
An unusual ylid selenium—carbon bond rupture on irradiation of 21 at 238 nm in chloroform was reported[17]. Dimethyl selenide (22) and phenacylcarbene (23) are the primary products. The latter trimerizes in two steps, via dibenzoylethylene (24), to trans-tribenzoylcyclopropane (25), as shown in equation 8.

$$Me_2Se=CHCOPh \xrightarrow[CHCl_3]{h\nu} Me_2Se + :CHCOPh \xrightarrow{:CHCOPh} PhCOCH=CHCOPh$$

(21)   (22)   (23)   (24)

(8)

(25)
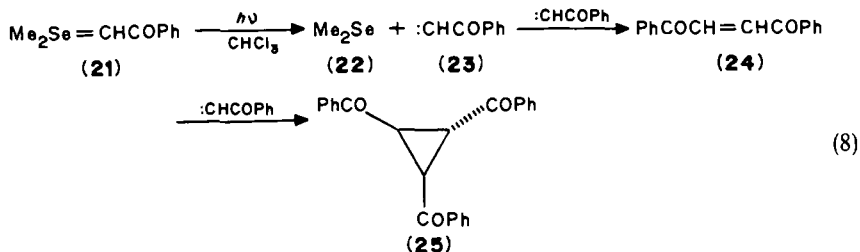
There are only a few known examples of the photochemical cleavage of a sigma bond between selenium and an aromatic carbon. Direct evidence for the homolysis of

bis(p-methoxyphenyl) selenide (**26**) to the selenide radical **27** was obtained from pulse radiolysis studies[18], in which the transition absorption spectrum of **27** (λ_{max}535nm) was observed in neutral or acidic methanolic solutions (equation 9). Similarly, pulse irradiated solutions of the diselenide **28** give the transient absorption spectrum of the diselenide radical **29** (λ_{max} 600nm) (equation 10). Here the spectrum of radical **27** also appeared as a result of the homolytic cleavage of the Se—Se bond. The decay of the 535nm absorption in irradiated solutions of **26** followed pseudo-first-order kinetics with a rate constant $k = 8 \times 10^5 \mathrm{lmol}^{-1}\mathrm{s}^{-1}$. Pulse radiolysis of methanolic solutions of bis(p-methoxyphenyl) telluride (**30**) similarly gave telluride radicals **31** (λ_{max} 508nm), which decay faster ($k = 1.5 \times 10^{10}\mathrm{lmol}^{-1}\mathrm{s}^{-1}$) (equation 11)[18].

$$\mathrm{Ar_2Se} \xrightarrow[\mathrm{MeOH}]{e_s^-} \mathrm{ArSe^{\cdot}} + \mathrm{ArH} \qquad\qquad (9)$$

$$\qquad (26) \qquad\qquad (27)$$

$$\mathrm{Ar_2Se_2} \xrightarrow[\mathrm{MeOH}]{e_s^-} \begin{array}{l} \mathrm{ArSeSe^{\cdot}} + \mathrm{ArH} \\ \quad (29) \\[2ex] \mathrm{ArSe^{\cdot}} + \mathrm{ArSeH} \\ \quad (27) \end{array} \qquad (10)$$

$$(28)$$

$$\mathrm{Ar_2Te} \xrightarrow[\mathrm{MeOH}]{e_s^-} \mathrm{ArTe^{\cdot}} + \mathrm{ArH} \qquad\qquad (11)$$

$$\quad (30) \qquad\qquad (31) \qquad\qquad \mathrm{Ar} = p\text{-methoxyphenyl}$$
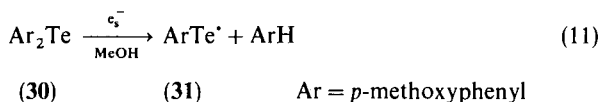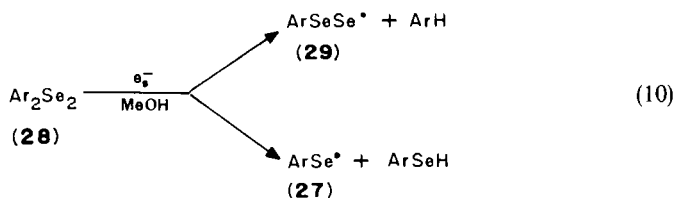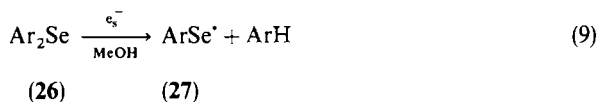
Cleavage of the Se—Ph bond was also observed in the sunlight-induced transfer reaction between triphenylselenonium fluoroborate (**32**) and triphenylphosphine (**33**) to form diphenyl selenide (**34**) and tetraphenylphosphonium fluoroborate (**35**)[19] (equation 12). The homolytic character of this reaction is evident from the isolation of small amounts of benzene, which apparently result from hydrogen abstraction from the solvent by phenyl radicals.

$$\mathrm{Ph_3SeBF_4} + \mathrm{Ph_3P} \xrightarrow[\text{acetone}]{\text{Sunlight}} \mathrm{Ph_2Se} + \mathrm{Ph_4PBF_4} + \mathrm{PhH} \qquad (12)$$

$$(32) \qquad (33) \qquad\qquad (34) \qquad (35)$$
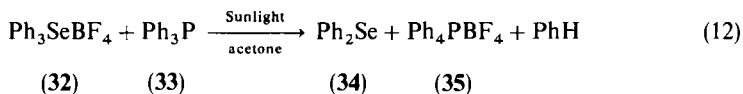
2. Cleavage of Se—Se and Te—Te bonds

Shortwave UV irradiation of diphenyl diselenide (**36**) in high vacuum gave phenylselenyl radicals (**37**), which were detected by ESR measurements (equation 13)[20]. These radicals are thermally more stable than the corresponding sulfide radicals, and recombine back to **36** only at temperatures above 77 K.

$$\mathrm{PhSeSePh} \xrightarrow{hv} \mathrm{PhSe^{\cdot}} \qquad\qquad (13)$$

$$(36) \qquad\qquad (37)$$

As has been shown above (equation 10), pulse radiolysis of bis(p-methoxyphenyl selenide) (**28**) affords selenide (**27**) and diselenide (**29**) radicals. The corresponding ditellurides (**38**) on radiolysis gave only telluride radicals (**31**), which absorb at λ_{max} 508 nm

(equation 14)[18].

$$ArTeTeAr \xrightarrow[\text{MeOH}]{e_s^-} ArTe^\cdot + ArTeH \qquad (14)$$

$$(38) \qquad\qquad (31)$$
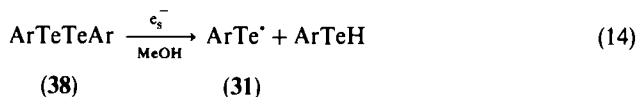
Ar = p-methoxyphenyl

A kinetic study of the photochemical degradation of bis(p-ethoxyphenyl telluride) (38, Ar = p-ethoxyphenyl) in toluene solutions containing ethanol revealed[21] that in the rigorous exclusion of oxygen no reaction occurred. However in the presence of even catalytic amounts of oxygen the ditelluride decomposes after a short induction period, with a rate half order in ditelluride (equation 15). The reaction is also first order in ethanol, but independent of temperature.

$$[Ar_2Te_2]^{1/2} = constant - k_{obs}t \qquad (15)$$

ESR findings indicate that a homolytic Te—Te bond cleavage took place, yielding ArTe radicals. Since the overall reaction is not independent of ditelluride concentration, two ditelluride molecules must be involved in the radical production. Molecular oxygen is obviously also involved at an early stage of the reaction. Consequently, a reaction sequence is proposed which includes the essential steps shown in equations 16–18. Both reaction products, 39 and 40, are unstable and oxidize immediately on exposure to oxygen, to give 41.

$$Ar_2Te^* + O_2 \longrightarrow Ar_2Te_2O_2 \qquad (16)$$

$$Ar_2Te_2O_2 + Ar_2Te_2 \longrightarrow 2ArTe^\cdot + Ar_2Te_2 + O_2 \qquad (17)$$

$$[2ArTe^\cdot + EtOH \longrightarrow ArTeCH(Me)OH + ArTeH \xrightarrow{[O]} (ArTe)_2O] \qquad (18)$$

$$(39) \qquad\qquad (40) \qquad\qquad (41)$$
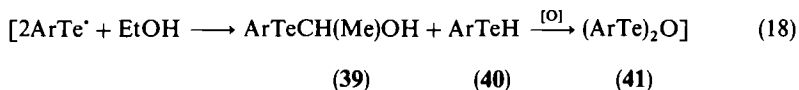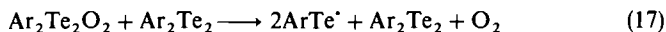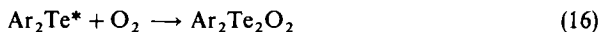
Ar = p-ethoxyphenyl

3. Cleavage of bonds between Se and other atoms

a. Selenium–sulfur.   Phenyl areneselenosulfonates (42) are unusually photosensitive. Irradiation of 42 through Pyrex, in degassed carbon tetrachloride, led to its complete decomposition. The identifiable products of decomposition were diphenyl diselenide (36) and arenesulfonic anhydride (43) (32% yield) (equation 19)[22]. These products are believed to arise as a result of the reaction sequence shown in equations 20–23, initiated by the homolytic photodissociation of 42 into PhSe and $ArSO_2$ radicals (equation 20). It should be noted that at some stage oxidation must occur, presumably of the intermediate dimer of $ArSO_2$ (equation 22).
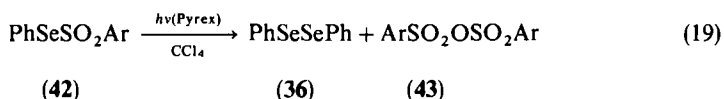
$$PhSeSO_2Ar \xrightarrow[\text{CCl}_4]{hv(Pyrex)} PhSeSePh + ArSO_2OSO_2Ar \qquad (19)$$

$$(42) \qquad\qquad (36) \qquad (43)$$

Ar = Ph, p-tolyl

$$PhSeSO_2Ar \longrightarrow PhSe^{\cdot} + ArSO_2^{\cdot} \tag{20}$$

$$PhSe^{\cdot} + PhSeSO_2Ar \longrightarrow PhSeSePh + ArSO_2^{\cdot} \tag{21}$$

$$2ArSO_2^{\cdot} \longrightarrow [ArSOOSO_2Ar] \xrightarrow{[O]} ArSO_2OSO_2Ar \tag{22}$$

$$2PhSe^{\cdot} \longrightarrow PhSeSePh \tag{23}$$
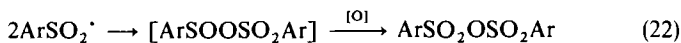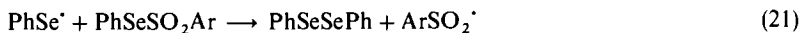
b. Selenium–germanium. The irradiation of triethylgermylselenol (**44**) in the presence of olefins usually gives addition products[23] (Section III.B). However, when **44** was irradiated in the presence of equimolar amounts of acrylonitrile, a 76.7% yield of hexaethyldigermselenane (**45**) was obtained, clearly indicating cleavage of the Se—Ge bond (equation 24).

$$Et_3GeSeH \xrightarrow{h\nu(Pyrex)} (Et_3Ge)_2Se \tag{24}$$

$$\begin{array}{cc} & 77\% \\ \textbf{(44)} & \textbf{(45)} \end{array}$$
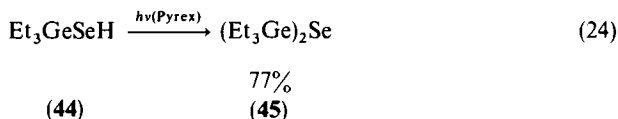
B. Photoeliminations

1. Deselenation and detelluration

The loss of a selenium or tellurium atom during the irradiation of organochalcogen compounds is a very common reaction. Early gas-phase flash photolysis studies of CSe_2[24,25] (equation 25) and $COSe$[24,26] (equation 26) revealed the presence of excited selenium atoms in the photolysis mixture. These may react with a variety of hydrocarbons and olefins to give insertion products, (Section III.D).

$$CSe_2 \xrightarrow{flash\ h\nu} CSe(X'\Sigma) + Se(4^3P_y) \tag{25}$$

$$COSe \xrightarrow{flash\ h\nu} CO + Se(4^1D_2) \tag{26}$$
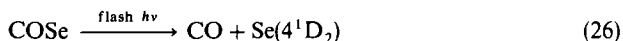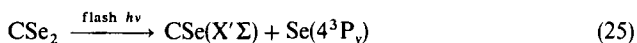
Flash photolysis of dimethyl telluride (**46**) is a useful source of triplet excited tellurium atoms (equation 27)[27]. Thus, inspection of flashed mixtures of **46** vapor (10^{-3}–10^{-5} Torr with CO_2 diluent), using kinetic absorption spectroscopy, showed intense atomic absorptions at $\lambda 214.3$ and 225.9 nm, corresponding to transitions of $Te(^3P_2)$, and at 238.6 and 238.3 nm, corresponding to $Te(^3P_1)$ and $(^3P_0)$, respectively. In addition, Σ–Σ type transitions of the Te_2 molecule appeared between 360 and 430 nm. At low initial pressures of **46**, the 216 nm absorption of the methyl radical was detected. From flash energy variations, the carrier of a series of four bands between 224 and 243 nm appears to be the primary photoproduct, the MeTe radical.

$$Me_2Te \xrightarrow[CO_2]{flash\ h\nu} Te(^3P_{2,1,0}) \tag{27}$$

$$\textbf{(46)}$$
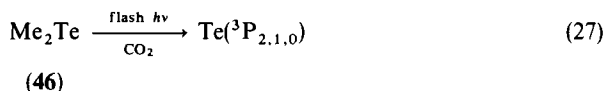
As an alternative source of Te atoms, the flash photolysis of H_2Te was examined. Ground-state and spin–orbit excited Te atoms were observed along with Te_2. A transient species absorbing at 215.5 nm was detected and was assigned as the HTe radical[27]. This

represents a unique case of a photohomolytic cleavage of a Te—H bond (equation 28).

$$H_2Te \xrightarrow{h\nu} HTe^{\cdot} + H^{\cdot} \longrightarrow Te \tag{28}$$
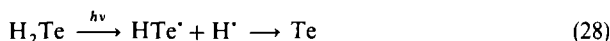
Dibenzyl diselenide (1) was the first organoselenium compound whose photochemistry was studied in solution[28]. Irradiation in benzene at 350 nm, in the absence of atmospheric oxygen, gave a 60% yield of isolable monoselenide (47) (equation 29).

$$PhCH_2SeSeCH_2Ph \xrightarrow[\text{PhH}]{h\nu \ (350\,nm)} PhCH_2SeCH_2Ph + Se \tag{29}$$

$$\textbf{(1)} \hspace{5cm} \textbf{(47)}$$
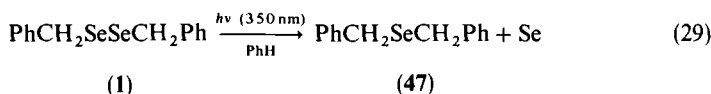
Detailed kinetic and mechanistic studies of the deselenation of 1 were carried out in acetonitrile using light of $\lambda > 280$ nm (Pyrex filter)[6]. First, it was established that 47 and a stoichiometric amount of red amorphous selenium are the sole products of the reaction. The observed quantum yield for the disappearance of 1 (at 313 nm) was $\phi = 0.16 \pm 0.02$ at low conversions, and the initial rates of the photodecomposition were found to be dependent on the light intensity, but not on the concentration (equation 30).

$$d(1)/dt = kI_a \tag{30}$$

where I_a = intensity of light absorption by 1;

$$PhCH_2SeSeCH_2Ph \underset{}{\overset{h\nu}{\rightleftharpoons}} 2PhCH_2Se^{\cdot} \tag{31}$$

$$\textbf{(1)} \hspace{4cm} \textbf{(48)}$$

$$PhCH_2SeSeCH_2Ph \underset{}{\overset{h\nu}{\rightleftharpoons}} PhCH_2^{\cdot} + PhCH_2SeSe^{\cdot} \tag{32}$$

$$\textbf{(1)} \hspace{3cm} \textbf{(49)} \hspace{1.5cm} \textbf{(50)}$$
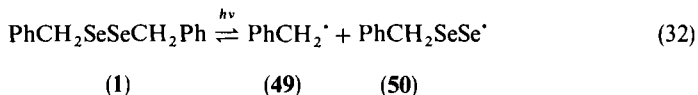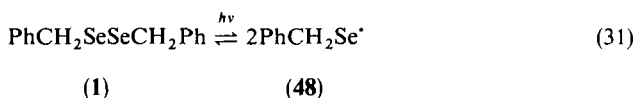
Since under the irradiation conditions ($\lambda 310$ nm ≈ 92 kcal) both the Se—Se bond (44 kcal) and the C—Se bond (57 kcal) may cleave, it is reasonable to suppose that the two primary processes involve homolytic cleavage of these bonds in 1 (equations 31 and 32). The presence of benzyl selenide radicals (48) in the reaction mixture was confirmed by trapping 48 with carbon tetrachloride, to give benzyl chloride. However, since the disappearance of 1 is dependent on the light intensity but not on the concentration, only the homolytic cleavage of the C—Se bond to produce benzyl (49) and benzyl diselenyl (50) radicals leads to products, whereas benzyl selenide (48) radicals are inactive except for recombination to 1. This is consistent with the non-chain radical mechanism shown in equations 33–40, for which the rate equation has the form depicted in equation 30, where $k = k_3/(k_1 + k_2 + k_3)$.

$$RSeSeR \xrightarrow{h\nu} RSeSeR^* \tag{33}$$

$$R = PhCH_2$$

$$RSeSeR^* \xrightarrow{k_1} RSeSeR \tag{34}$$

$$RSeSeR^* \xrightarrow{k_2} 2RSe^{\cdot} \tag{35}$$

$$RSeSeR^* \xrightarrow{k_3} R^{\cdot} + RSeSe^{\cdot} \tag{36}$$

$$RSeSe^{\cdot} \xrightarrow{k_4} RSe^{\cdot} + Se \tag{37}$$

$$R^{\cdot} + RSeSeR \xrightarrow{k_5} RSe^{\cdot} + RSeR \tag{38}$$

$$R^{\cdot} + RSe^{\cdot} \xrightarrow{k_6} RSeR \tag{39}$$

$$2RSe^{\cdot} \xrightarrow{k_7} RSeSeR \tag{40}$$

An important conclusion that can be drawn from the above scheme is that benzylselenyl radicals (**48**) do not dissociate to Se and benzyl radicals under normal photolytic conditions. However, in the presence of Ph_3P, the diselenation reaction takes a different course[29]. In addition to the expected dibenzyl selenide (**47**) and triphenylphosphine selenide (**52**), bibenzyl (**51**) is formed (equation 41). Further, the quantum yields for disappearance of **1** are dependent on the concentration of Ph_3P, and rise to $\phi > 1.0$. This suggests a radical chain mechanism, shown in equations 42–46, in which benzylselenyl radicals (**38**), obtained from the homolytic dissociation of **1**, play a crucial part in the reaction.

$$PhCH_2SeSeCH_2Ph + Ph_3P \xrightarrow[\text{MeCN}]{hv} PhCH_2SeCH_2Ph + PhCH_2CH_2Ph + Ph_3PSe$$

$$\text{(1)} \qquad\qquad\qquad\qquad \text{(47)} \qquad\qquad \text{(51)} \qquad \text{(52)}$$

$$\tag{41}$$

$$RSeSeR \longrightarrow 2RSe^{\cdot} \tag{42}$$

$$RSe^{\cdot} + Ph_3P \longrightarrow Ph_3PSeR \tag{43}$$

$$Ph_3PSeR \longrightarrow R^{\cdot} + Ph_3PSe \tag{44}$$

$$R^{\cdot} + RSeSeR \longrightarrow RSeR + RSe^{\cdot} \tag{45}$$

$$2R^{\cdot} \longrightarrow RR \tag{46}$$

Dibenzyl ditelluride (**53**) and diethyl ditelluride (**54**), like their selenium counterparts, react quantitatively under UV irradiation to give tellurium and the corresponding tellurides (**55 and 56**)[30,31] (equation 47). The benzyl derivatives photolyse more rapidly than the corresponding ethyl compounds[31]. Dibenzyl telluride (**55**) itself is both thermal and light sensitive, decomposing readily to Te and bibenzyl (**51**). Cleavage of the ditellurides, like that of selenides, is accelerated in the presence of tertiary phosphines (**57**), affording the corresponding phosphine tellurides (**58**). The latter decompose back to **57** and Te, forming an equilibrium mixture shown in equation 48. However, unlike selenides, the increase in reaction rates is not marked, suggesting that C—Te bond cleavage in alkyltellurium compounds predominates over the rupture of Te—Te bonds. In general, it appears that the difference in reactivity between the selenium and tellurium compounds lies in the fact that Se—Se bond cleavage occurs more readily than that of a C—Se bond, whereas the opposite is true for the tellurium analogs.

$$RTeTeR \xrightarrow[\text{CDCl}_3]{hv} RTeR + Te \tag{47}$$

$$\text{(53)} \qquad\qquad \text{(55)} \qquad R = PhCH_2$$
$$\text{(54)} \qquad\qquad \text{(56)} \qquad R = Et$$

$$RTeTeR + R^1R^2R^3P \xrightarrow{hv} RTeR + R^1R^2R^3PTe \rightleftharpoons R^1R^2R^3P + Te \qquad (48)$$

$$(57) \qquad\qquad (58)$$

$$R = Et, PhCH_2; \ R^1 = R^2 = Ph, \ R^3 = Me; \ R^1 = R^2 = Ph, \ R^3 = CH_2PPh_2$$

An interesting photoextrusion of selenium from bis(9-anthrylmethyl selenide) (59) in the presence of Ph_3P has been reported to give two isomeric dimers, hydrocarbons 60 and 61, in a ratio of 3:1 (equation 49)[32,33]. The proposed mechanism involves the initial deselenation of 59 to the anthrylmethyl radical 62, which first dimerizes to a mixture of hydrocarbons 63 and 64, followed by a thermal intramolecular 4 + 2 cycloaddition (Diels–Alder reaction) of 63 to give 60, and a photochemical 4 + 4 cycloaddition of 64[34] to dimer 61.

$$(49)$$
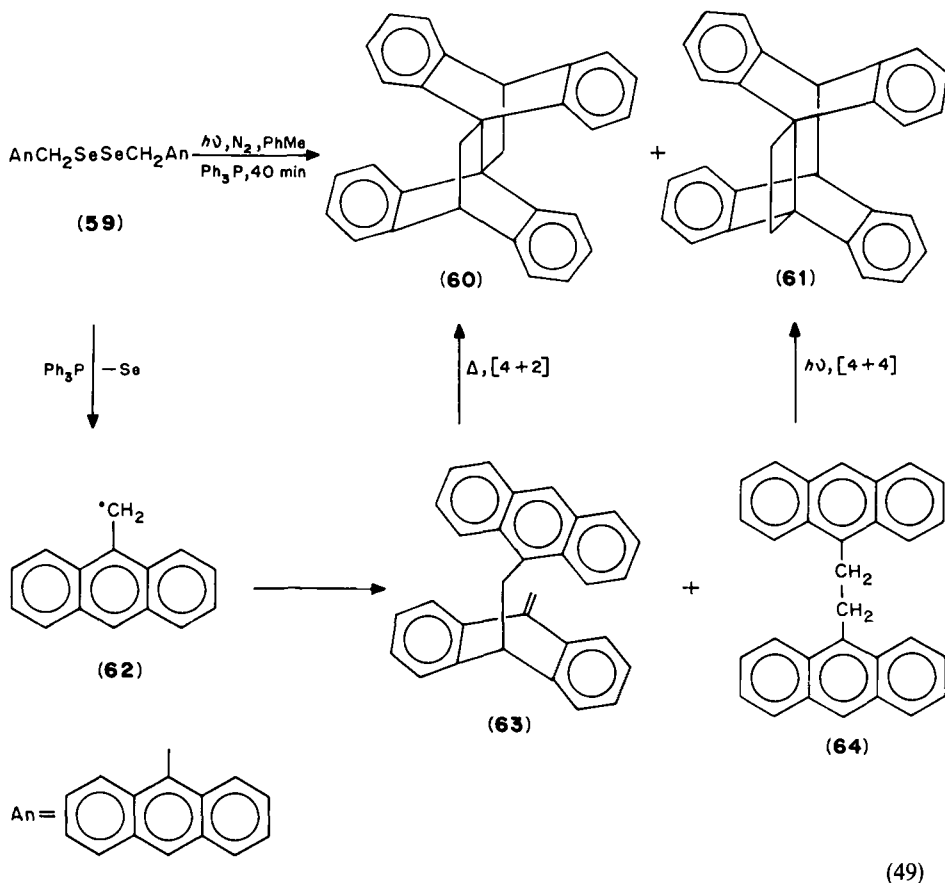
The photolysis of bis(2-cyanoethyl) selenide (65) and bis[2-(methoxycarbonyl)ethyl] selenide (69) gave a complex mixture of products derived from the homolytic cleavage of the Se—C bonds[35]. The composition of the mixture was strongly solvent dependent. In methanol, 65 decomposed mainly to elemental Se and traces of H_2Se and acrylonitrile (66) (equation 50). In THF solutions, the major product was bis(2-cyanoethyl selenide) (67)

together with small amounts of adduct **68**, H_2Se and **66** (equation 51). Photolysis of **69** in methanol solutions afforded mainly Se together with small amounts of methyl adipate (**70**) and methyl acrylate (**71**). In THF solutions, moderate amounts of **70** were obtained with essentially quantitative formation of elemental Se (equation 52).

$$Se(CH_2CH_2CN)_2 \xrightarrow[\text{MeOH}]{h\nu} Se + H_2Se + CH_2 = CHCN \tag{50}$$

<div align="center">

(**65**)   (**66**)

66% traces traces

</div>

$$Se(CH_2CH_2CN)_2 \xrightarrow{h\nu}_{THF} Se + (SeCH_2CH_2CN)_2 + \tag{51}$$

33% 66%   6%

(**67**)   (**68**)

$$Se(CH_2CH_2COOMe)_2 \xrightarrow{h\nu} Se + (CH_2CH_2COOMe)_2 + CH_2 = CHCOOMe$$

<div align="center">

(**69**)   (**70**)   (**71**)

</div>

MeOH:	54%	1%	1%	(52)
THF:	100%	10%	traces	
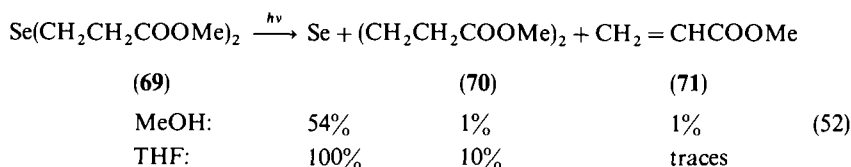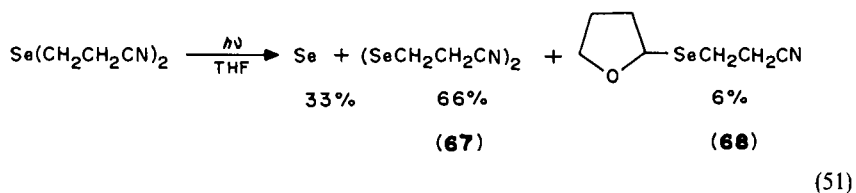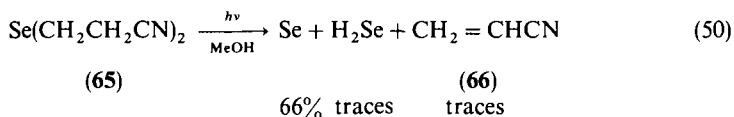
Excitation of bis(benzoylmethyl)tellurium dichloride (**72**) with 313 nm light in degassed solutions of benzene, perfluorobenzene or acetonitrile yielded chloroacetophenone (**73**) and tellurium as the principal photoproducts[36]. In addition, smaller amounts of acetophenone (**74**) and dibenzoylethane (**75**) were obtained (equation 53). When the photolysis was performed in hydrogen-donating solvents such as tetrahydrofuran, acetophenone (**74**) and tellurium were the two major products formed. Trace amounts of **73** and 2-phenylacetyltetrahydrofuran (**76**) were also identified in this reaction.

$$(PhCOCH_2)_2TeCl_2 \xrightarrow{h\nu} PhCOCH_2Cl + PhCOMe + Te$$

<div align="center">

(**72**)   (**73**)   (**74**)

</div>

$$PhCOCH_2CH_2COPh \qquad \qquad CH_2COPh \tag{53}$$

(**75**)   (**76**)
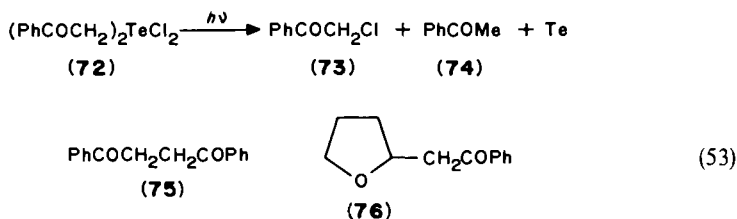
Quantum yields (in acetonitrile) for acetophenone formation are less than those for chloroacetophenone. The extrapolated minimum quantum yields for **73** and **74** are 0.01 and 0.1, respectively. These values correspond to non-free-radical concerted processes that are independent of the concentration of **72**. In the presence of the efficient radical trap CCl_4, the quantum yield of **73** increases, whereas that of **74** decreases to the limiting value of 0.01 ($[CCl_4] > 5$ M).

No room temperature emission was observed for **72**, but at 77 K in methyltetrahydrofuran glass, phosphorescence is detected with quantum yield $\phi_p = 0.18$ and lifetime $\tau_p = 24$ ms. The spectroscopic triplet is assigned as originating principally from the $^3\pi,\pi^*$

state with appreciable $^3n, \pi^*$ character. The triplet state of **72** ($E_T = 72$ kcal) cannot be quenched by molecules with lower energy triplet states such as naphthalene ($E_T = 61$ kcal) and fluorene ($E_T = 68$ kcal), but the reaction can be sensitized by the higher energy 9-xanthone ($E_T = 74$ kcal).

These results are consistent with a mechanism in which the decomposition of the triplet π, π^* state of **72** may lead to products **73** and **74** by a concerted type II γ-hydrogen abstraction and by β-cleavage reactions. They may also be derived by reactions of phenacyl radicals **77** (produced from β-cleavage) which abstract hydrogen from the solvent or a chlorine atom from **72**. Recombination of **77** with solvent radicals affords **76**. In inert solvents **77** recombines to form dibenzoylethane (**75**). Tellurium metal formation may be accounted for by disproportionation of $TeCl_2$ (equations 54–57).

$$\textbf{72*} \xrightarrow[\text{type II}]{} \text{PhCOMe} + [Cl_2TeCHCOPh] \qquad (54)$$

$$\textbf{(74)}$$

$$\textbf{72*} \longrightarrow \text{PhCOCH}_2\cdot + TeCl_2 \xrightarrow[\beta\text{-cleavage}]{} TeCl_4 + Te + \text{PhCOCH}_2CH_2COPh$$

$$\textbf{(77)} \hspace{6cm} \textbf{(75)}$$

$$(55)$$

$$\text{PhCOCH}_2^{\cdot} + \underset{O}{\bigcirc} \longrightarrow \textbf{74} + \underset{O}{\bigcirc}\cdot \xrightarrow{\textbf{77}} \textbf{76} \qquad (56)$$

$$\text{PhCOCH}_2\cdot + \textbf{72} \longrightarrow \textbf{73} \qquad (57)$$
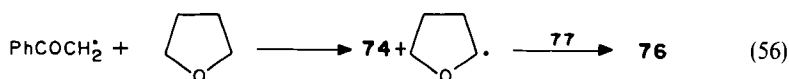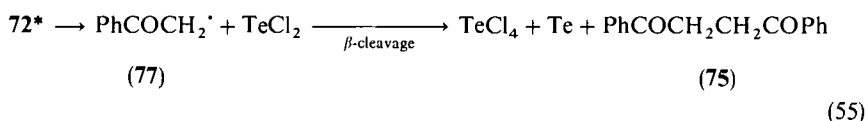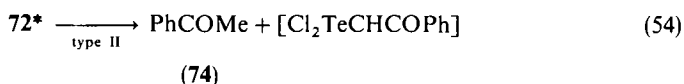
Kinetic expressions for the quantum yields of acetophenone and chloroacetophenone formation were derived using steady-state approximations for excited states and radicals[36]. The quantum yield of **74** in good hydrogen-donating solvents was predicted to be proportional to the concentration of **72**. In poor hydrogen-donating solvents the quantum yields of **73** (ϕ_{ca}) and **74** (ϕ_a) were expected to be linearly dependent on the initial concentration of **72**, and on the inverse square root of the absorbed light (ϕ_a, $\phi_{ac} \propto [\textbf{72}]/I_a^{1/2}$). These predictions were verified experimentally[36].

Photochemical deselenation has been observed in systems in which the selenium atom is flanked by two vinylic carbons. Thus, the flash photolysis of selenophene (**77**) diluted with argon resulted in two groups of transient absorption bands in the 350–390 nm region, due to vibrationally excited levels of the Se_2 ground state[37]. A new band system was also observed in the 397–418 nm region which was attributed to the remaining C_4H_4 fragment, whose structure was not identified (equation 58).

$$\underset{Se}{\bigcirc} \xrightarrow{\text{flash } h\nu} Se_2(B^3\Sigma_4^- - X^3\Sigma_g^-) + C_4H_4 \qquad (58)$$

$$\textbf{(77)}$$
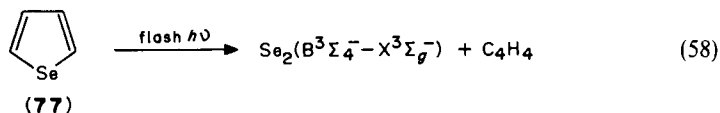
The solution photochemistry of 2-phenylselenophene (**78**) resulted in the formation of a mixture containing selenium and phenylvinylacetylene (**79**) as the deselenation products, together with the isomeric 3-phenylselenophene (**80**) (Section IV.A) (equation 59)[38].

Irradiation of 2-phenyltellurophene (**81**) gave only the fragmentation products, tellurium and **79** (equation 60)[38].

$$5 \quad (78) \xrightarrow[\text{Et}_2\text{O}]{h\upsilon} \quad PhC\equiv CCH=CH_2 + Se + (80) \quad (59)$$

$$(81) \xrightarrow[\text{Et}_2\text{O}]{h\upsilon} \quad PhC\equiv CCH=CH_2 + Te \quad (60)$$
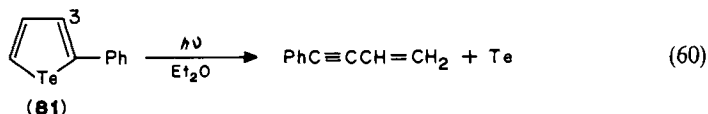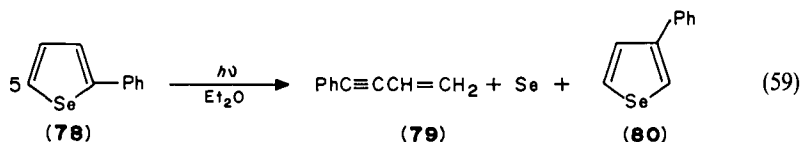
Deuterium labeling experiments with 5-d-**78** and 3,4,5-d_3-**81** revealed that the formation of **79** did not arise from intramolecular hydrogen shift in the intermediate radical but rather via hydrogen exchange with the solvent. The mechanistic scheme proposed for the deselenation (equation 61) involves the initial cleavage of the Se—C bond to form the diradical **82**, which loses a hydrogen atom to either an excited starting material or a solvent radical, forming the vinyl selenide radical **83**. This monoradical then extrudes selenium to give **84**, which in turn abstracts a hydrogen from the solvent, to give **79**.

$$(78) \xrightarrow{h\upsilon} (82) \xrightarrow{-H^\bullet} (83)$$

$$\xrightarrow{-Se} (84) \xrightarrow[\text{(solvent)}]{+H^\bullet} (79) \quad (61)$$
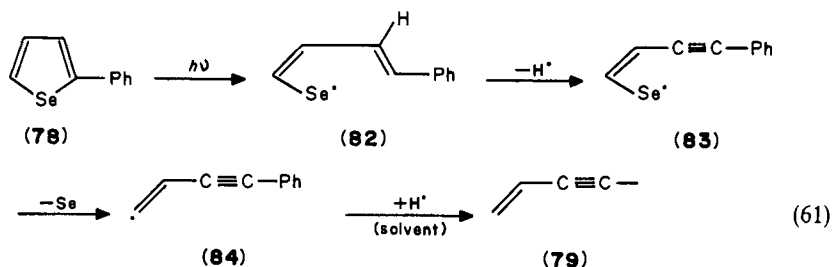
Two interesting variations of selenium extrusion in related divinyl derivatives are worth mentioning. First, the irradiation of the 2,1,3-benzoselenadiazole 1-oxide (**85**) in methylene chloride solutions, which gave benzofurazan (**87**) in 94% yield (equation 62)[49], has been shown to occur in two steps via cyclization of the intermediate **86** (Section II.B.3). The second deselenation is that of 3,3'-bis(1-methylindolyl) selenide (**88**), which on irradiation in benzene afforded the biindolyl **89** and 1-methylindole (**90**)[40] (equation 63). In this case the first step is a homolytic cleavage.

$$(85) \xrightarrow[\text{CH}_2\text{Cl}_2]{h\upsilon} (86) \longrightarrow (87) \quad (62)$$

$$(88) \xrightarrow[\text{PhH}]{h\upsilon} (89) + (90) \quad (63)$$
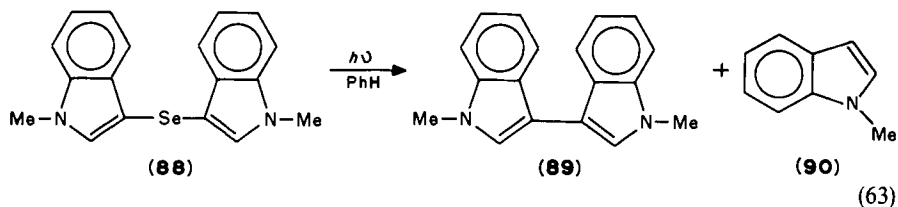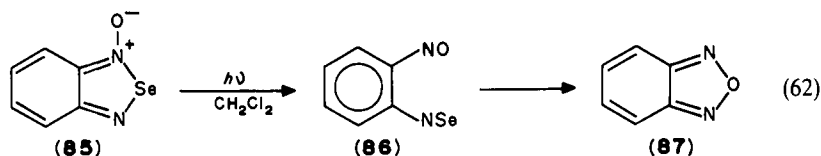
2. Nitrogen eliminations

The photofragmentation of 1,2,3-selenadiazole (91) and its derivatives has been studied extensively in the last decade. Interest has been focused mainly on the detailed mechanism of nitrogen elimination in conjugated cyclic selenium compounds vis-à-vis analogous heterocyclic systems. Irradiation (235–280 nm) of argon or nitrogen matrix-isolated 1,2,3-selenadiazole (91) at 8 K produced selenoketene (92), ethynylselenol (93) and a photolabile species, identified spectroscopically as the selenirene (95) (equation 64)[41]. The reaction progress was monitored by IR spectroscopy.

$$\underset{(91)}{\left[\begin{array}{c}N\\ \\ \\ Se\end{array}\right.}\quad\xrightarrow[\text{8 K, Ar}]{h\nu}\quad \underset{(92)}{CH_2=C=Se} \;+\; \underset{(93)}{CH\equiv CSeH} \;+\; \underset{(94)}{CH\equiv CH} \;+\; \underset{(95)}{\left[\!\!\!\triangleright Se\right.} \qquad (64)$$
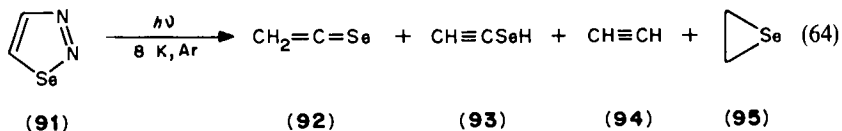
Irradiation of the mixture of products at 275–325 nm led to the conversion of 91 into selenoketene and acetylene. If, however, irradiation was continued, using light of 235–280 nm, the intensity of the IR bands characteristic of 92 and 94 was reduced, whereas the bands assigned to 95 reappeared and those belonging to 93 were enhanced. This suggests that 93 is not a primary product but a photoproduct of 95.

The question of whether selenirene (95) is a primary product of 91 was clarified only recently by a combination of trapping and labeling experiments[42]. It was found that irradiation $(290 \pm 10\,\text{nm})$ at room temperature of 91 (λ_{max} 285 nm, ε 905 lmol^{-1} cm^{-1}) at low concentrations (ca. 5×10^{-4}M) in cyclohexane or diethyl ether–isopentane–ethanol (5:5:1) (EPA), and in the presence of 1% diethylamine afforded only diethylselenoacetamide (96) in 90–100% yield. The quantum yield of disappearance of 91 is independent of the diethylamine concentration and is not quenched by oxygen. This implies that 91 undergoes a unimolecular fragmentation from the singlet excited state to form selenoketene (92) (either directly or via short-lived intermediates), which subsequently traps diethylamine to give 96 (equation 65).

$$\underset{(91)}{\left[\begin{array}{c}N\\ \\ \\ Se\end{array}\right.}\quad\xrightarrow[\substack{20\,^\circ\text{C or}\\ EPA}]{h\nu}\quad \underset{(92)}{CH_2=C=Se}\quad\xrightarrow{Et_2NH}\quad \underset{(96)}{CH_3\underset{\underset{Se}{\|}}{C}NEt_2} \qquad (65)$$
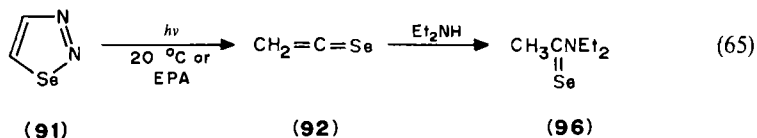
When the photolysis is carried out with the 5-^{13}C-labeled 91 under the same conditions, no scrambling is observed, and the label appears solely on the amide carbon. However, if 91 is irradiated in a EPA glass or PVC film at liquid nitrogen temperature (80 K), and the selenoketene thus formed is further irradiated before quenching with diethylamine, scrambling is observed. These experiments show that selenirene (95) is not a primary photoproduct of 91 but is formed as an unstable intermediate in the photolysis of ketene (92) (equation 66). At room temperature 92 is too labile to undergo further photorearrangement and no exchange of carbons takes place. However, at 80 K 92 is stable enough to undergo further photoisomerization to 95, which in turn rearranges thermally back to carbon-randomized selenoketene (92). It should be noted that unlike the photolysis at 8 K under solid conditions, no selenirene could be detected with 80 K matrix irradiation, nor could ethynylselenol (93) or acetylene by observed. Therefore, 93 is indeed a true photoproduct of 91[41]. These results are in accord with those obtained for the thiazole analogs[43].

$$\text{(91)} \quad \xrightarrow[-N_2]{h\nu} \quad CH_2={}^{13}C=Se \quad \xrightleftharpoons{h\nu\,(80\ K)} \quad \text{(95)}$$

$$\downarrow \quad Et_2NH$$

$$CH_3\overset{13}{C}NEt_2 \atop \underset{Se}{\|}$$

$$\xrightarrow{} \quad {}^{13}CH_2=C=Se \qquad (66)$$

$$\downarrow \quad Et_2NH$$

$${}^{13}CH_3\overset{}{C}NEt_2 \atop \underset{Se}{\|}$$
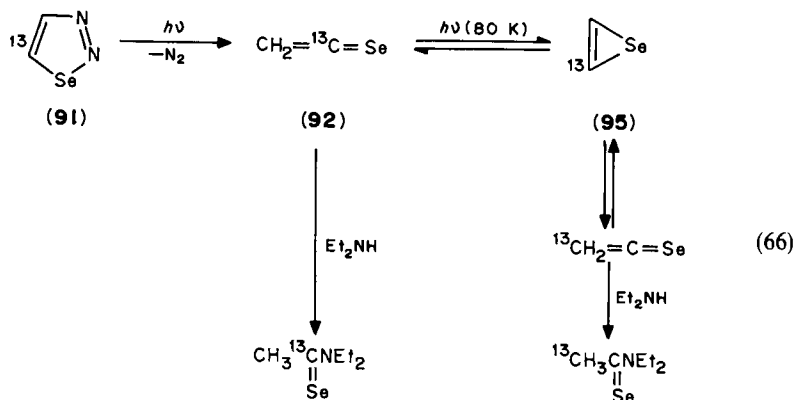
In a related study[44], matrix- isolated cyclopenteno-1, 2, 3-selenadiazole (97) in argon at 12 K was subjected to UV irradiation ($\lambda < 300$ nm), giving trimethyleneselenoketene (98) (equation 67) as the sole product.

$$\text{(97)} \quad \xrightarrow[\text{argon}]{h\nu\,(12\ K)} \quad \text{(98)} \quad =C=Se \qquad (67)$$
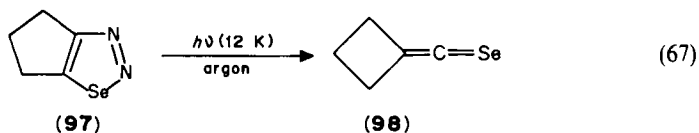
Substitution of the selenadiazole ring by electron-withdrawing groups such as ethoxycarbonyl (99), arylsulfonyl (109) or phenyl (104), while not affecting the primary photoextrusion of nitrogen, results in the isolation of products different from those derived from the parent compound. Thus, irradiation of 99 in benzene gave a 1:1 mixture of the two isomeric selenafulvenes 100 and 101, in 18% (R = H) and 12% (R = Me) yields[45] (equation 68). The mechanism of this reaction is assumed to involve extrusion of nitrogen to produce diradical 102, which undergoes a Wolff rearrangement to the ketene 103 (the same steps which presumably occur in the parent compound 91). The two intermediates 102 and 103 combine in a formal 3 + 2 cycloaddition to give the products shown in equation 68.

$$\text{(99)} \quad \xrightarrow[PhH,-N_2]{h\nu} \quad \text{(100)} \quad + \quad \text{(101)} \qquad (68)$$

$$R = H, Me$$

$$\downarrow -N_2$$

$$\text{(102)} \quad \xrightarrow{} \quad \text{(103)}$$
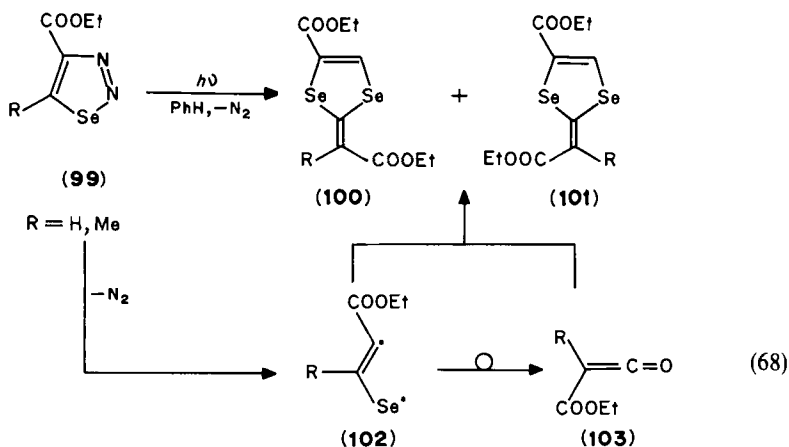
The analogous photolysis of 4, 4-diphenyl-1, 2, 3-selenadiazole (104) in the presence of oxygen was reported[46] to give tetraphenylselenafulvene (105), diphenylacetylene (106), benzil (107) and benzophenone (108) (equation 69).

$$PhC \equiv CPh + PhCOCOPh + Ph_2CO \quad (69)$$

(106)   (107)   (108)
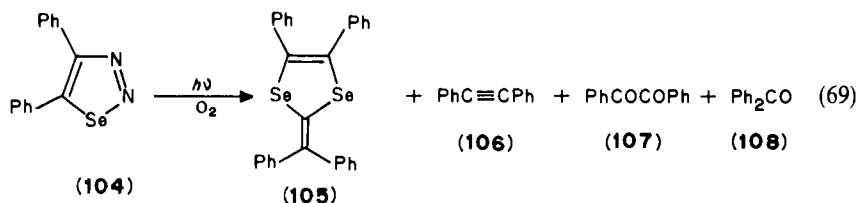
5-Arylsulfonyl-1, 2, 3-selenadiazoles are reported to possess antibacterial and antifungal activity. When the 5-(p-toluenesulfonyl)-1, 2, 3-selenadiazoles (109) were photolysed in benzene, good yields of the corresponding sulfonylacetylenes (110) were isolated (equation 70)[48].

$$p-Tol-SO_2C \equiv CR \quad (70)$$

(110)

R = Me   42 %

R = Ph   64 %
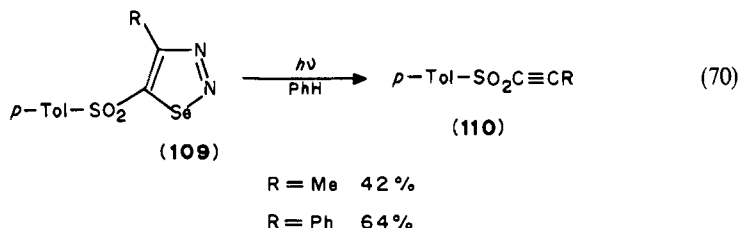
Although diazoketones seem to be good candidates for photochemical extrusion of nitrogen to form carbenes or ketenes (by subsequent rearrangement), there is only a single case in which such a reaction was utilized with the heavier organochalcogen compounds. Thus, the irradiation of the *ortho*-substituted diazoacetophenone 111 in dry benzene afforded telluro-3-coumaranone (112), albeit in poor yield (4%)[49] (equation 71). It should be noted that when the reaction was carried out under thermal, CuO-catalysed conditions, substantially higher yields of 112 (and also of the analogous selenocoumaranone) were obtained[49]. The mechanism of this intramolecular carbene reaction is not clear, although attempts have been made to understand the details in the oxygen analogs[50].

$$o-BuTeC_6H_4COCH_2N_2 \xrightarrow[PhH]{h\nu} \quad (71)$$

(111)   (112)
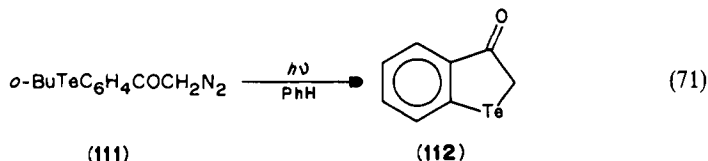
3. Cycloreversions

The most extensive photochemical studies on cycloreversion reactions have been performed on isomers of selenadiazoles in which there is at least one Se—N bond in the molecule. Except for a few cases, the primary photochemical process in selenadiazoles is a formal 3 + 2 cycloreversion. In 1, 2, 3-selenadiazoles (previous section) this results in nitrogen elimination. The 1, 2, 5-selenadiazoles (113) and their 1, 2, 4-isomers (114) eliminate the corresponding nitriles.
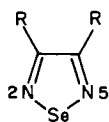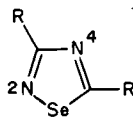
(113)   (114)

Irradiation at room temperature of 1, 2, 5-selenadiazoles (115–117) in 95% ethanol at 300 ± 20 nm produced elemental selenium and nitriles 118–120, respectively, in high chemical and quantum yields, as shown in equation 72^{51-53}.

$$\xrightarrow[\text{25 °C,EtOH}]{h\upsilon(320nm)} \quad \text{RCN} + \text{Se}$$ (72)
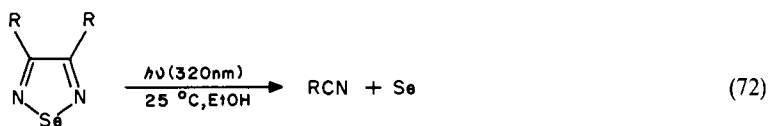
(115)	(118)	R = H	85%;	$\Phi_r 0.71$	(285 nm)
(116)	(119)	R = Me	100%;	$\Phi_r 0.80$	(290 nm)
(117)	(120)	R = Ph	100%;	$\Phi_r 0.96$	(317 nm)

The multiplicity of the excited states involved in the reactions was determined from quenching and sensitization experiments. The rate of photolysis of the aliphatic selenadiazoles 115 (in heptane) and 116 (in benzene) was found to be insensitive to 1 atm oxygen ($E_s = 23$ kcal) or piperylene ($E_T = 57$–59 kcal) at concentrations up to 0.3M. However, the reactions could be triplet-sensitized by xanthone ($E_T = 74$ kcal). Therefore, although the reactions may occur from either a singlet or triplet excited state, the triplet state is apparently not populated upon direct excitation at room temperature, and the photoactive state in these reactions is the singlet.

The photolysis of diphenylselenadiazole (117) in ethanol was partially quenched by oxygen ($\phi_r = 0.33$). The degree of quenching of 117 (in benzene) was studied as a function of added piperylene. The Stern–Volmer plot indicated that two photoactive states (S_1 and T_1) are involved in the unsensitized reaction, and only the T_1 state is quenched by piperylene. The ratio of triplet to singlet reaction, $T_1/S_1 = 4$, was deduced from the kinetic expression^{51}, and the lifetime (τ) of T_1 in benzene at room temperature was calculated to be in the range 1.6×10^{-7} s $< \tau < 1.6 \times 10^{-6}$ s.

Both selenadiazoles 116 and 117 phosphoresce in EPA (at 77 K), whereas the parent diazole (115) does not. Compound 116 emitted at λ_{max} 455 nm (excited at 280–290 nm) with a quantum yield $\phi_p = 0.14$. The calculated lifetime of the triplet state was $\tau_p = 2.5 \times 10^{-3}$ s. For 117, the emission was measured at λ_{max} 538 nm (excited at 310–320 nm) with a quantum yield $\phi_p = 0.33$ and a lifetime of $\tau_p = 1.7 \times 10^{-3}$ s. These results suggest that the lowest triplet state of the selenadiazoles is π, π^* in character.

Low-temperature experiments provided an insight into the transient species formed in the photolysis. Irradiation of 117 was performed in PVC or in EPA (diethyl ether – isopentane–ethanol, 5:5:2) at 85 K and in solid nitrogen at 20 K, and the reaction was followed by UV and IR spectroscopy. In EPA with irradiation at 300 nm, new absorptions appeared at 254, 325 (sh), 357 and 384 nm. Simultaneously, characteristic absorptions of benzonitrile (120) appeared. On prolonged photolysis (or heating above 240 K) the former absorptions disappeared with the concomitant enhancement of the intensity of benzonitrile absorption bands. Similar results were obtained with irradiation in PVC and in nitrogen. The IR spectrum consists of two bands in the 2300–1900 cm^{-1} region, benzonitrile bands at 2235 cm^{-1} and a band at 2200 cm^{-1} assigned to the transient

benzonitrile selenide (121, R = Ph), which disappeared on continuous irradiation or heating.

$$RC{\equiv}\overset{+}{N}-\overset{-}{S}e$$
(121)
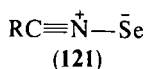
R = H, Me, Ph

Similar low-temperature experiments were carried out in PVC, EPA and argon, to detect the transient nitrile selenides obtained from the aliphatic selenadiazoles 115 and 116. The absorption bands assigned to HCNSe appear at 237 and 255 (sh) nm in PVC, and those assigned to MeCNSe appear to 233 and 252 nm. Interestingly, the IR spectra in both experiments (in argon) display a doublet at 2046 cm^{-1}, characteristic of CN radicals of unknown origin[51].

Diphenyl-1, 2, 4-selenadiazole (122) exhibits similar behavior to that of the 1, 2, 5-isomer (117)[51,52]. The photolysis of 122 at room temperature in ethanol, using Pyrex-filtered light (λ 300 nm), produced benzonitrile (120) quantitatively, with a low quantum yield of ϕ_r = 0.085 (at 310nm) (equation 73). Attempts to trap the intermediate benzonitriles selenide (121, R = Ph) [k(decay) = 10 960 $\pm$ 140 s^{-1} at 25 °C)[53] with dimethyl acetylenedicarboxylate failed. The photolysis could not be quenched with piperylene, and could not be sensitized by xanthone. Therefore, the photoactive state is the excited singlet state[52]. However, absorption spectra taken during the photolysis of 122 at 85 K in PVC film showed absorptions due to PhCNSe, identical with those exhibited in the irradiation of 117 under the same conditions. A similar spectrum was also obtained in frozen EPA at 85 K. IR spectra taken in a solid nitrogen matrix at 20 K again proved the presence of the transient PhCNSe, by showing the characteristic 2200 cm^{-1} absorption band.

$$\text{(122)} \xrightarrow[\text{EtOH}]{h\nu} \text{PhCNSe} + \text{PhCN} \xrightarrow{h\nu \text{ or } \Delta} \text{PhCN} + \text{Se} \qquad (73)$$
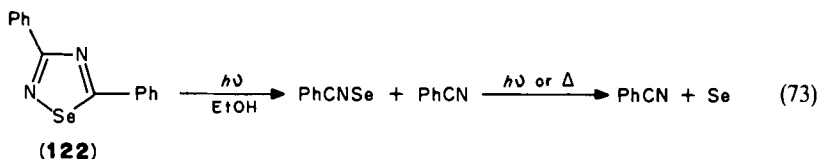
4. Cheletropic reactions

2, 1, 3-Benzoselenadiazole (123) does not undergo the usual ring cleavage observed in 1, 2, 5-selenadiazoles (previous section). Instead, irradiation of 123 in 95% ethanol through a Pyrex filter at room temperature led to slow extrusion of selenium and the formation of the photoequilibrium mixture of the three isomeric hexadienedinitriles 124–126[51], in a formal cheletropic reaction[54] (equation 74).

$$\text{(123)} \xrightarrow[\text{25 °C,EtOH}]{h\nu} \text{(124)} + \text{(125)} + \text{(126)} \qquad (74)$$

9%   23%   18%

(124)   (125)   (126)
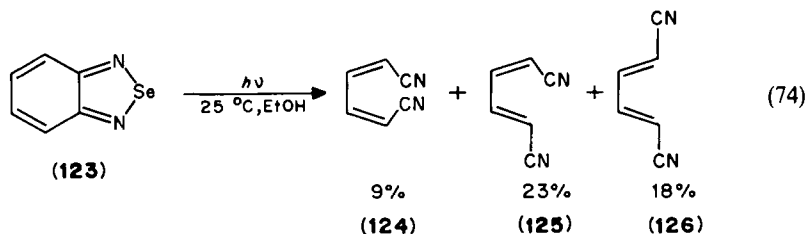
Highly substituted 2,5-dihydro-1,3,4-selenadiazoles (127) are the only members of this heterocyclic ring system which are known to be photoreactive[55]. On irradiation at 300 nm in pentane solutions, these selenadiazoles undergo a cheletropic deselenation to give tetrasubstituted azines (128) in good yields (equation 75). It is interesting that under thermal conditions a two-fold extrusion reaction occurred with loss of both nitrogen and selenium, affording the corresponding highly crowded tetrasubstituted olefins.

$$\text{(75)}$$

(127)   (128)

R = alkyl, cycloalkyl
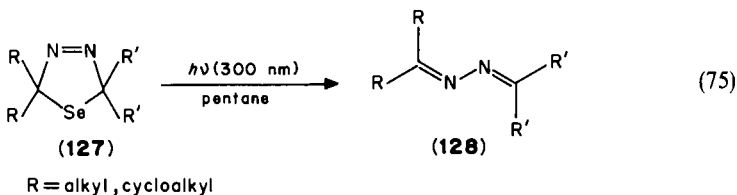
An unusual variation of a photochemical cheletropic reaction in which a phosphorus bridge is eliminated has recently been described[56]. Irradiation in methanol of the adducts 129 and 130, obtained by thermal Diels – Alder cycloaddition of phenyl selenoxophosphole with maleic anhydride and phenylmaleimide, respectively, gave the corresponding dihydrophthalic anhydride 131 and phthalimide (132) together with dimethyl phenylselenophosphonate (135) (equation 76). The unstable phenylselenoxophosphan 133 was shown to be the primary photoproduct of the elimination. It first adds methanol to form 134, which in turn reacts photochemically with methanol to give 135.

(129) X = O
(130) X = NPh

(131)
(132)

(133)

MeOH

(135)   (134)

$$\text{(76)}$$
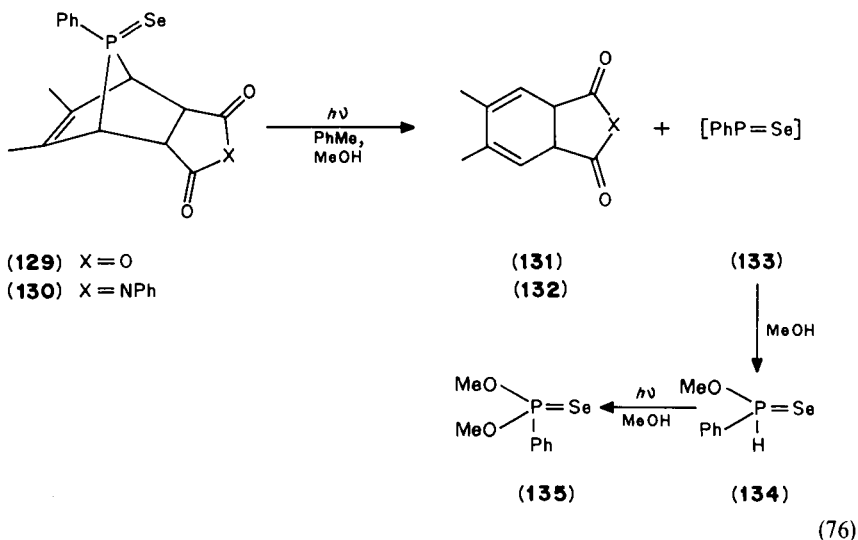
III. PHOTOASSOCIATIVE PROCESSES

In many reactions described in this section the primary photoproducts result from homolytic cleavage of organochalcogen σ bonds. Nevertheless, such reactions will be covered here if the chalcogenide radicals thus formed react with ground-state molecules to form new chalcogen—carbon σ bonds.

A. Photosubstitution

1. Nucleophilic substitution

a. Aromatic substitutions. Photolysis of aryl halides in the presence of nucleophiles leads to substitution by a radical chain mechanism commonly known as the aromatic S_{RN} 1 reaction (equation 77)[57,58].

$$ArX + Nu^- \xrightarrow{h\nu} ArNu + Y^- \qquad (77)$$

The reaction mechanism involves an initiation step in which an electron is transfered from the nucleophile to the excited aryl halide, forming a radical ion $ArX^{-\cdot}$ (equation 78), which enters into a three step propagation cycle depicted in equations 79–81.

$$ArX + Nu^- \longrightarrow ArX^{-\cdot} + Nu^\cdot \qquad (78)$$

$$ArX^{-\cdot} \longrightarrow Ar^\cdot + X^- \qquad (79)$$

$$Ar^\cdot + Nu^- \longrightarrow ArNu^{-\cdot} \qquad (80)$$

$$ArNu^{-\cdot} + ArX \longrightarrow ArNu + ArX^{-\cdot} \qquad (81)$$

The use of phenyl selenide (137)[59,60] and phenyl telluride (142)[59,61] as nucleophiles in the photostimulated nucleophilic substitution provides a simple and direct route for the synthesis of symmetrical and unsymmetrical diaryl selenides and tellurides. The reactions are usually carried out in liquid ammonia solutions, with Pyrex-filtered irradiation at $\lambda < 350$ nm.

The reactivity order of the nucleofugal group in the reaction of $PhSe^-$ with a series of aryl halides, as determined from the chemical yields, decreases in the order $I > Br > Cl$. Naphthalene derivatives were found to be more reactive than benzene derivatives with the same leaving group (equation 82).

$$ArX + PhSe^- \xrightarrow[\text{liq NH}_3 \text{ (Pyrex)}]{h\nu(\lambda < 350 \text{ nm})} ArSePh^- + X^- \qquad (82)$$

$$(136) \quad (137) \qquad\qquad\qquad (138)$$

ArX	Yields	
(a) PhCl	–	1%
(b) PhBr	1%	4%
(c) PhI	55%	66%
(d) 1-chloronaphthalene	73%	88%
(e) 4-chlorobiphenyl	52%	59%
(f) 9-bromophenanthrene	72%	85%
(g) 2-chloroquinoline	40%	54%
(h) 4-chlorobenzophenone	–	5%

The above results conform with the general photo-S_{RN} 1 mechanism outlined above and parallel the reactions observed with the sulfur analogs[62–64]. However, there appears to be one exceptional case, 4-chlorobenzophenone, which with selenide gave very poor yields compared with sulfide, probably because of competing nucleophilic addition of $PhSe^-$ to the carbonyl group[59] (equation 83).

$$4-ClC_6H_4COPh + PhSe^- \xrightarrow{\Delta} 4-ClC_6H_4C\overset{\displaystyle O^-}{\underset{\displaystyle SePh}{\big|}}Ph \qquad (83)$$

The photostimulated reaction of $PhSe^-$ with dihaloarenes[59] gave the disubstituted products. Use of p-bromoiodobenzene (139) as substrate afforded 70% yield of p-bis(phenylselenyl)benzene (140) and > 80% of iodide and bromide ions. Only traces of the monoadduct 141 were observed, although some of the starting material (12%) was recovered (equation 84). This suggests a propagation mechanism (equations 85–88) in which the radical anion of the monosubstituted product (equation 86) decomposes to the p-(phenylselenyl)phenyl radical and Br^- (equation 87) much faster than electron transfer to the substrate.

$$4-IC_6H_4Br + PhSe^- \xrightarrow{h\nu} 1,4-(PhSe)_2C_6H_4 + Br^- + I^- + 4-BrC_6H_4SePh \qquad (84)$$

$$\text{(139)} \qquad\qquad\qquad \text{(140)} \qquad\qquad\qquad \text{(141)}$$

$$4-BrC_6H_4I^{-\cdot} \rightarrow 4-BrC_6H_4{}^\cdot + I^- \qquad (85)$$

$$4-BrC_6H_4{}^\cdot + PhSe^- \rightarrow 4-BrC_6H_4SePh^{-\cdot} \qquad (86)$$

$$4-PhSeC_6H_4Br^{-\cdot} \rightarrow 4-PhSeC_6H_4{}^\cdot + Br^- \qquad (87)$$

$$4-PhSeC_6H_4{}^\cdot + PhSe^- \rightarrow 4-PhSeC_6H_4SePh^{-\cdot} \qquad (88)$$

The photonucleophilic substitution reaction of aryl halides with phenyl telluride (142) is in general more efficient than the analogous reaction with $PhSe^-$ [59]. The reaction with bromobenzene gave a 20% yield of diphenyl telluride (143), and a 90% yield of 143 was obtained starting from iodobenzene. However, with more nucleofugal aryl halides such as p-iodoanisole and with 1-chloro- or 1-bromo-naphthalene, two unexpected products, 145 and 143, were observed, indicating the existence of mechanistic pathways which enable the scrambling of the aryl groups (equation 89).

$$ArX + PhTe^- \xrightarrow[\text{liq. } NH_3]{h\nu} Ph_2Te + ArTePh + Ar_2Te \qquad (89)$$

	(142)	(143)	(144)	(145)
ArX		Yields		
(a) bromobenzene		20%	—	—
(b) iodobenzene		90%	—	—
(c) p-iodoanisole		15%	73%	11%
(d) 1-chloronaphthalene		9%	41%	6%
(e) 1-bromonaphthalene		16%	53%	16%

The remarkable difference in behavior between the two nucleophiles was ascribed to the reversibility of coupling in the case of $PhTe^-$ (equation 90)[59]. The radical anion formed from coupling of the initially formed aryl radical with $PhTe^-$ may undergo three competing reactions: reversion to starting material (k_r), fragmentation to form aryltelluride ion and phenyl radical (k'_r) and electron transfer to form aryl phenyl telluride. The two new species formed, $ArTe^-$ and $Ph^\cdot$ may recombine (k'_c) to the aryl phenyl telluride radical anion or, alternatively, react with $Ar^\cdot$ and $PhTe^-$, respectively, to give the symmetrical tellurides. The reason why the phenylselenyl anion does not undergo nucleophilic scrambling reactions is that the fragmentation of the initially formed mixed radical anion

is much slower than electron transfer, $k'_f \ll k_t[\text{ArX}]$, and thus only the straightforward substitution product is formed.

$$\text{Ar}^{\bullet} + {}^{-}\text{TePh} \underset{}{\overset{k_f}{\rightleftharpoons}} (\text{ArTePh})^{-\bullet} \underset{k'_c}{\overset{k'_f}{\rightleftharpoons}} \text{ArTe}^{-} + \text{Ph}^{\bullet} \qquad (90)$$

$$\downarrow k_f[\text{Arx}]$$

$$\text{ArTePh}$$

It is important to note from the above mechanistic interpretation that by decreasing the bond dissociation energy of the C—E bond (E = Se, Te), the chances of competing scrambling reactions increases. On the other hand, the reduction potentials of the aromatic compounds will be of importance in the electron-transfer processes. The reduction potentials of aromatic compounds are related to their π^* MO energy levels. The more negative the reduction potential, the higher is the π^* in energy. The bond dissociation energy parallels the σ^* MO energy levels and decreases on going down the Periodic Table. Hence, in reactions of a particular aryl radical with PhE$^-$ nucleophiles, the difference in energy between σ^* and π^* MOs decreases from Se to Te, and the competition of bond fragmentation becomes more important[57]. Indeed, when the photoreaction of PhSe$^-$ was carried out with 4-iodoanisole and 2-bromopyridine, scrambling mixtures were obtained (equation 91)[65]. Moreover, use of iodobenzene and 1-adamantyl selenide (1-AdSe$^-$) (146) as nucleophile gave an equimolar mixture of the three corresponding selenides 147–149 (equation 92)[66]. The same reaction with 1-adamantyl telluride (1-AdTe$^-$) gave only 143 (80%) and 150 (16%) (equation 93).

In order to quantify further the mechanistic interpretation, competition experiments were carried out under conditions of irreversible coupling, using the reaction between various nucleophiles PhE$^-$ (E = S, Se, Te) with 2-quinolyl radicals. The results indicate increasing reactivity on going down Group 6A in the order PhO (0.0) < PhS (1.0) < PhSe (5.8) < PhTe (28)[65].

$$\text{ArX} + \text{PhSe}^{-} \xrightarrow[\text{liq. NH}_3, \, -33\,°\text{C}]{h\nu} \text{Ph}_2\text{Se} + \text{ArSePh} + \text{Ar}_2\text{Se} \qquad (91)$$
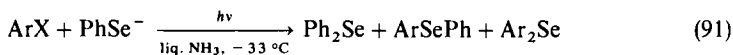
4-iodoanisole	20%	25%	19%
2-bromopyridine	5%	72%	2%

$$\text{PhI} + \text{1-AdSe}^{-} \xrightarrow{h\nu}_{\text{NH}_3} \text{Ph}_2\text{Se} + \text{1-AdSePh} + (\text{1-Ad})_2\text{Se} \qquad (92)$$

$$\quad\quad (146) \quad\quad\quad\quad (147) \quad\quad (148) \quad\quad\quad (149)$$

$$\text{PhI} + \text{1-AdTe}^{-} \xrightarrow{h\nu}_{\text{NH}_3} \text{PhTe} + \text{1-AdTePh} \qquad (93)$$

$$\text{1-Ad} = \text{1-adamantyl} \quad\quad\quad\quad (143) \quad\quad (150)$$
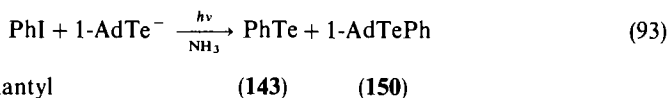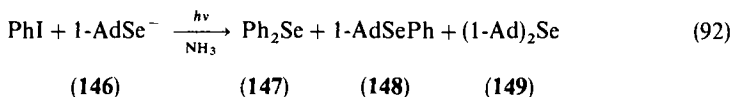
Nucleophilic substitution of aryl halides by selenocyanate ion (151) may also be induced by UV light in aqueous *tert*-butanol. Irradiation of 151 with 2-amino-5-chlorobenzonitrile and 1-chloro-2-naphthylamine gave the corresponding selenocyanates (152), whereas the

photolysis with 4-chloroanisole and 5-bromo-2-(dimethylamino)pyrimidine afforded the corresponding diaryl diselenides (153) (equation 94)[67]. The mechanism of these reactions proceeds probably via aromatic $S_{RN}1$ substitution. The diaryl diselenides may be derived from recombination of ArSe· formed by cleavage of the intermediate aryl selenocyanate radical anion (equation 95).

$$ArX + SeCN^{-} \xrightarrow[\textit{t-BuOH}]{h\nu} \begin{array}{l} \nearrow ArSeCN \quad \textbf{(152)} \\ \\ \searrow ArSeSeAr \quad \textbf{(153)} \end{array} \qquad (94)$$

$$ArX + SeCN^{-}$$
$$\textbf{(151)}$$

$$Ar^{·} + SeCN^{-} \rightarrow ArSeCN^{-·} \rightarrow ArSe^{·} + CN^{-} \rightarrow ArSeSeAr \qquad (95)$$
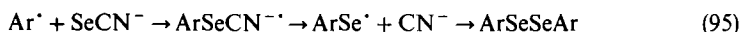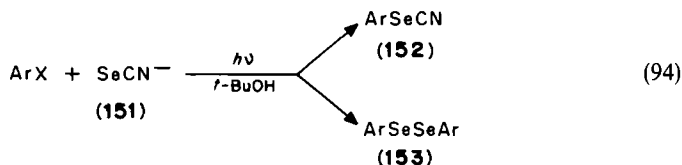
b. *Aliphatic substitution.* Photochemical reactions of alkyl halides in the gas phase[68,69] and in solution[70,71] usually involve homolytic cleavage of carbon—halogen bonds. For example, direct chemical evidence for the intermediacy of trifluoromethyl radicals has been provided in the photolysis of CF_3I with halobenzenes[72]. When perfluoroalkyl iodides (154) are photolysed with dimethyl telluride (155) at 310 nm, good conversions of the iodides into perfluoroalkyl substituted tellurides (156 and 157) was observed (equation 96)[73]. When equimolar ratios of telluride to iodide were used, tellurium metal separated from the reaction mixture. However, when excess of iodide was utilized (3:1 molar ratio), iodine was formed.

$$R_{F}I + Me_{2}Te \xrightarrow{h\nu(310 \text{ nm})} R_{F}TeMe + (R_{F})_{2}Te \qquad (96)$$

$$\textbf{(154)} \quad \textbf{(155)} \qquad\qquad \textbf{(156)} \qquad \textbf{(157)}$$

$$R_{F} = CF_{3}, C_{2}F_{5}$$
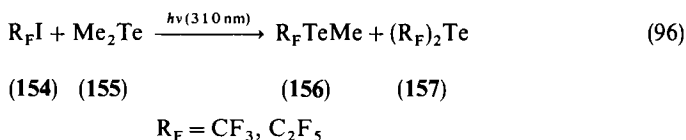
Trifluoromethyl radicals generated by photolysis of CF_3I in liquid ammonia may also be trapped efficiently (34–83%) by selenophenols (158) to give the corresponding trifluoromethyl aryl selenides (159) (equation 97)[74]. Similarly, irradiation of $PhSe^{-}$ (produced in liquid ammonia from Ph_2Se_2 and Na metal) with perfluoroalkyl iodides (154) gave the corresponding perfluoroalkyl selenides (160) (equation 98)[74].

$$CF_{3}I + 4-RC_{6}H_{4}SeH \xrightarrow[\text{liq. NH}_3]{h\nu} 4-RC_{6}H_{4}SeCF_{3} \qquad (97)$$

$$\textbf{(158)} \qquad\qquad\qquad \textbf{(159)}$$

$$R = H, Br, Me, CF_{3}$$

$$R_{F}I + PhSe^{-} \xrightarrow[\text{liq. NH}_3]{h\nu} PhSeR_{F} \qquad (98)$$

$$\textbf{(154)} \quad \textbf{(137)} \qquad\qquad \textbf{(160)}$$

$$R_{F} = CF_{3}, C_{3}F_{7}$$
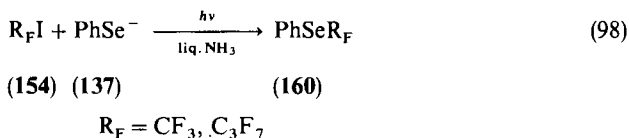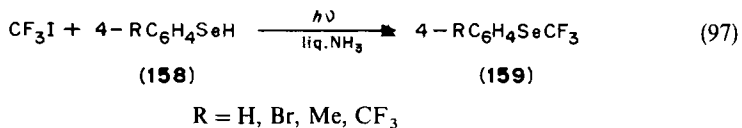
It is reasonable to suppose that the reactions in liquid ammonia proceed by an $S_{RN}1$ type chain mechanism whereby the initially formed alkyl radicals react with aryl selenide anion

to give the corresponding radical anion, which decays to the product by electron transfer (ET) (equation 99).

$$R^{\cdot} + ArSe^{-} \rightarrow RSeAr^{-\cdot} \xrightarrow{ET} RSeAr \tag{99}$$

It is well known that bridgehead-substituted halides are very unreactive towards nucleophilic substitution reactions[75]. It has recently been reported, however, that 1-haloadamantanes and 9-halotriptycene react with nucleophiles by the photochemical $S_{RN}1$ mechanism[76,77]. 1-Iodoadamantane (1-AdI) (161) reacts with disodium selenide and telluride under photolytic conditions in ammonia to give, after air oxidation, bis(1-adamantyl selenide) and bis(1-adamantyl telluride) (162) in good yields (equation 100). In both cases the reaction mixture also contained moderate yields of the hydrocarbon adamantane (163). 1-Adamantyl selenide and telluride anions (164) are believed to be the primary photosubstitution products, which dimerize oxidatively to the observed products (162) (equation 101). Adamantane was probably obtained from the intermediate adamantyl radicals by reaction with the solvent.

$$1\text{-AdI} + E^{2-} \xrightarrow[NH_3]{h\nu} 1\text{-AdEEAd-1} + AdH + I^{-} \tag{100}$$

(161)   (162)   (163)

(a) E = Se   46%   23%   70%
(b) E = Te   47%   20%   69%

$$1\text{-AdI} + E^{2-} \xrightarrow[S_{RN}1]{h\nu} 1\text{-AdE}^{-} + I^{-} \xrightarrow{[O]} 1\text{-AdEEAd-1} \tag{101}$$

(161)   (164)   (162)
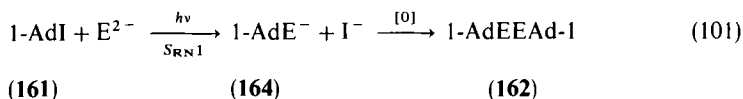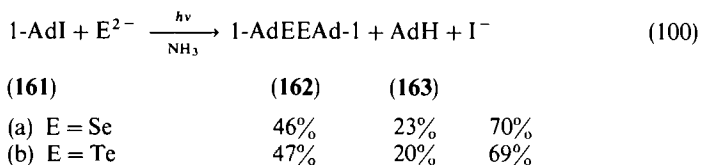
The photostimulated reaction of 1-iodoadamantane with PhS^{-} gave three products (147–149), the same scrambling mixture that was obtained when iodobenzene reacted with 1-AdSe^{-} (equation 92), but in a different ratio (equation 102)[66]. Similarly, the photolysis of 1-AdI with PhTe^{-} gave a different ratio of the same two products (143 and 145) which were obtained (equation 93) in the reaction of PhI with 1-AdTe^{-} (equation 103). With 1-naphthyl selenide ion (165), only the unsymmetrical selenide 166 was observed (equation 104), and no selenides were formed in the photolysis of 1-AdI with 1-AdTe^{-}.

$$1\text{-AdI} + PhSe^{-} \xrightarrow[liq. NH_3]{h\nu} Ph_2Se + 1\text{-AdSePh} + (1\text{-Ad})_2Se \tag{102}$$

(161)   (147)   (148)   (149)
                relative yields: 10%   74%   16%

$$1\text{-AdI} + PhTe^{-} \xrightarrow{h\nu} Ph_2Te + 1\text{-AdTePh} \tag{103}$$

                               (143)   (158)
                relative yields: 31%   39%

$$1\text{-AdI} + 1\text{-NaphSe}^{-} \xrightarrow{h\nu} (1\text{-Naph})Se(1\text{-Ad}) \tag{104}$$

(165)   (166)
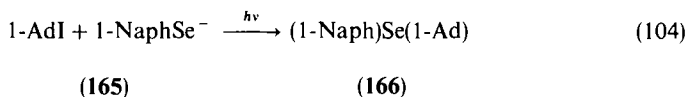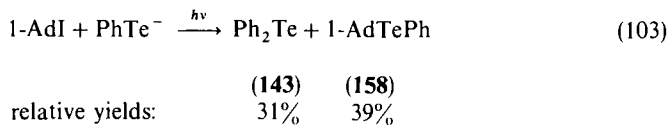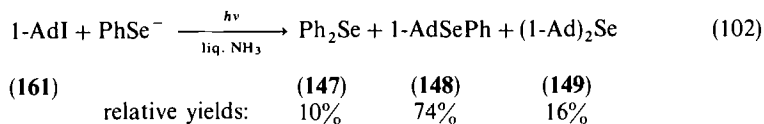
These results confirm the mechanistic scheme outlined in equation 105, in which an equilibrium is generally established between the mixed aralkyl radical ion **167** and the two ion – radical pairs which are obtained from the alternative photostimulated reactions.

Fragmentations of **167** on both sides permit the formation of the symmetrical scrambling products, and compete with electron transfer to form the mixed product. Since the rates of electron transfer from **167** to the substrate halides should be similar, and probably diffusion controlled, the relative amount of scrambling products will be determined by the different fragmentation rates of the R—E $[k_f(RE)]$ and Ar—E $[k_f(ArE)]$ bonds in **167**[66]. The ratio of fragmentation rates for the adamantyl – phenyl pair, $k_f(AdE)/k_f(PhE)$, was found to be 3.7 (E = S), 9.5 (E = Se) and 13 (E = Te). This increase in the ratio of fragmentation rates on going from sulfur to tellurium suggests that in the photostimulated reactions the products obtained depend on the energy levels of the σ^* and π^* of the C—E bonds of the radical anion intermediate[66,77].

$$RX + ArE^- \qquad\qquad\qquad RE^- + ArX$$

$$R^\bullet + ArE^- \xrightarrow{k_f(RE)} (R-E-Ar)^{-\bullet} \xrightarrow{k_f(ArE)} RE^- + Ar^\bullet \qquad (105)$$

$$(\mathbf{167})$$

$$ET \,\big\downarrow k_f[RX]$$

$$R-E-Ar$$
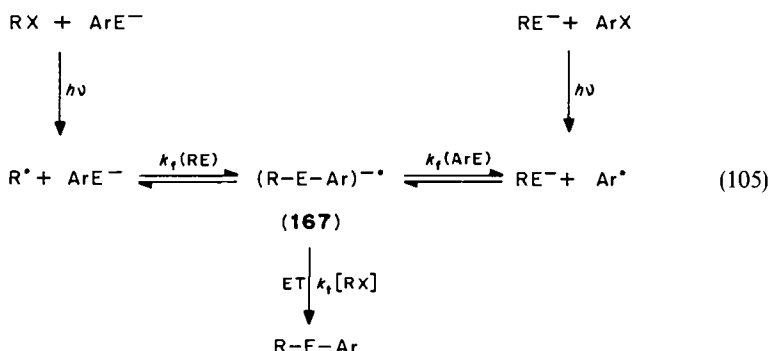
c. Intramolecular substitution. Excitation of *Se*-aryl esters of aromatic selenoacids **168**, which are *ortho*-substituted by appropriate leaving groups, often results in cyclization by intramolecular substitution. This reaction provides an important synthetic entry to novel heterocyclic seleno compounds.

$$ArCOSeAr'$$
$$(\mathbf{168})$$
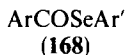
In the first typical example, selenoxanthone (**170**) was obtained in 19% yield by irradiating through quartz a benzene solution of *Se*-phenyl 2-chloroselenobenzoate (**169**) with a high-pressure mercury lamp (equation 106)[11]. Similarly, irradiation of the 2-chloroselenonicotinate ester (**171**) leads via loss of HCl to a mixture of selenoxanthone (**13**), (25%) and bis(*p*-tolyl selenide) (**7**) (57%) (equation 107)[14,78]. The selenophene analog **173** was obtained in low yields (4%) together with **7** (66%) irradiation of the *Se-p*-tolyl ester of 3-bromoselenophene-2-selenocarboxylic acid (**172**) (equation 108)[79].

$$2\text{-ClC}_6\text{H}_4\text{COSePh} \xrightarrow[\substack{PhH \\ (-HCl)}]{h\nu} \qquad (106)$$

$$(\mathbf{169}) \qquad\qquad\qquad (\mathbf{170})$$

(107)

(108)
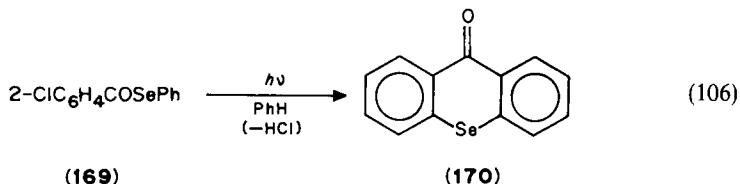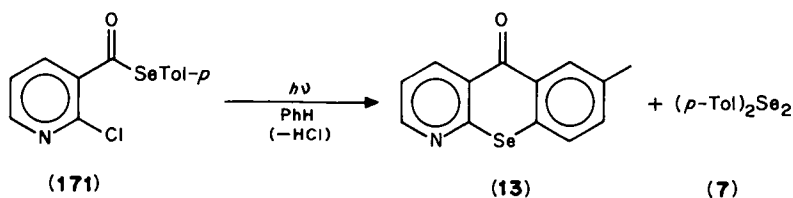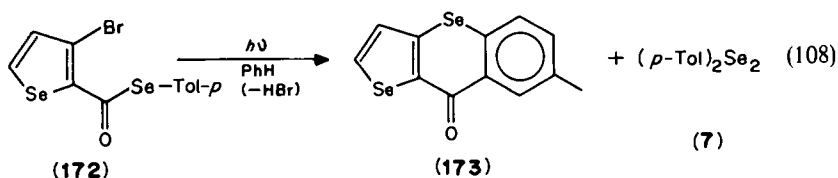
While the mechanistic details of these reactions are not yet completely understood, it is reasonable to assume that cyclization occurs in two steps. First, a photochemical Fries rearrangement (Section IV.A) of the selenoester **174** to the selenolketone **175** takes place, followed by intramolecular nucleophilic photo-substitution to give the selenoxanthone **176** (equation 109).
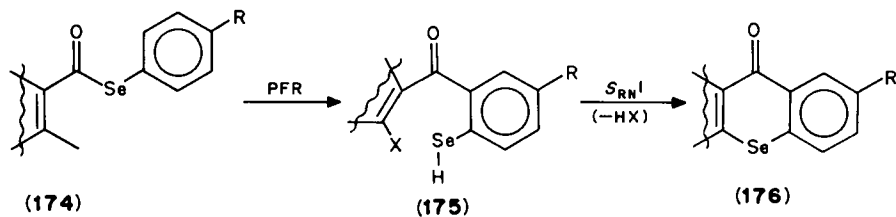
(109)

Photocyclization of aromatic selenoesters may also be achieved, albeit in low yields, when the *ortho*-halogen atom of the selenoester is replaced with a sulfoxide group, as in **8**[12] (equation 110), or a selenide group, as in **12**[14] (equation 111). Thus, photolysis of 2-(methylsulfinyl)selenobenzoate (**8**) afforded a mixture containing 3% of selenoxanthone (**177**)[12] together with other major products which arise from photofragmentation (Section II.A.1). Similarly, irradiation of selenonicotinic ester **12** gave 15% yield of **13**[14]. Here, however, an alternative mechanistic pathway has been proposed[14], which involves a photoinduced homolytic fragmentation of **12** to radicals **178** and **179**, followed by an intramolecular Friedel – Crafts cyclization[80] of **178** to **13** and dimerization of **179** to the diselenide **7** (equation 111).

(110)

$$hv \atop PhH$$

(12)   (178)   (179)

FC

$(p\text{-Tol})_2Se_2$

(13)   (7)

(111)
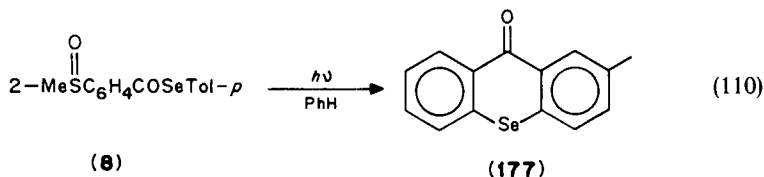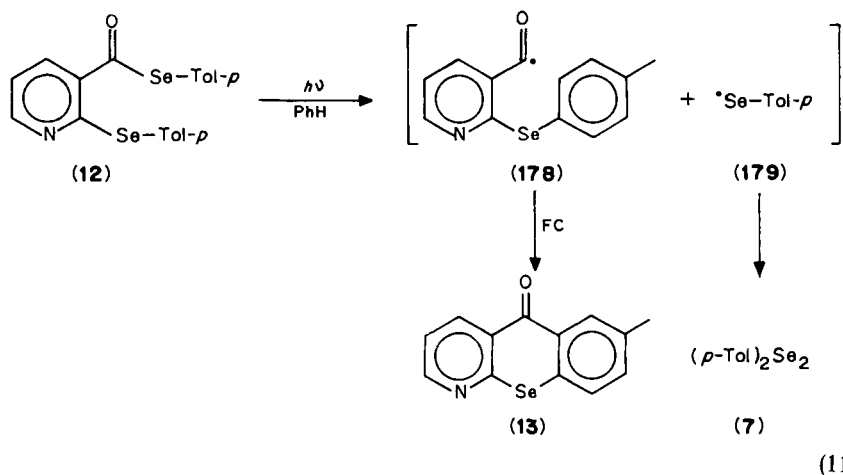
An interesting example in which competition between a photo-Fries rearrangement and Friedel–Crafts acylation apparently occurred has been reported for the photoinduced reaction of 10 (equation 112)[13]. On irradiation, two isoelectronic heterocyclic systems were formed in a 2:3 ratio; the selenopyrone 180 via the photo-Fries pathway and the thiopyrone 11 by the Friedel–Crafts mechanism. These products were accompanied by the corresponding disulfide and the diselenide. Further experimental evidence for the occurrence of both mechanistic pathways in this reaction was deduced from the observation that when the aromatic sulfide moiety in 10a was replaced by the inferior methyl sulfide leaving group of 10b, no cyclization products were detected and only the diselenide 7 could be isolated from the reaction mixture.

$$hv \atop PhH$$

(10)   22%   14%

(a), R = p-Tol   (11)   (180)

(b), R = Me

+ $(p\text{-Tol})_2Se_2$ + $(p\text{-Tol})_2S_2$

22%   35%   (112)

(7)   (181)
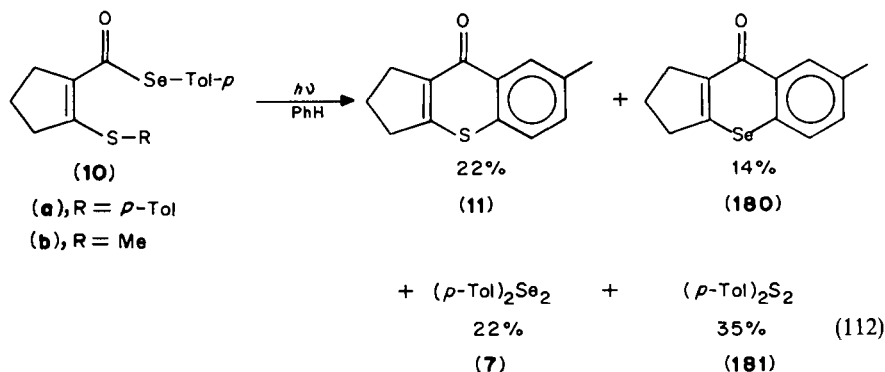
Telluroesters do not usually undergo photochemical cyclization reactions, although both fragmentation (Section II.A.1) and photo-Fries rearrangements (Section IV.A.1) have often been observed in these compounds. However, the methylthio-substituted telluroester 19 undergoes photocyclization to give, among other products, 22% of the unexpected thioxanthone 20 (equation 113)[16]. Here, unlike with the selenoester 181, the rearrangement is followed by displacement of the tellurium by sulfur. The rearrangement products, 182 and 183, also readily undergo photocyclization to thioxanthone 20, demonstrating again the ability of excited sulfides to displace tellurides[16].
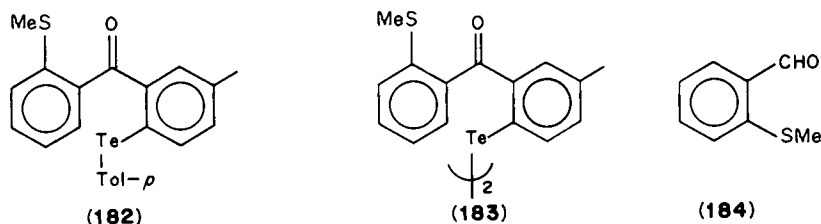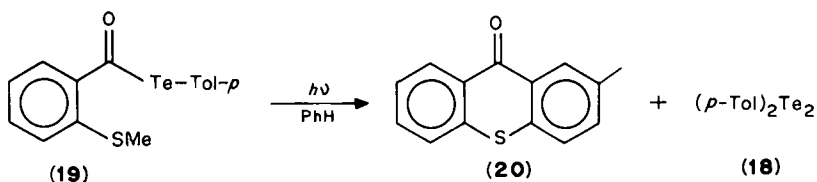
(113)

A unique example of a photocyclization at an unsubstituted vinylic carbon of a selenophene ring has been reported[79]. Irradiation of the selenoester **185** in benzene (Solidexglas filter) afforded the novel 6-methyl-4H-selenolo[2,3-b][1]benzoselenin-4-one (**186**) in 16% yield, together with diselenide **7** (34%) and selenophene-3-carboxaldehyde (**187**) (2%) (equation 114). A similar reaction occurred when the analogous selenophene thioester **188** photocyclized to thieninone (**189**) (equation 115)[81]. In both cases a formal oxidation by loss of a hydrogen molecule occurred, but this could not be established experimentally.
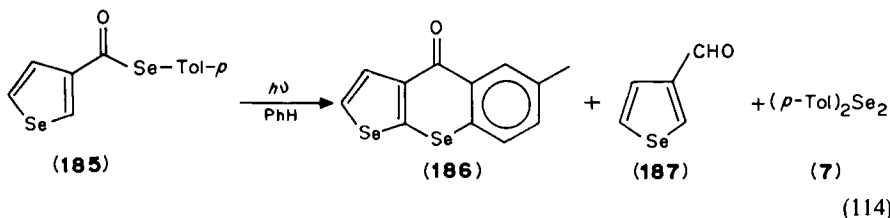
(114)
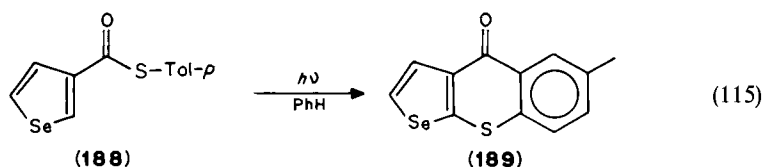
(115)

2. Organometallic substitutions

a. Free-radical displacements. Free-radical chain reactions involving substitution at a metal center may in general be separated into bimolecular homolytic substitutions (S_H2) and addition–elimination reactions, represented by equations 116 and 117, respectively. Such radical chain reactions are formally analogous to the well known S_N2 and S_N1

heterolytic reactions, and have ample precedence in the free-radical chemistry of organometallic compounds[82].

$$LMR + X^{\cdot} \xrightarrow{\ S_H2\ } LMX + R^{\cdot} \tag{116}$$

$$LMR + X^{\cdot} \xrightarrow{\ \text{addition}\ } [LMRX] \xrightarrow{\ \text{elimination}\ } RX + LM^{\cdot} \tag{117}$$
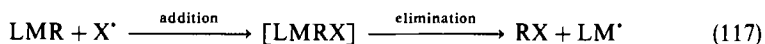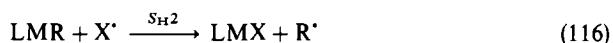
Vinylmercury halides (190) readily undergo photostimulated free-radical chain substitution reactions in the presence of bis(phenyl selenide) and bis(phenyl telluride) to give the corresponding vinyl phenyl selenides and tellurides (191) and mercury(II) salts (192) in high yields (equation 118)[83]. The reactions were carried out in benzene solutions using a 275-W sunlamp at 34–45 °C, and were completely inhibited by radical quenchers such as di-tert-butyl nitroxide and galvinoxyl.

$$RCH = CHHgCl + PhEEPh \xrightarrow[\text{PhH}]{hv} RCH = CHEPh + PhEHgCl \tag{118}$$

(190)		(191)	(192)
		yield	
R = H,	E = Se	91%	
R = t-Bu,	E = Se	95%	
R = Ph,	E = Se	90%	
R = t-Bu,	E = Te	89%	
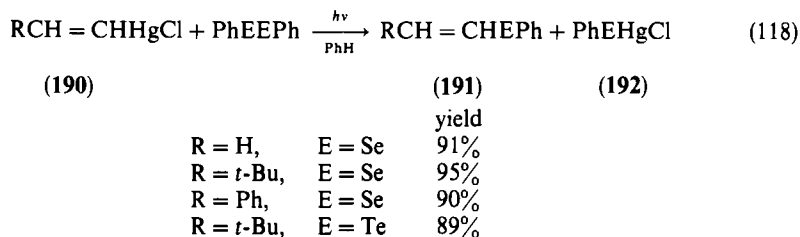
Since these reactions fail to occur with benzyl- or phenyl-mercury halides, the initial formation of a carbon-centered radical intermediate to propagate an S_H2 reaction was excluded. Instead, a free-radical addition–elimination[82,84] mechanism was suggested, with initiation by the photohomolytic cleavage of the chalcogenide (equation 119), and the subsequent propagation sequence shown in equations 120–121.

$$PhEEPh \xrightarrow{\ hv\ } PhE^{\cdot} \tag{119}$$

$$(E = Se, Te)$$

$$RCH = CHHgX + PhE^{\cdot} \longrightarrow RCHCH(EPh)HgX \longrightarrow RCH = CHEPh + HgX^{\cdot} \tag{120}$$

$$HgX^{\cdot} + PhEEPh \longrightarrow PEHgX + PhE^{\cdot} \tag{121}$$
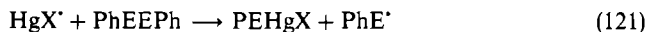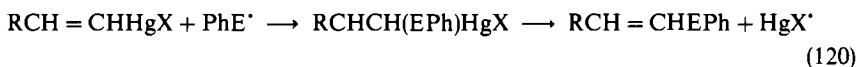
Irradiation of allyltributylstannane (193) with PhSeSePh in benzene (Pyrex filter) afforded allyl phenyl selenide (194) and the selenide 195 (equation 122)[85]. The reaction did not occur in the dark, but was initiated by azobis(isobutyronitrile) (AIBN) at 70 °C. The photostimulated reaction was completely inhibited by nitroxide or galvinoxyl. When crotyltributylstannane (196) was irradiated with bis(phenyl sulfide), the allylic rearrangement product 197 was obtained (equation 123).

$$CH_2 = CHCH_2SnBu_3 + PhSeSePh \xrightarrow[\text{PhH}]{hv\ (\text{Pyrex})} PhSeCH_2CH = CH_2 + Bu_3SnSePh$$

(193)	(36)	(194)	(195)

$$\tag{122}$$

$$MeCH = CHCH_2SnBu_3 + PhSSPh \xrightarrow{h\nu} PhSCH(Me)CH = CH_2 + Bu_3SnSePh$$

(196)   (197)
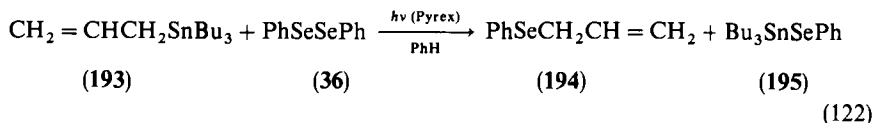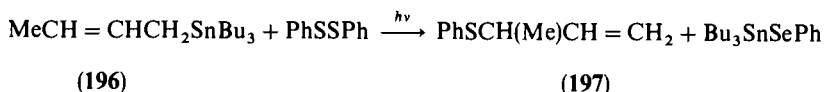
(123)

These results suggest that unlike the vinyl mercurials **190**, the stannanes operative via an S_H2 free-radical chain mechanism induced by PhSe radicals. Propagation is achieved by allylic displacement of a Bu_3Sn radical, followed by reaction of the latter with the diselenide to regenerate PhSe radicals (equations 124 and 125).

$$PhSe^{\bullet} + CH_2 = CHCH_2SnBu_3 \longrightarrow PhSeCH_2CH = CH_2 + Bu_3Sn^{\bullet} \qquad (124)$$

$$Bu_3Sn^{\bullet} + PhSeSePh \longrightarrow Bu_3SePh + PhSe^{\bullet} \qquad (125)$$
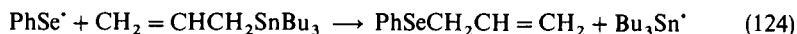
A closer look at the intermediate radicals obtained during the photochemical metal displacement with selenide was provided by studies of the photoinduced reaction of bis(phenyl selenide) (**36**) with alkyl, allyl and allenyl derivatives of bis(dimethylglyoximato)pyridinecobalt(III) complexes (**198**) (cobaloximes). When equimolar amounts of the optically active (R)-s-octyl-cobaloxime (**198a**) and **36** in dichloromethane were irradiated through pyrex with tungsten light, the racemic s-octyl phenyl selenide **199a** was obtained in 62% yield, together with phenylselenyl-cobaloxime (**200**) (equation 126)[86]. Good yields of selenides were also obtained from benzylic and allylic cobaloximes **198b–d**.

$$RCo(dmgH)_2py + PhSeSePh \xrightarrow[CH_2Cl_2]{h\nu} PhSeR + PhSeCo(dmgH)_2py \qquad (126)$$
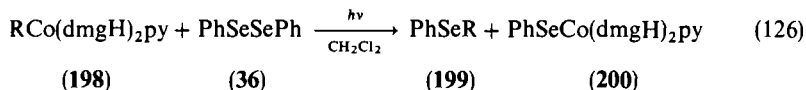
(198)   (36)   (199)   (200)

(a) R = (R)-s-octyl   R = racemic s-octyl
(b) R = PhCHMe
(c) R = $Me_2C = CHCH_2$
(d) R = $PhCH = CHCH_2$

In all the above reactions only a single isomeric selenide (**199**) was observed. However, when the but-2-enyl-cobaloxime **201** was irradiated, two isomers, **202** and **203**, were isolated (equation 127). The allenyl-cobaloxime **204** likewise gave two isomers, propadienyl selenide (**205**) and propynyl selenide (**206**) (equation 128).

$$MeCH = CHCH_2Co(dmgH)_2py + PhSeSePh \xrightarrow{h\nu} MeCH = CHCH_2SePh$$

(201)   (202)

$$+ CH_2 = CHCH(Me)SePh + 200$$

(203)

(127)

$$Me_2C = C = CHCo(dmgH)_2py + PSeSePh \xrightarrow{h\nu} Me_2C = C = CHSePh +$$

(204)   (205)

$$HC \equiv CC(Me)_2SePh + 200$$

(206)
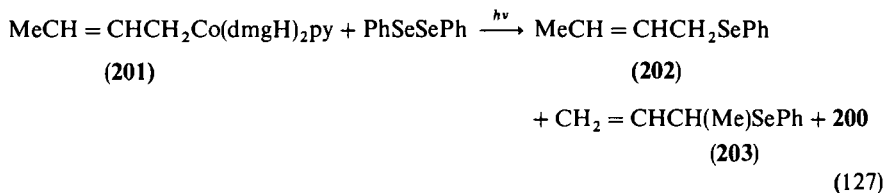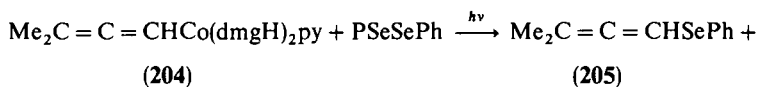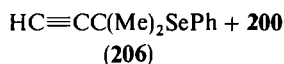
(128)

Based on the fact that cobaloximes readily form radicals under photolytic conditions[87], a non-chain free-radical mechanism is suggested (equations 129–131)[86], in which an initial photoinduced homolysis of the cobaloximes takes place to give the corresponding alkyl radicals, which attack diphenyl diselenide to form alkyl phenyl selenide and phenyl selenide radicals. The latter recombine with the metal fragment to form phenyl selenide cobaloxime. The formation of isomeric mixtures of selenides in the reaction of **201** and **204** supports this mechanism, although a combination of the S_H2[82,85] and addition–elimination[83,84] pathways cannot be excluded. However, racemization of the (R)-s-octyl group during the photolysis of cobaloxime **198a** seems to exclude these pathways and to favor the non-chain mechanism suggested.

$$RCo^{III}(dmgH)_2py \longrightarrow R^{\cdot} + Co^{II}(dmgH)_2py \tag{129}$$

$$R^{\cdot} + PhSeSePh \longrightarrow RSePh + PhSe^{\cdot} \tag{130}$$

$$Co^{III}(dmgH)_2py + PhSe^{\cdot} \longrightarrow PhSeCo(dmgH)_2py \tag{131}$$
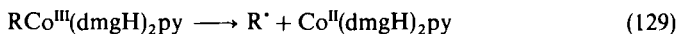
Aromatic ligands are photolytically displaced by selenides in zirconocene derivatives[88]. Irradiation of heptane solutions of diphenylzirconocene (**207**) with bis(phenyl selenide) (**36**) afforded bis(phenylselenyl)zirconocene (**208**) and biphenyl (equation 132). No reaction occurred in the dark. With dimethylzirconocene (**209**), monosubstitution by a PhSe group took place thermally in the dark, forming the thermally stable monoselenide **210** (equation 133), which on irradiation with **36** gave the expected **207**. These reactions are assumed to proceed via the bimolecular homolytic substitution (S_H2) mechanism.

$$(132)$$

$$(\eta^5\text{-}RC_5H_4)ZrMe_2 + PhSeSePh \xrightarrow{\Delta} (\eta^5\text{-}RC_5H_4)_2Zr(SePh)Me + PhSeMe \tag{133}$$

$$\textbf{(209)} \qquad\qquad\qquad\qquad \textbf{(210)}$$

$$(\eta^5\text{-}RC_5H_4)_2Zr(SePh)Me + PhSeSePh \xrightarrow{h\nu} (\eta^5\text{-}RC_5H_4)_2Zr(SePh)_2 \tag{134}$$

$$\textbf{(210)} \qquad\qquad\qquad\qquad\qquad \textbf{(208)}$$
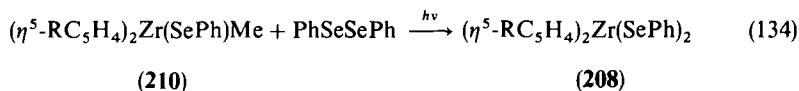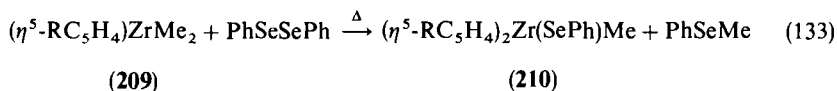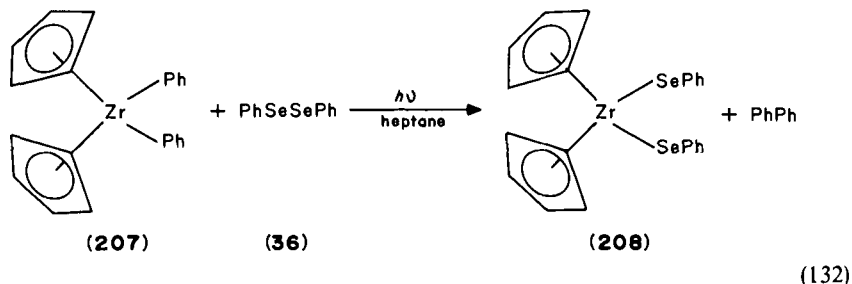
R = H, t-Bu

The same group[89] succeeded in achieving photosubstitution of phenyl and methyl groups in zirconocene and hafnocene derivatives using elemental (grey) selenium. Thus, when pentane solutions of **211** (M = Zr, Hf) were irradiated with UV light in the presence of grey selenium, a dinuclear selenium-bridged complex (**212**) was isolated, together with an equimolar amount of biphenyl. The same products were obtained when the dimethyl analogs $(\eta^5\text{-}t\text{-}BuC_5H_4)_2M(CH_3)_2$ (M = Zr, Hf) were irradiated in the presence of Se, and

when **208** was irradiated with **211** (equations 135 and 136). The yields were lower, however, and the by-products were not characterized.

$$(\eta^5\text{-}t\text{-BuCp})_2\text{MPh}_2 + \text{Se (grey)} \xrightarrow{h\nu} [(\pi^5\text{-}t\text{-BuCp})_2\text{M}(\mu\text{-Se})]_2 + \text{PhPh} \qquad (135)$$

$$\textbf{(211)} \qquad\qquad\qquad\qquad \textbf{(212)}$$

$$(\eta^5\text{-}t\text{-BuCp})_2\text{MPh}_2 + (\eta^5\text{-}t\text{-BuCp})\text{M}(\text{SePh})_2 \xrightarrow{h\nu} [(\eta^5\text{-}t\text{-BuCp})_2\text{M}(\mu\text{-Se})]_2 \quad (136)$$
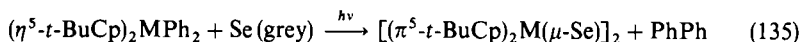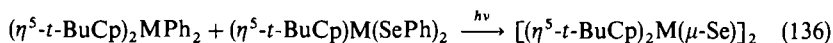
$$\textbf{(211)} \qquad\qquad \textbf{(208)} \qquad\qquad\qquad \textbf{(212)}$$
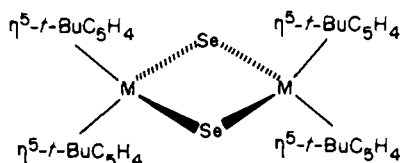
M = Zr, Hf

(212)
M = Zr, Hf

b. Ligand-exchange reactions. Photochemical exchange of ligands in metal carbonyl complexes is a common practice in organometallic chemistry[90]. The photoinduced exchange of ligand carbonyls with selenide and telluride groups has recently regained substantial interest. As with many other radical substitution reactions, the major source of these chalcogenide groups comes from the homolytic cleavage of diselenides and ditellurides.

An early study reported[91] that photolysis of **213** and **214** in the presence of hexafluorodimethyl diselenide (**215**) gave the binuclear diamagnetic complexes **216** and **217**, respectively (equations 137 and 138). It has been deduced from the spectroscopic data that these complexes contain bridging CF_3Se groups and terminal CO groups. A tentative free-radical mechanism is suggested in which $SeCF_3$ radicals combine with $M(CO)_n$ fragment (M = Fe, $n = 4$; M = Mn, $n = 5$) to give a labile metal selenide $[M(CO)_n(SeCF_3)]$ which dimerizes to the products with the expulsion of CO.

$$\text{Fe(CO)}_5 + \text{CF}_3\text{SeSeCF}_3 \xrightarrow[\text{CH}_2\text{Cl}_2,\text{ hexane}]{h\nu} [\text{Fe(CO)}_3(\mu\text{-SeCF}_3)]_2 \qquad (137)$$

$$\textbf{(213)} \qquad \textbf{(215)} \qquad\qquad\qquad\qquad \textbf{(216)}$$

$$\text{Mn}_2(\text{CO})_{10} + \text{CF}_3\text{SeSeCF}_3 \xrightarrow{h\nu} [\text{Mn(CO)}_4(\mu\text{-SeCF}_3)]_2 \qquad (138)$$

$$\textbf{(214)} \qquad\qquad\qquad\qquad \textbf{(217)}$$

More recently, a cubane-type tetranuclear cluster **218** was isolated[92] in the photolysis of **214** in the presence of PhSeSePh (equation 139). In addition, small amounts of the dinuclear complex **219** were isolated. Attempts to prepare mixed metal compounds having both sulfur and selenium bridges in the same molecule by irradiating **214** in the presence of both diphenyl diselenide and disulfide failed. Only the selenium derivatives **218** and **219** were obtained[93].

$$Mn_2(CO)_{10} + PhSeSePh \xrightarrow[\text{pentane}]{hv} [Mn(CO)_3(\mu\text{-}SePh)]_4 + [Mn(CO)_4(\mu\text{-}SePh)]_2$$

(214)   **(218)**   **(219)**
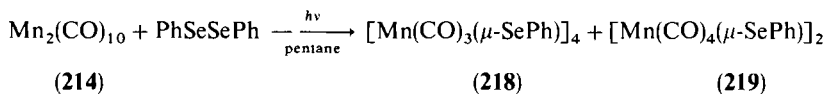
(139)
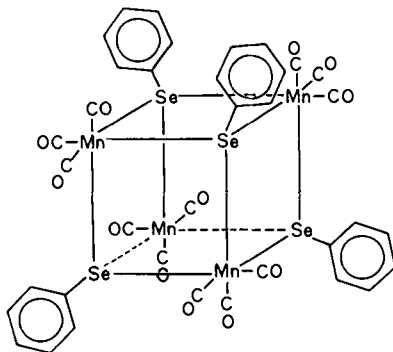
(218)

Structure suggested for
$[Mn(CO)_3SeC_6H_5]_4$

With Group VIB carbonyls, the dimolybdenum complexes **221** and **222** were isolated when the corresponding dimolybdenum hexacarbonyl complex **220** was irradiated with PhEEPh (E = Se, Te) (equation 140)[94]. The reaction proceeded in two steps, photolysis of **220** giving **221** as the primary product, followed by decarbonylation of the latter in vacuum under mild thermolysis conditions. The structure of **222** was deduced from the IR and mass spectra.

$$[(\eta^5\text{-}MeCp)Mo(CO)_3]_2 \xrightarrow[\text{toluene}]{hv \atop +(PhE)_2,} [(\eta^5\text{-}MeCp)Mo(CO)_2(\mu\text{-}EPh)]_2$$

(220)   **(221)**

$\Big\downarrow -CO$ (140)

E = Se, Te $[(\eta^5\text{-}MeCp)Mo(CO)(\mu\text{-}EPh)]_2$

MeCp = methylcyclopentadienyl   **(222)**
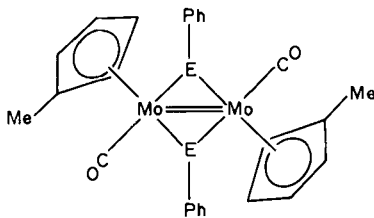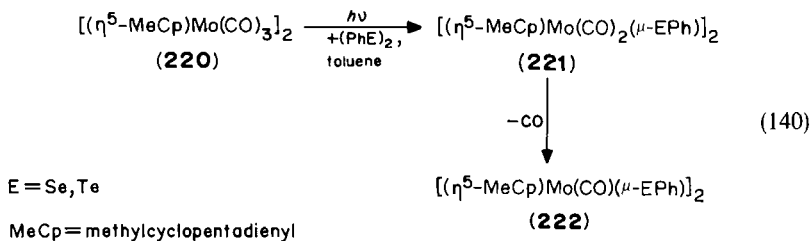
(222)
E = Se, Te
Structure suggested for
$[(\eta^5\text{-}MeCp)Mo(CO)(\mu\text{-}EPh)]_2$

Substitution of a carbonyl group by dimethyl selenide and telluride (and also sulfide) to give cyclopentadienyliron fluoroborate complexes (224) was accomplished by irradiation at room temperature of dichloromethane solutions of complexes 223 and the corresponding chalcogenides[95] (equation 141). The half-life of the exchange reaction in going from sulfur to tellurium compounds increases in the order $\tau_{1/2} = 1.7\,h\,(S) < 2.3\,h\,(Se) < 11.6\,h\,(Te)$. This reflects the affinity of the donor element to the coordination center of the complexes, which decreases in the order $S < Se < Te$.

In a closely related study, and under similar conditions, one phosphite group of 225 was substituted photochemically by dimethyl selenide or telluride, giving 226 (equation 142)[96].

(141)

(223)

E = S, Se, Te

(142)

(225)   (226)

E = S, Se, Te;   R = Me, Ph
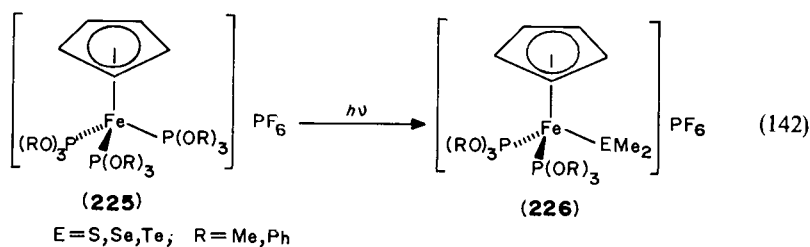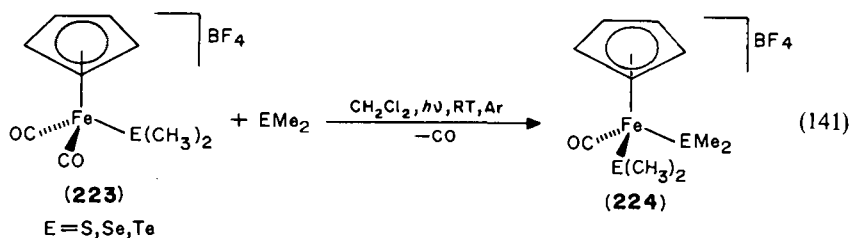
The first stable tellurophosphosphorane complex (229) were prepared in almost quantitative yields by irradiation of Group VIB transition metal hexacarbonyls (227) with tri-*tert*-butyltellurophosphorane (228) in THF (equation 143)[97]. The complex products (229) are fairly stable in air. The X-ray crystal structure of $W(CO)_5(R_3PTe)$ (R = *t*-Bu) exhibited a short W–Te bond (2.875 Å) and a W—Te—P angle close to 120°, suggesting an sp^2-type tellurium atom and double bond character of the W—Te bond[97].

$$M(CO)_6 + R_3PTe \xrightarrow[THF]{h\nu} M(CO)_5(R_3PTe)$$ (143)

(227)   (228)   (229)

M = Cr, Mo, W; R = *t*-Bu
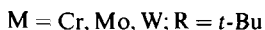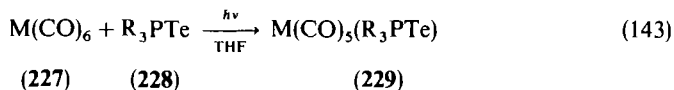
The X-ray structure of the selenium-bridged dinuclear rhenium complex 232 (E = Se) has been established[98]. Compound 232 was obtained when 230 was irradiated in THF solution. The key intermediate in the photolysis of 230 is the labile rhenium complex 231, in which one of the original carbonyls is replaced by a THF molecule. This complex has been shown to react thermally with elemental selenium or tellurium to give the bridged products 232. This may represent a general mechanism of photoinduced carbonyl exchange reactions (equation 144).

(230)

E = S, Se, Te

(231)

(144)

(232)
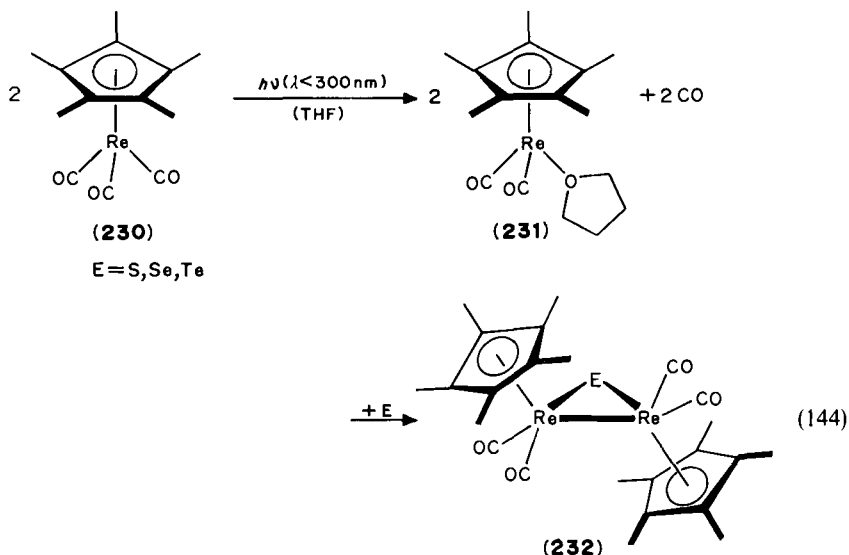
B. Photoaddition Reactions

Photolysis of silicon- and germanium-bonded selenols with olefins affords anti-Markovnikov addition products which result from homolytic cleavage of the Se—H bond[23]. Triethylsilaneselenol (233) reacts with styrene (234, R = Ph) and with hexene (234, R = Bu), giving the 1:1 adducts 235 in 90% and 72% yield, respectively (equation 145). Similarly, triethylgermaneselenol (236) reacts with styrene to give triethyl(phenethylselenyl)germane (237, R = Ph). However, the reaction of 236 with ethyl acrylate (234, R = COOEt) gave both the expected 3-[(triethylgermyl)selenoyl]propionate (237, R = COOEt) and 45 (equation 146). Irradiation of 236 with acrylonitrile (66) resulted in the isolation of only the symmetrical product 3,3′-selenodipropionitrile (67) (equation 147). The presence of these products in the reaction mixture clearly indicates that cleavage of the Ge–Se bond competes with that of the Se—H bond (Section II.A.3b).

$$Et_3SiSeH + CH_2 = CHR \xrightarrow{hv \text{ (Pyrex)}} Et_3SiSeCH_2CH_2R \qquad (145)$$

(233)   (234)   (235)

$$R = t\text{-Bu, Ph}$$

$$Et_3GeSeH + CH_2 = CHR \xrightarrow{hv} Et_3GeSeCH_2CH_2R + (Et_3Ge)_2Se \qquad (146)$$

(236)   (234)   (237)   (45)

$$R = Ph, COOEt$$

$$Et_3GeSeH + CH_2 = CHCN \xrightarrow{hv} Se(CH_2CH_2CN)_2 + 45 \qquad (147)$$

(66)   (67)

Se-Phenyl areneselenosulfonates (**42**), unlike their thiosulfonate analogs, are extremely photosensitive and undergo facile homolytic cleavage of the Se—S bond. In the presence of alkenes, addition of selenosulfonate across the alkene double bond occurs in an anti-Markovnikov fashion, giving β-phenylseleno sulfones (**238**) (equation 148)[22]. No reaction was observed with tetrasubstituted alkenes such as 2, 3-dimethylbut-2-ene. The experimental results are compatible with a free-radical chain reaction mechanism as shown in equation 149. When the intermediate sulfone radical is highly stabilized, as in the case of the reaction with 1, 1-diphenylethylene (**239**), the unsaturated sulfone **240** is formed together with diphenyl diselenide, presumably via an addition–elimination type of reaction as shown in equation 50. Such unsaturated sulfones are important synthetic intermediates and may be prepared from selenosulfones (**238**) by oxidative elimination[22,99,100].

$$PhSeSO_2Ar + CH_2 = CHR \xrightarrow[CCl_4]{h\nu} ArSO_2CH_2CH(R)SePh \qquad (148)$$

$$\textbf{(42)} \qquad\quad \textbf{(234)} \qquad\qquad\qquad \textbf{(238)}$$

$$Ar = p\text{-tolyl}; \ R = n\text{-Bu, Ph}$$

$$PhSeSO_2Ar \xrightarrow{h\nu} PhSe^{\cdot} + ArSO_2^{\cdot}$$

$$ArSO_2^{\cdot} + CH_2 = CHR \longrightarrow ArSO_2CH_2\overset{\cdot}{C}HR$$

$$ArSO_2CH_2\overset{\cdot}{C}HR + PhSeSO_2Ar \longrightarrow ArSO_2CH_2CH(R)SePh + ArSO_2^{\cdot} \qquad (149)$$

$$ArSO_2^{\cdot} + CH_2 = CPh_2 \longrightarrow ArSO_2CH_2\overset{\cdot}{C}Ph_2 \xrightarrow{-H^{\cdot}} ArSO_2CH = CPh_2 \qquad (150)$$

$$\textbf{(239)} \qquad\qquad\qquad\qquad\qquad \textbf{(240)}$$

When a large excess of olefin over selenosulfonate was used, polymerization occurred. Thus, irradiation of **42** in 10-fold excess of hex-1-ene gave polymers of general structure **241**.

$$ArSO_2(CH_2CH)_n SePh$$
$$|$$
$$n\text{-Bu}$$
$$n > 1$$
$$\textbf{(241)}$$

The photoaddition of **42** to cyclohexene was found to be highly stereospecific, giving rise to 80% of the *trans*-adduct **242** (equation 151) with no significant amounts of the *cis*-adduct. Free-radical additions to cyclohexene are highly stereoselective, exhibiting a strong preference for axial attack on both the olefinic double bond and the derived radical intermediate[101,102]. Therefore, radical **243**, being formed by axial attack of $ArSO_2^{\cdot}$ on cyclohexene, must undergo chain transfer with **42** to give **242** more rapidly than ring flip to the conformationally more stable radical **244**. Otherwise, the *cis*-isomer **245** would have been formed (equation 152).

$$(151)$$

$$\textbf{(42)} \qquad\qquad\qquad \textbf{(242)}$$

(152)

Further information regarding the reactivity of the intermediate arylsulfonyl radical in the chain transfer process is provided from studies of the photoinduced selenosulfonation of non-conjugated dienes[22,103]. Photoaddition of **42** to hepta-1,6-diene (**246**) in CCl_4 (equation 153) afforded a mixture of three products in a ratio depending on the initial concentration of reactants. At 1 M the open-chain products **247** and **248** predominate over the cyclic product **249** (9:1 ratio), while in more dilute solutions (0.1 M) equal amounts of open-chain to cyclic products are observed[103]. This indicates that **42** is reactive enough as a chain-transfer agent to compete with the transannular reaction to give **249**.

(153)

Likewise, free-radical addition of **42** to cycloocta-1,5-diene (**250**) gives a mixture of approximately equal amounts of the 1,2-adduct **251** and the 1,5-transannular product **252** (equation 154)[22].

(154)

It is instructive to compare the reactivity of selenosulfonates (**42**) with other chain-transfer agents such as HBr and CCl_4. Photoaddition of HBr to cycloocta-1,5-diene (**250**) is reported to give only 1,2-adducts[104], whereas free-radical addition of CCl_4 to **250**

afforded only 1, 5-transannular products[105,106]. The formation of both **251** and **252** in the reaction of **42** with **250** shows that the reactivity of these reagents as chain-transfer agents decreases in the order HBr > ArSO$_2$SePh > CCl$_4$.

The relative rate of the chain-transfer capability of **42** compared with cyclobutane ring cleavage is demonstrated in the photoinduced arylsulfonation of β-pinene (**253**)[103]. Photoaddition of **42** (Ar = p-Tol) in CCl$_4$ solution afforded 91% of the rearranged p-menthene derivative **256** (equation 155). This result demonstrates that cleavage of the initial cyclobutylcarbonyl radical **254** to the p-menthenyl radical **255** is faster than the transfer reaction of this radical with **42**. Unrearranged 1, 2-adducts were observed only with extremely reactive chain-transfer agents such as thioacetic acid[107].

(155)
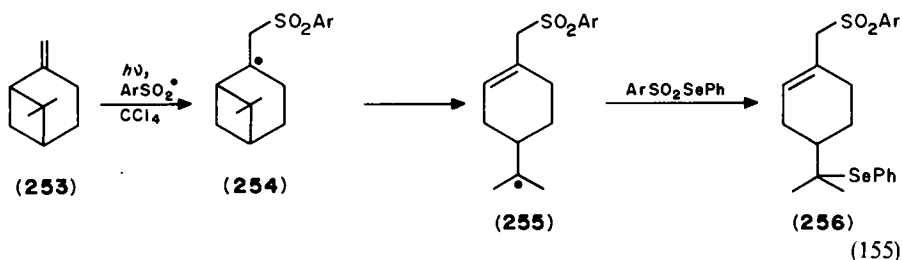
The chain-transfer reactivity of selenosulfonate **42** (Ar = p-Tol) was studied in the norbornane – nortricyclane system. The interconversion between radicals **258** and **259** is known to be very rapid, with the nortricyclenyl radical being favored at equilibrium[108,109]. Photoaddition of **42** (Ar = p-Tol) to norbornadiene (**257**) gives a 75% yield of a mixture of adducts consisting of ca. 90% of **261** and **262** and only 10% of **260**. This ratio is virtually the same as that found in the photoaddition of PhSO$_2$Br to norbornadiene at similar dilutions[110]. This suggests a similar chain-transfer reactivity of the two reagents. However, the ratio between the two cyclic systems is quite different from that (27:73) found for the corresponding addition of PhSO$_2$I[110], indicating that the iodide is a much more reactive chain-transfer agent. It is also interesting that the ratio between the exo-**261** and endo-**262** tricyclanes (6:4) is not significantly different from the ratio (4:3) of the arenesulfonyl bromide counterparts[111]. This indicates that a change in the group transferred to the nortricyclic radical **259** from Br to PhSe has little effect on the preference of exo vs. endo transfer.

(156)
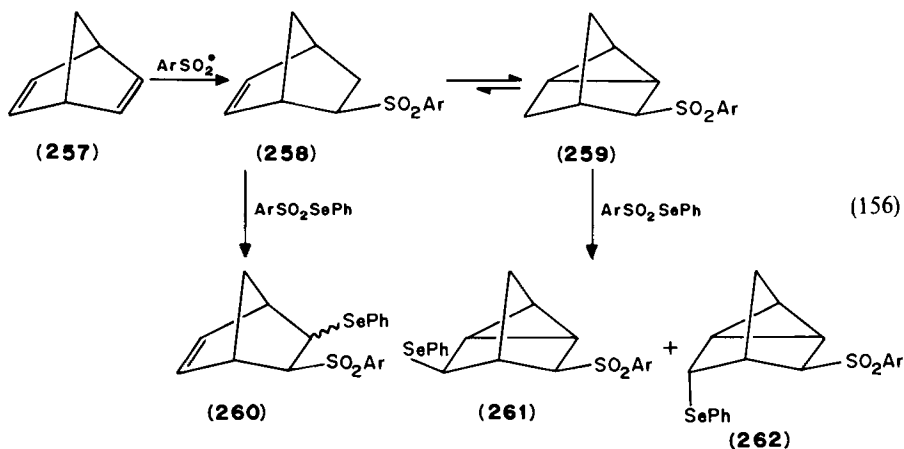
Selenosulfonation of olefins may also be effected by alkaneselenosulfonates such as *Se*-phenyl-1-dodecaneselenosulfonate (263), which adds to cyclohexene in the usual 1,2-manner in 71% yield[103]. On the other hand, the photolysis of the corresponding benzylsulfonate 264 in the presence of cyclohexene did not result in an addition product. Instead, benzyl phenyl selenide (265) was isolated in high yields. Apparently, the benzylsulfonyl radical initially formed undergoes rapid desulfonylation to the more stable benzyl radical, which undergoes a transfer reaction with another molecule of selenosulfonate in preference to addition to an alkene molecule (equation 157).

$$C_{12}H_{25}SO_2SePh \qquad PhCH_2SO_2SePh$$
$$(263) \qquad\qquad (264)$$

$$PhCH_2SO_2^{\bullet} \rightarrow PhCH_2^{\bullet} + SO_2$$

$$PhCH_2^{\bullet} + PhCH_2SO_2SePh \rightarrow PhCH_2SePh + PhCH_2SO_2^{\bullet} \qquad (157)$$
$$(265)$$
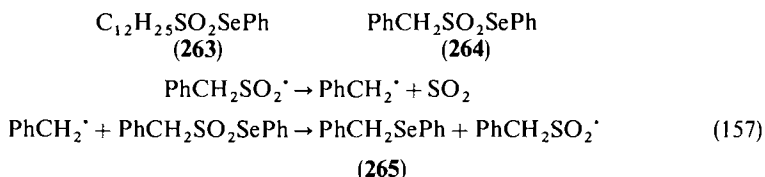
Another variation of the selenosulfonation reaction was observed in the photolysis of bis(*p*-tolylsulfonyl) selenide (266)[103] with cyclohexene (equation 158). In addition to the expected 1,2-adduct 267, the diselenide 268 and some elemental selenium precipitate were obtained. The diselenide 268 is believed to be formed from the primary selenosulfonate product 267 in a subsequent photodissociation of the Se—S bond, followed by dimerization. Interestingly, the photoinduced reaction of 266 with styrene gave only high yields of the selenide 269 and none of the expected primary 1,2-addition product (equation 159).

$$PhCH = CH_2 \xrightarrow[266]{hv} (ArSO_2CH_2CHPh)_2Se \qquad (159)$$
$$(269)$$
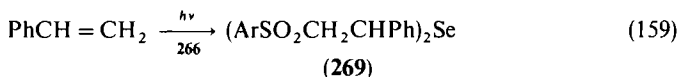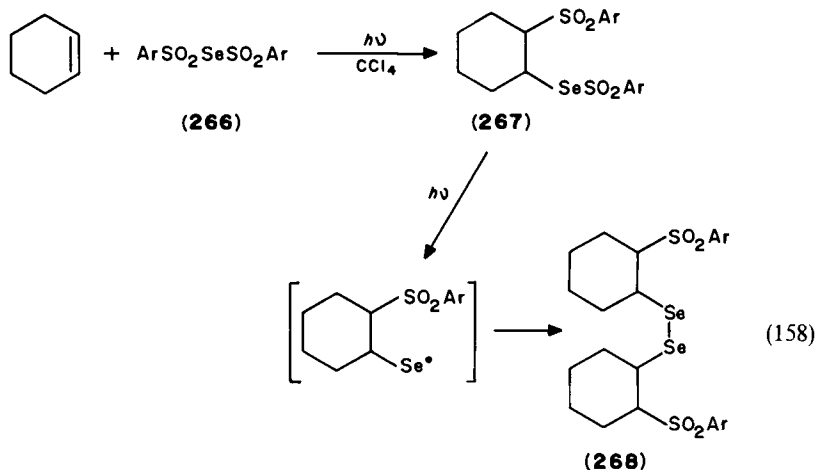
We conclude this section with the unusual photoaddition of ArSe radicals 271 (Ar = Ph, *o*-NO$_2$C$_6$H$_4$) to nitrosodurene (270)[112], which gave the corresponding spin adducts 272 (equation 160). Experiments were performed in a quartz cell at − 50 °C. The ESR spectra of these selenylnitroxide radicals show hyperfine coupling with ^{77}Se ($\alpha = 7.8$–8.7 G), indicating a low spin density on the selenium. Similar results were obtained when diphenyl

selenide was photolysed in the presence of **270**. This reconfirmed previous evidence of the homolytic nature of the cleavage of Se—Se and Se—C bonds in aromatic diselenides.

$$
\text{(270)} \quad + \quad \text{ArSe}^\bullet \quad \xrightarrow[-50\ ^\circ C]{h\nu(\text{quartz})} \quad \text{(272)} \tag{160}
$$

(270)   **(271)**   **(272)**

$$Ar = Ph, o\text{-}O_2NC_6H_4$$
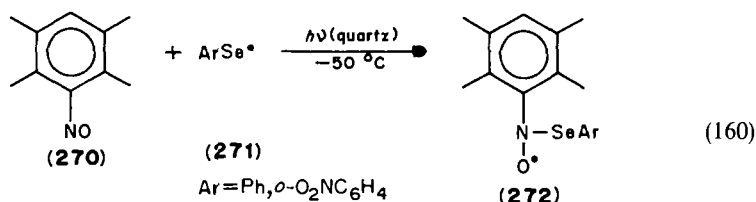
C. Photocycloadditions

All photocycloadditions of organoselenium compounds involve the 2 + 2 cycloaddition of olefins and ketones to selenophene **(273)** and benzo[*b*]selenophene **(274)** derivatives. Olefins yield cyclobutanes[113] and ketones yield oxetanes (Paterno–Buchi reaction)[114]. Light-induced cycloaddition reactions of tellurophene derivatives are as yet unknown. Both tellurophene **(275)** and 2,5-diphenyltellurophene **(276)** were stable under irradiation conditions in which selenophene derivatives react[115,116].

(273)   **(274)**   **(275)**   **(276)**
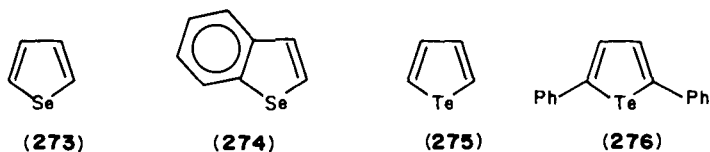
The benzophenone triplet-sensitized reaction of equimolar amounts of selenophene **(273)** and 2,3-dimethylmaleic anhydride **(277)** gave high yields of the 2 + 2 anti-adduct **278**, accompanied by the minor diadduct **279** in which two anhydride molecules add to the selenophene, one with *exo*- and the other with *endo*-stereochemistry (equation 161)[117].

$$
\text{273} + \quad \text{(277)} \quad \xrightarrow[PhH]{h\nu(Ph_2CO)} \quad \text{(278)} \quad + \quad \text{(279)} \tag{161}
$$
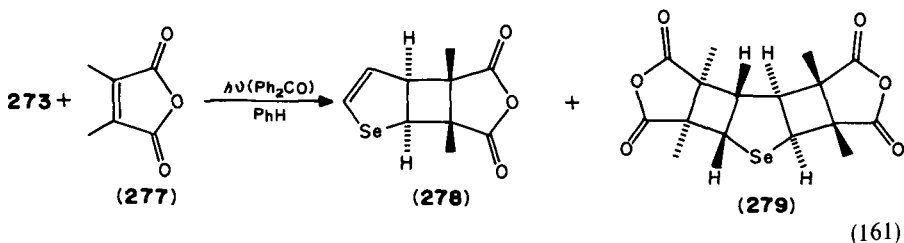
2,3-Dimethylmaleic anhydride **(277)** undergoes photosensitized 2 + 2 cycloaddition also with benzo[b]selenophene **(274)** and with the two selenophthenes **281** and **283**. Benzoselenophene (equation 162) and the selenophthene **281** (equation 163) gave the corresponding monoadducts **280** and **282**, whereas the selenophthene **283** (equation 164) gave a mixture of the monoadduct **284** and diadduct **285**[118].

$$
\text{274} + \text{277} \quad \xrightarrow[PhH]{h\nu(Sen.)} \quad \text{(280)} \tag{162}
$$

(Sen. = photosensitizer)   **(280)**

(163)

(281)   (282)

(164)

(283)   (284)

(285)
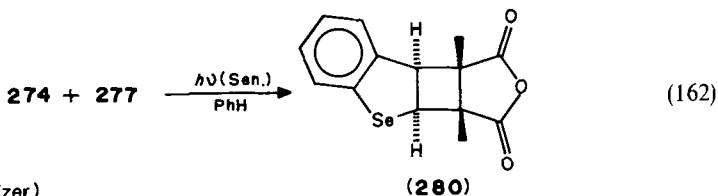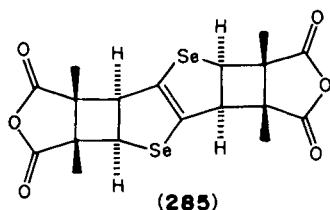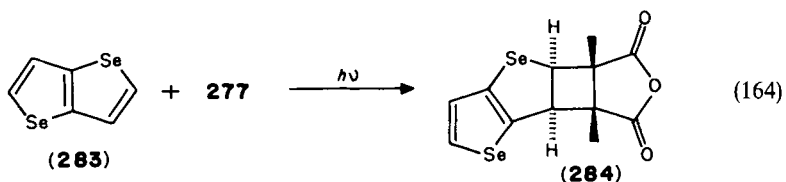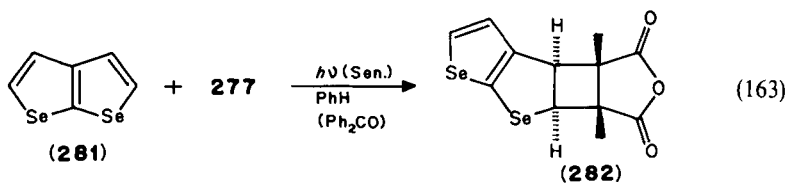
Acetophenone-sensitized photocycloaddition of the benzoselenophene derivatives **286** (triplet energy $E_T = 69$ kcal) with 1, 2-dichloroethylene (**287**) (*cis* and *trans* isomers) gave a mixture of cyclobutanes **288** and **289** (equation 165)[119]. As with the sulfur analogs[120], four such isomeric 2 + 2 adducts may be obtained, a pair of *trans*- and *cis-exo* isomers **288** and a pair of *trans*- and *cis-endo* isomers **289**. A mixture of all four isomeric products was obtained only in the photoreaction of **286c**. Three isomers were identified in the reaction of the monomethyl derivatives **286a** and **286b**, and two isomers were detected with 3-acetoxybenzoselenophene (**286d**). A single isomeric 2 + 2 adduct was observed in the photoexcitation of **286e**.

(286)   (287)

(a) $R^2 = H, R^3 = Me$

(b) $R^2 = Me, R^3 = H$

(c) $R^2 = R^3 = Me$

(d) $R^2 = H, R^3 = OCOMe$

(e) $R^2 = Me, R^3 = OCOMe$

trans- and *cis-exo*

(288)

(165)

trans- and *cis-endo*

(289)
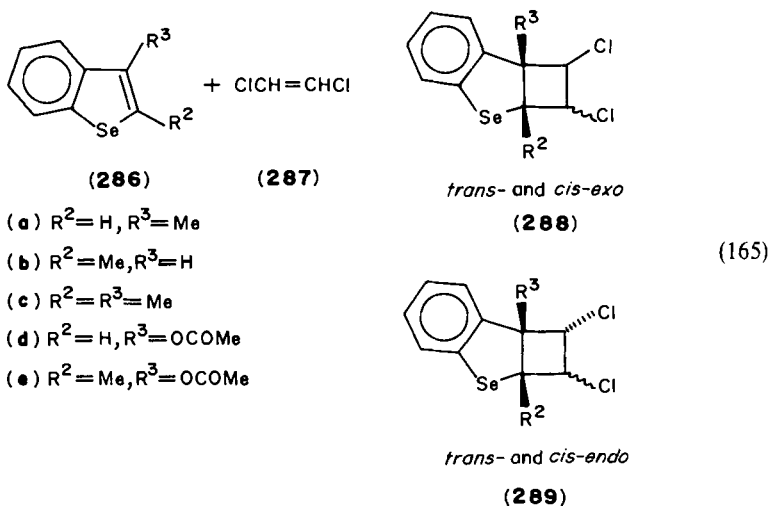
The structural assignment of the various isomers is based on a comparative NMR analysis with the sulfur analogs[120]. The two major isomers usually observed are believed to be the *trans-* and the *cis-exo-288* isomers. *Cis-endo-289* is assumed to be formed in low yields (1–3%) and *trans-289* is rarely observed. However, this generalization should be treated with some caution since an unequivocal X-ray structure study showed that the two acetoxy adducts isolated from the reaction of **286d** were the two *trans-*cyclobutane isomers **288d** and **289d**[119].

Unlike 1,2-dichloroethylene and 2,3-dimethylmaleic anhydride, which give isolable 2 + 2 adducts, dimethyl acetylenedicarboxylate (**290**) reacts photochemically with benzoselenophene (**274**) and its 3-methyl derivative (**286a**) in the presence of acetophenone as a triplet sensitizer to give esters of 1,2-naphthalenedicarboxylic acid (**292**)[119] (equation 166). This unusual reaction has an analogy in the sulfur series[121,122], where the same products **292** were obtained. However, in contrast to the sulfur counterparts, where the intermediate **291** (with S instead of Se) could be isolated and pyrolysed to **292**, **291** itself is apparently an unstable primary product and undergoes a spontaneous thermal deselenation to **292**.

$$(166)$$
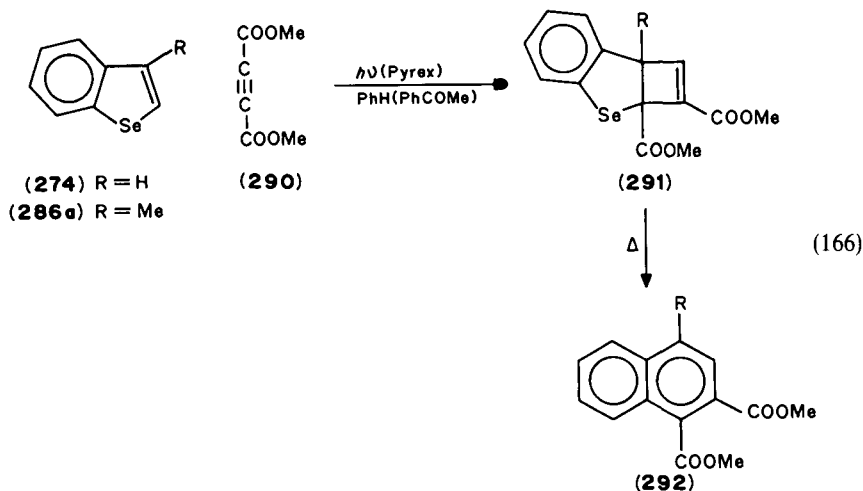
The mechanism by which the cyclobutene **291** was obtained is obscure. Three possible pathways have been proposed for the sulfur analogs[122], but none is conclusive. The preferred mechanism is shown in equation 167.

R = COOMe

$$(167)$$
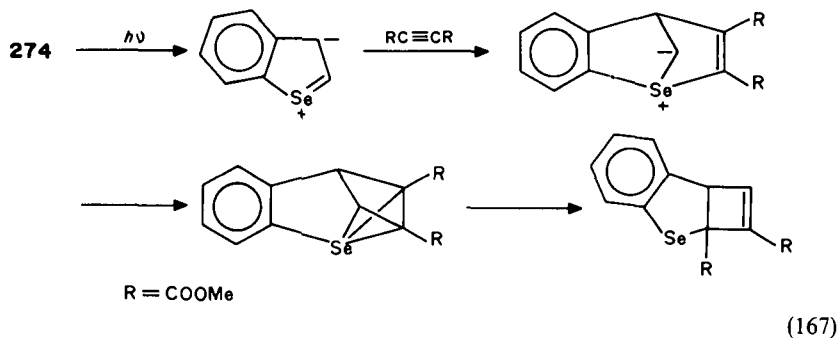
The reluctance of unsubstituted selenophene, thiophene and tellurophene to photo-dimerize or give oxetanes was first attributed to their aromatic character[116,123]. Later[115,124,125], however, it was shown that the lack of reactivity results from the ability of these compounds to act as quenchers of the ketones used. In order to test the quenching ability of selenophene on the excited state of benzophenone, a kinetic study of the photoreduction of benzophenone by isopropanol in the presence of selenophene was carried out[124]. Stern–Volmer plots of ϕ_o/ϕ_Q versus $[Q]$ (where ϕ_o and ϕ_Q are the quantum yields for the photoreduction of benzophenone in the absence and presence of the quencher, respectively, and $[Q]$ is the concentration of selenophene as quencher) indicate that selenophene and also thiophene, pyrrole and imidazole derivatives are good quenchers of the triplet state of benzophenone. It is perhaps important to mention that unlike imidazole and the thiophene derivatives, which give a normal linear Stern–Volmer plot, selenophene and pyrrole derivatives gave quadratic plots. This is consistent with a mechanism in which an exciplex $(Q-B)^*$ is initially formed between triplet benzophenone (^3B) and ground-state selenophene (Q), and subsequently quenched by another quencher molecule. The Stern–Volmer equation will then obtain the quadratic form shown in equation 168[126].

$$^3B + Q \longrightarrow (Q-B)^* \overset{Q}{\longrightarrow} B + Q^* + Q \tag{168}$$

$$\phi_o/\phi = (1 + k_q\tau[Q])(1 + k'_q\tau'[Q])$$
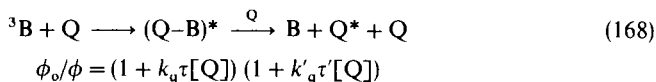
Although unsubstituted selenophene, like thiophene, is inert towards $2 + 2$ cycload-ditions with benzophenone, 2-methylselenophene (293) is active. Irradiation of 293 in benzene using benzophenone as sensitizer gave 34% of the oxetane 294 (equation 169)[127]. Thiophene has been shown to require two methyl groups in order to participate in the Paterno–Buchi oxetane cycloaddition[128].

$$\tag{169}$$

(293)   **(294)**
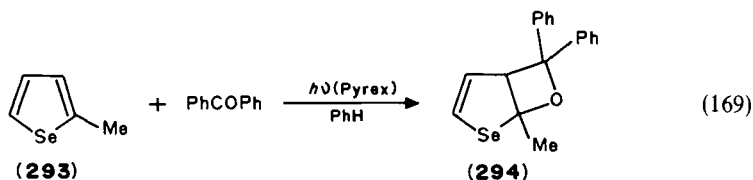
D. Insertion Reactions

Diazomethane (295) reacts with dibenzyl diselenide (1) in sunlight to give quantitatively the insertion product 296 (equation 170)[129]. The corresponding ditelluride 53 undergoes the same insertion reaction in the dark.

$$PhCH_2SeSeCH_2Ph + CH_2N_2 \xrightarrow[Et_2O,\,0°C]{sunlight} (PhCH_2Se)_2CH_2 \tag{170}$$

$$\quad\quad (1) \quad\quad\quad\quad (295) \quad\quad\quad\quad\quad (296)$$
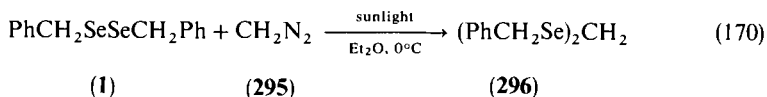
A plausible reaction pathway involves light-induced homolytic cleavage of the Se—Se bond of 1 (Section II.A.2), forming benzyl selenide radicals, which react with diazometh-ane to give a labile diazo radical. Loss of nitrogen and recombination with a benzylselenyl radical affords the observed product (equation 171). Other mechanistic pathways, such as the initial formation of carbene cannot be entirely ruled out.

$$(PhCH_2Se)_2 \xrightarrow{h\nu} PhCH_2Se^{\cdot} \xrightarrow{CH_2N_2^{\cdot}} PhCH_2SeCH_2N_2^{\cdot}$$

$$\xrightarrow{-N_2} PhCH_2SeCH_2^{\cdot} \xrightarrow{PhCH_2Se^{\cdot}} (PhCH_2Se)_2CH_2 \tag{171}$$
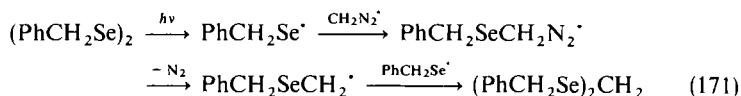
In the gas phase, atomic selenium was monitored in flashed CSe_2 and $COSe$ (Section II.B.1) by kinetic absorption spectroscopy, and its rate of reaction with alkanes and alkenes was measured in the temperature range 302–412 K[24–26]. The excited $Se(4^1D_2)$ atoms insert into the C—H bond of saturated hydrocarbons such as propane, cyclopropane, cyclobutane, ethane and isobutane, and also possibly into the Si—H bonds of methylsilane[26]. When mixtures of COSe and propane were flashed, no hexane was formed, although small amounts of HSe were detected. This indicates that selenomercaptan formation in these reactions is a single-stage process (equation 172). Had it been a two-step hydrogen abstraction followed by combination of HSe and C_3H_7, hexane formation would have been expected.

$$RH + COSe \xrightarrow{\ h\nu\ } RSeH + CO + Se_2 \tag{172}$$
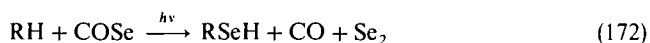
Generation of excited selenium atoms in the presence of olefins resulted in the formation of adducts which are probably the corresponding episelenides (297) (equation 173)[24,25]. The activation energies were shown to correlate with the olefin ionization potentials. All the episelenides were found to be unstable at room temperature but could be trapped at 77 K in a fast flow system. They decay at room temperature with half-lives between 30 ms and a few seconds. Decomposition of the episelenides, if it occurs in the gas phase, is probably bimolecular, giving Se_2 and two olefin molecules.

$$R^1R^2C{=}CR^3R^4 \ + \ Se \ (4^1D_2) \ \longrightarrow \ \underset{\textbf{(297)}}{\overset{\displaystyle R^2\!\!\diagdown\!\!\underset{Se}{\diagup}\!\!\diagup R^4}{}} \tag{173}$$

$$R^1R^2C{=}CR^3R^4 \ + \ Te \ (^3P_2) \ \longrightarrow \ \underset{\textbf{(298)}}{\overset{\displaystyle R^2\!\!\diagdown\!\!\underset{Te}{\diagup}\!\!\diagup R^4}{}} \tag{174}$$
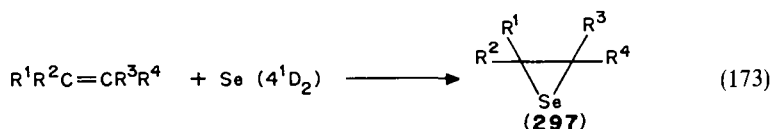
Similarly, flashing dimethyl telluride produced excited $Te(^3P_2)$ atoms (Section II.B.1), which in the presence of olefins give unstable adducts. These adducts have lifetimes of several milliseconds, and have been assigned as the corresponding epitellurides 298 (equation 174)[26,27]. The formation of the transient epitelluride molecules has been confirmed by kinetic mass spectrometry, and has been shown to be slower and more selective than the addition of O, S or Se atoms to olefins. It is interesting that the rate constants for the addition of $Te(^3P_2)$ to tetramethylethylene $3.9 \times 10^9\,l\,mol^{-1}\,s^{-1}$ (25 °C) and $2.6 \times 10^9\,l\,mol^{-1}\,s^{-1}$ (80 °C) correspond to an activation energy $E_a = -1.6 \pm 1.4\,kcal\,mol^{-1}$, which is the first reported case of a negative temperature coefficient for an addition reaction in its second-order region[27].

IV. PHOTOREARRANGEMENTS AND PHOTOISOMERIZATIONS

A. Rearrangements

There are in principle two groups of rearrangement reactions, those in which a bond between a chalcogen and another atom is cleaved during the reaction, and others in which the bonds to selenium or tellurium remain intact and rearrangement occurs at a different

molecular site. It is often observed that primary rearrangement products in which an Se—C bond was cleaved are air sensitive and can be isolated only as oxidation products. In other cases further photochemical (or thermal) transformations occur.

Photolysis of 2-phenylselenophene (**78**) in dilute ethereal solutions gave a 15% yield of the isomeric 3-phenylselenophene (**80**) together with deselenation products (equation 175)[38]. The corresponding 2-phenyltellurophene, however, gave only fragmentation products (Section II.B.1). 3-Phenylselenophene (**80**) proved to be stable and could not be rearranged back to **78** under the reaction conditions. It is assumed that the rearrangement occurs in a manner analogous to that suggested for thiophene rearrangements (equation 176)[130]. This involves cleavage of the Se—C bond to form the intermediate cyclopropenyl selone **299**, which rearranges by a formal 1,3-sigmatropic shift to **80**[38].

$$\textbf{78} \xrightarrow[\text{Et}_2\text{O}]{h\nu} \textbf{80} \qquad (175)$$

$$(176)$$
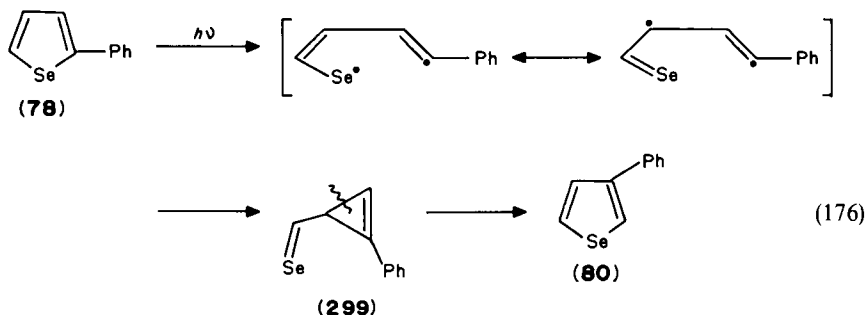
The photoinduced electrocyclic ring opening of selenochromene **300** was examined as a potential photochromic system in relation to the oxygen and sulfur analogs (equation 177)[131]. Irradiation of **300** (R = H) ($c = 10^{-4}$ mol l^{-1}) in glass solutions (isopentene–isopropanol, 5:2) at 313 nm resulted in color formation. The UV spectrum displayed characteristic features (λ_{max} 355 and 660 nm) of the conjugated system **301** observed for the lower chalcogen chromenes. However, unlike these chromenes no fluorescence of **300** was detected and the reaction could neither be sensitized nor quenched by triplet donors or acceptors. Further, unlike the lower analogs the characteristic bleaching of the solutions by thermal recyclization of **301** could only be effected at temperatures above 150 K. It was concluded that the selenochromenes **300** differ in their photochromic properties, and perhaps also in their photocoloring mechanism, from the corresponding chromenes and thiochromenes.

$$(177)$$
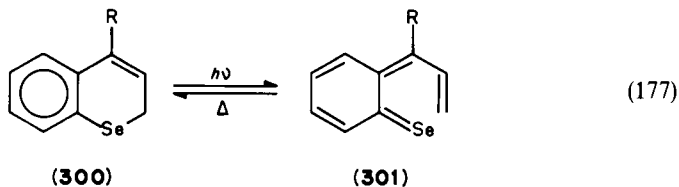
The photorearrangement of alkyl phenyl selenides **302** led via a formal 1,3-alkyl shift to *ortho*-substituted phenyl selenols **303**. These selenols oxidize during workup, and were

isolated as the corresponding diselenides **304** (equation 178)[132]. By application of this reaction to phenyl ribosyl selenide derivatives (**302b** and **c**), pseudonucleosides (C-nucleosides) of potential biological interest were obtained as mixtures of α- and β-anomers.

$$\text{PhSeR} \xrightarrow[\text{\it t-BuOH}]{\text{\it hv(quartz)}} 2-RC_6H_4SeH \longrightarrow 2-RC_6H_4SeSeC_6H_4R-2$$

(302)   (303)   (304)

(**a**) R=CH$_2$Ph

(**b**) R=

(178)

(**c**) R=
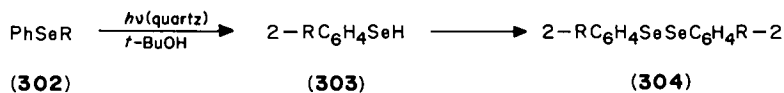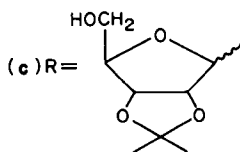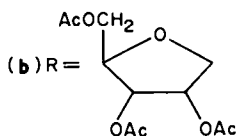
A useful photochemical route to substituted benzyl **306** and 1-naphthyl isoselenocyanate **308** from the easily accessible selenocyanates **305** and **307** has been reported (equations 179 and 180)[133]. The photochemical transformation is carried out by irradiation through quartz of 0.1–1.0mM solutions of the selenocyanates in dry acetic acid with a high-pressure mercury lamp. A photoequilibrium is reached in which the isoselenocyanates predominate. This formal sigmatropic 1,3-benzyl shift may occur by a concerted pathway or via homolytic Se—C bond cleavage to benzyl and selenocyanate radicals, which then recombine at either carbon or nitrogen.

(305)   (306)

(179)
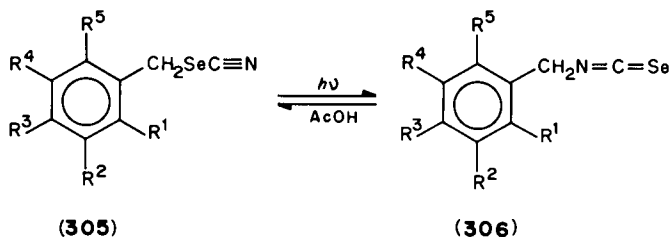
$R^{1,2,3,4,5} = H$

$R^{1,2,4,5} = H, R^3 = Cl$

$R^{1,2,4,5} = Me, R^3 = Br$

$R^{1,2,3,5} = Me, R^4 = Cl$

$R^{1,3,5} = Me, R^{2,4} = H$

$R^{1,2,3,4,5} = Me$

$$(180)$$
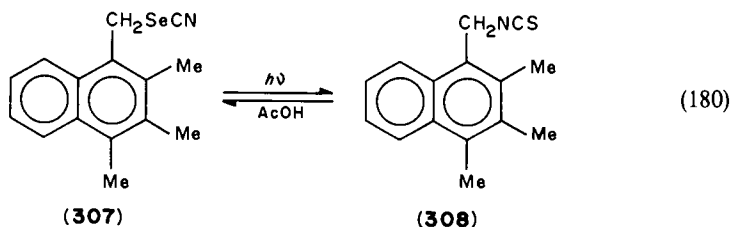
Aromatic selenoesters undergo an efficient photo-Fries rearrangement[134] to ketones. In the first published example of a seleno-photo-Fries reaction[11], Se-p-tolyl selenobenzoate (309, R = H) was irradiated in benzene at room temperature, affording a complex mixture containing the substituted benzophenone 310 (R = H) together with p-selenocresol (311, R = H), benzaldehyde (312, R = H) and the two diselenides 313 and 7 obtained by oxidative dimerization of the corresponding selenols (equation 181). Similarly, the selenophthalic ester 309 (R = COOMe) rearranges photochemically to the benzophenone 310 (R = COOMe), which was isolated as the diselenide 313 (R = COOMe)[135]. When the *ortho*-position of the selenoester is substituted by appropriate leaving groups, such as halogens, the reaction could not be stopped at the rearrangement step but instead selenoxanthones derived from further intramolecular substitution were obtained (see Section III.A.1.c). If the *ortho*-position was substituted by an aromatic selenide or telluride group, photo-Friedel–Crafts reaction occurred without rearrangement (see Section II.A.1).

$$(181)$$
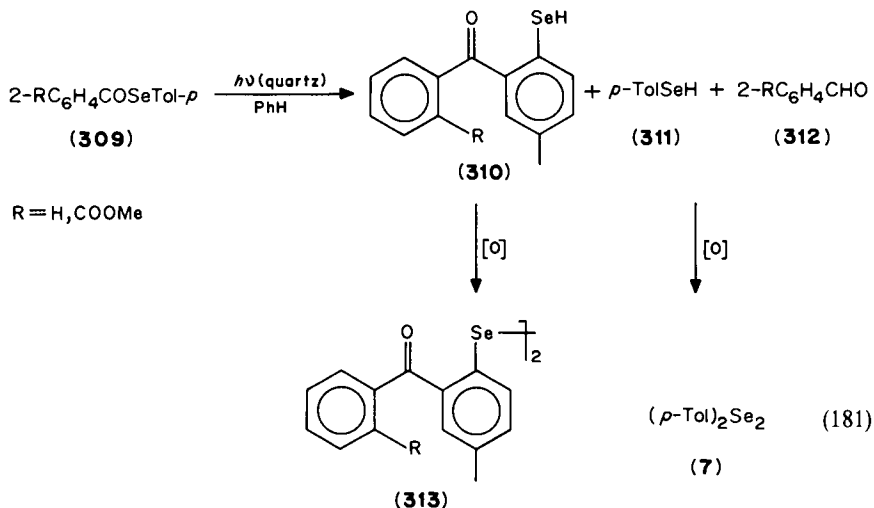
These results suggest that the primary photoreaction involves a homolytic cleavage of the CO—Se bond of the ester 314 to form the acyl (315) and selenyl (316) radicals, which recombine to give the benzophenone 317 (equation 182). Hydrogen abstraction from the solvent by the selenyl radical 316 gives 311, and that by the acyl radical 315 gives 312.

Photo-Fries rearrangement is also observed with the telluroesters 14, albeit in low yields compared with the competitive fragmentation reactions (see Section II.A.1)[15,16]. These reactions follow essentially the same route as those of selenoesters 309 with perhaps one exception, namely the isolation of small amounts of the mixed monotelluride 320 from the reaction mixture. This is presumably obtained by combination of the telluride fragment

radical 16 with the rearranged telluroketone radical 318, forming 319, which loses one tellurium atom photochemically to form 320 (equation 183).

(182)

(183)

Irradiation of selenofenchone (321) into its S_2 (π, π^*) excited state (λ_{max} 272 nm) results in the formation of the three products, 323, 324 and 325, in approximately a 1:1:0.1 ratio[136]. On the basis of the analogous thiofenchone photochemistry, it was suggested that selenofenchone gives as a primary irradiation product the rearranged cyclopropylselenol 322, which on further reaction apparently yields the observed diselenides. In none of the experiments, however, could any 322 be detected (equation 184).

While irradiation of 321 at 268 nm gave a quantum yield of disappearance of $\phi_2 = 5 \times 10^{-3}$, no conversion was observed on irradiation at 620 nm. This implies that the quantum yield of disappearance following excitation into the S_1 state of 321 is less than $\phi = 6 \times 10^{-4}$. Fenchone itself does not undergo this type of rearrangement reaction, presumably because the S_2 (π, π^*) state is too short-lived and the S_1 (n, π^*) state possesses the wrong geometry for β-hydrogen abstraction to occur[136]. In selenofenchone (and thiofenchone[137]), if the S_2 state is π, π^* in nature, the partially filled, and hence electrophilic, π orbital is of the correct geometry to insert into the β C—H bond.

A new method of preparing alkenes from alkanoic acids has been described recently[138], utilizing a Hunsdiecker-type photodecarboxylative rearrangement of carboxylic esters of 2-selenopyridine N-oxide (326) to 2-pyridylselenides (327) (equation 185). This decarboxylative rearrangement was shown to proceed efficiently with simple saturated aliphatic acid derivatives (e.g. 328 ⟶ 329) (equation 186), steroidal acid derivatives (e.g. 330 ⟶ 331) (equation 187) and amino acid derivatives (e.g. 332 ⟶ 333) (equation 188), and

(184)

is of particular importance for chiral molecules since the configuration of the allylic carbon of the olefinic product is retained. Since decarboxylation can also be effected thermally in refluxing benzene, the mechanism is assumed to involve a free-radical pathway. However, unlike the radicals obtained from esters of the thio derivatives[139], the radicals derived from the selenoesters could not be intercepted.

(185)

(186)
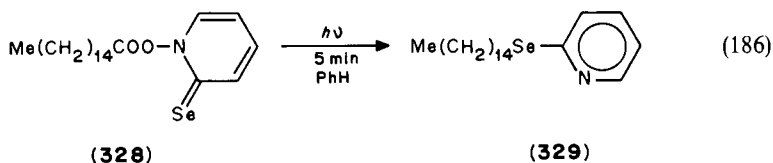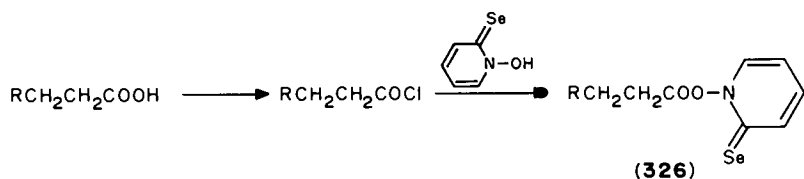
Irradiation ($\lambda > 390$ nm) of 2,1,3-benzoselenadiazole 1-oxide (85) produced benzofurazan (87) (see Section II.B.1)[39,140]. Flash photolysis of 85 in both aerated and degassed solutions (96% ethanol and cyclohexane) using Pyrex-filtered light ($\lambda > 300$ nm) gave rise to absorptions due to the transient 86 obtained by 6-electron cycloreversion, which decayed in a first-order reaction. From the UV spectra it was concluded that the same

(330)

$$\xrightarrow[\text{PhH}]{h\upsilon}$$

(331)

(187)

(332)   **(333)**

(188)

$$R^1 = Me, R^2 = PhCH_2O$$
$$R^1 = CH_2Ph, R^2 = t\text{-Bu}$$
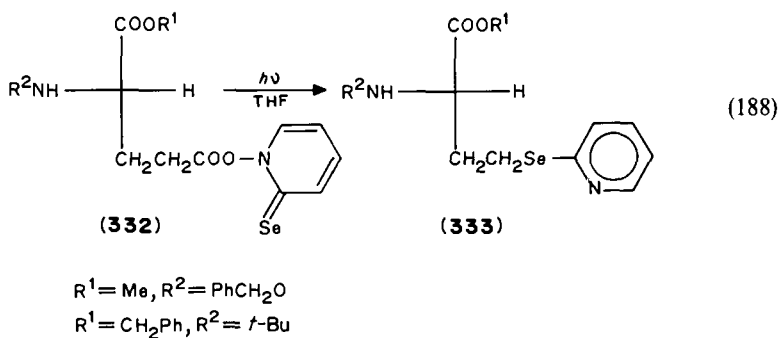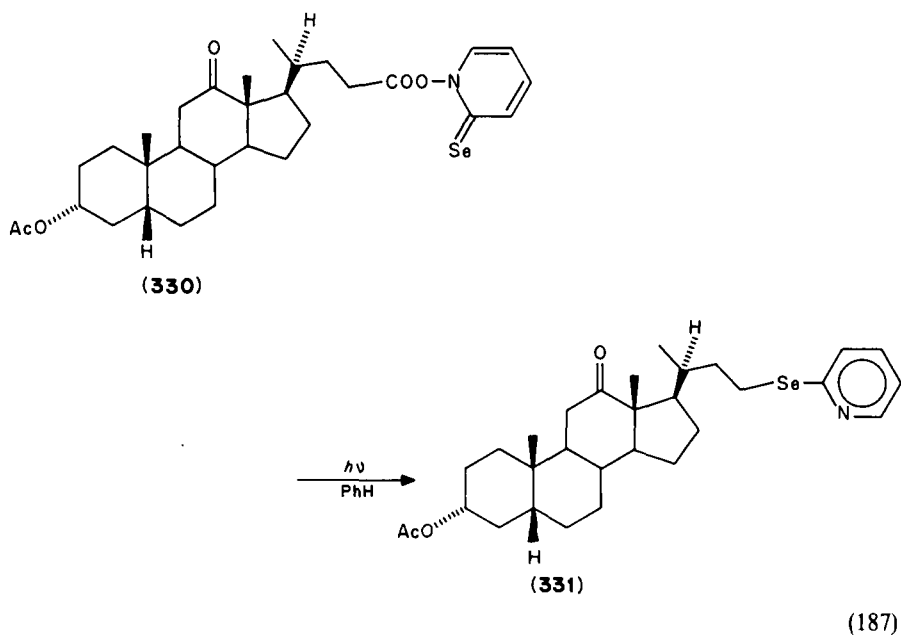
transient is formed at low and room temperatures. Transient **86** extrudes selenium and cyclizes to give the isolable furazan **87**[53] (equation 189).

(85)   **(86)**   **(87)**
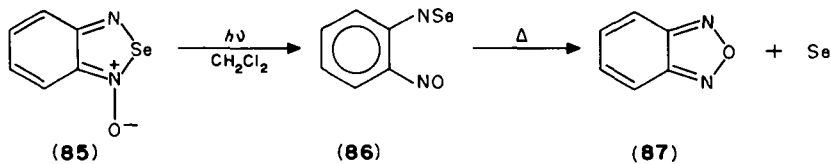
(189)

Selenophene dicarboxaldehydes **334** and **337** undergo an intramolecular photo-Cannizaro disproportionation, analogous to the photochemical transformation of

phthalaldehyde[141], to the corresponding γ-lactones 335–338 as shown in equation 190 and 191[142].

(190)

(334)   **(335)**   **(336)**

(191)

(337)   **(338)**
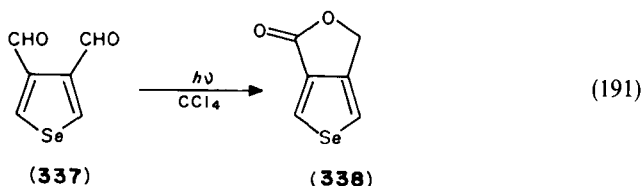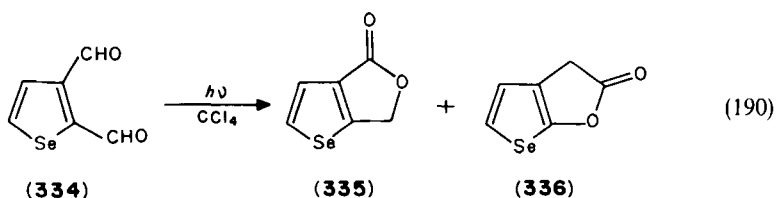
The phenyl selenide substituted acetylacetone 2 undergoes an acid-catalysed photocyclization to the dihydro benzoselenophene 341, which dehydrates under the reaction conditions to give 2-acetyl-3-methylbenzo[b]selenophene (342) in 60% yield[10]. The mechanism for this transformation presumably involves a photoinduced electrocyclic reaction of the enol 339 to the selenocarbonyl ylid 340, which undergoes a further 1,4-hydrogen shift to the dihydroselenophene 341 (equation 192). Analogous cyclizations with divinyl systems having heteroatoms other than selenium, such as oxygen[143], sulfur[144] and nitrogen[145], have also been reported.

(2)   **(339)**   **(340)**

(341)   **(342)**

(192)
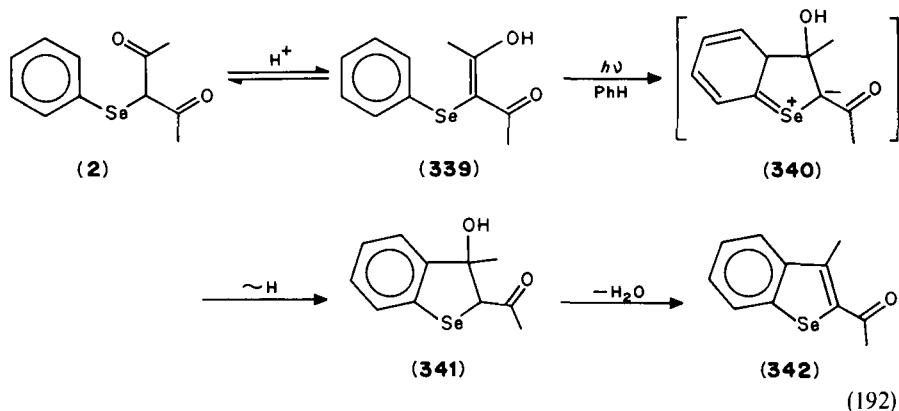
In a search for dibenzoheteroazepines having pharmacodynamic activity, a series of 9-azido-9-arylselenoxanthenes (343) and their oxygen and sulfur analogs were photolysed[146,147] (equation 193). Irradiation of 9-azido-9-phenylselenoxanthene (343, X = Se, Ar = Ph) gave a 70% yield of a mixture containing 60% of the dibenzoselenoazepine 344 (X = Se, Ar = Ph) and 40% of the isomeric anil 345[146]. When 9-azido-9-(4-pyridyl)selenoxanthene (343, X = Se, Ar = 4-pyridyl) was irradiated, 32% of the selenoazepine 344 (X = Se, Ar = 4-pyridyl) was obtained together with 25% of the isomeric

anil **345**[147]. The best results were obtained when 1-methylnaphthalene was added to the irradiated reaction mixture. It is considered to serve as both a singlet sensitizer and triplet quencher, and as such it serves as a protector for the reaction products[147]. The mechanism of these rearrangements probably involves a photoelimination of nitrogen to give a nitrene (or nitrenoid) followed by either a ring enlargement to the azepine **344** or aryl 1,2-migration to the anil **345**. The fact that the migration aptitude of the aryl group (4-pyridyl) remains constant, regardless of the nature of the heterocycle, appears to support a concerted mechanism[147,148].

$$X = O, S, Se$$
$$Ar = Ph, 4\text{-pyridyl}$$

(193)

Irradiation ($\lambda > 220\,nm$) of propadieneselone (**346**) matrix isolated in argon at 12 K gives propyneselenal (**347**) (selenal C=Se stretching band at 1058 cm^{-1})[44]. The formation of **347** may involve either a 1,3-hydrogen shift, or loss of selenium giving allenylidene (**348**), which rearranges to propargylene (**349**) and recombines with selenium (equation 194). The starting material (**346**) was obtained by flash vacuum thermolysis of cyclopenteno-1,2,3-selenadiazole (Section II.B.2).

$$CH_2 = C = C = Se \quad \xrightarrow[\sim 1,3\text{-H}]{hv\,(12\,K)} \quad HC \equiv CCH = Se$$

(**346**)   (**347**)

(194)

$$CH_2 = C = C\colon \quad \xrightarrow{\sim H} \quad CH \equiv CCH\colon$$

(**348**)   (**349**)

B. *Cis–Trans* Isomerization

The photoisomerization of selenoindigo (**350**) was studied as a potential photochromic indigoid[149]. Typical of the majority of photoisomerizable indigoids, *trans*-selenoindigo shows a red fluorescence at about 620 nm on irradiation at its principal visible absorption band. By irradiation of **350** in toluene at 562 nm a photostationary state (**350** ⇌ **351**) was achieved (equation 195). The solution contained 57% of the *trans* isomer **350**, compared with 41% of the *trans* thio-analog at photoequilibrium (542 nm). The photoequilibrium mixture is solvent dependent, containing more of the *cis* isomer in chloroform than in toluene. This has been attributed to the lowering of the quantum yield for *cis–trans* photoisomerization on changing the solvent to chloroform.

(350)   **(351)**   (195)

The quantum yields for the *trans–cis* ($\phi_t = 0.025$ at 562 nm) and *cis–trans* ($\phi_c = 0.275$ at 485 nm) photoisomerizations, respectively, coincide with the values obtained for ϕ_t and ϕ_c of the thio analogs. However they differ considerably from the quantum yield of isomerization of the oxoindigoid ($\phi_t = 0.63$ at 413 nm, $\phi_c = 0.35$ at 396 nm). The quantum yields for *cis–trans* photoisomerizations over spectral regions which include long-wavelength absorption remained constant.

The photoelectron spectra of several aryl alkyl selenides have been measured[150]. Some show evidence of the existence of two predominant rotamers, one with a maximum p–π overlap and one with minimal overlap. It has been shown that steric factors affect the rotamer population while the detection of rotamers by the photoelectron technique is dependent on electronic factors.

The photoelectron spectra of simple selenium-substituted olefins has been studied[151] and compared with other push–pull olefins containing electron-donor (e.g. thio and amino) and -acceptor (e.g. cyano, carbonyl and carboxyl) groups. In olefins with electron-donating groups ionization potentials (IPs) decrease with the IPs of the corresponding atoms, namely in the order S < Se < N. Similarly, the IPs and electron affinities of chalcogen cyanates and isocyanates[152] and also those of non-isomerizable chalcogen heterocyclic olefins[153,154] have been determined by UV photoelectron spectroscopy.

A useful photoinduced diphenyl diselenide-catalysed isomerization of the Δ^6-double bond of ergocalciferol **(352)** to 5,6-*trans*-ergocalciferol **(353)**[155] was reported (equation 196). This reaction probably proceeds via the addition of phenylselenyl radical to $C_{(19)}$, isomerization of the derived allylic radical and loss of the phenylselenyl radical. An analogous double-bond isomerization of (−)-caryophyllene to (−)-isocaryophyllene was reported using diphenyl disulfide[156].

(352)   **(353)**   (196)
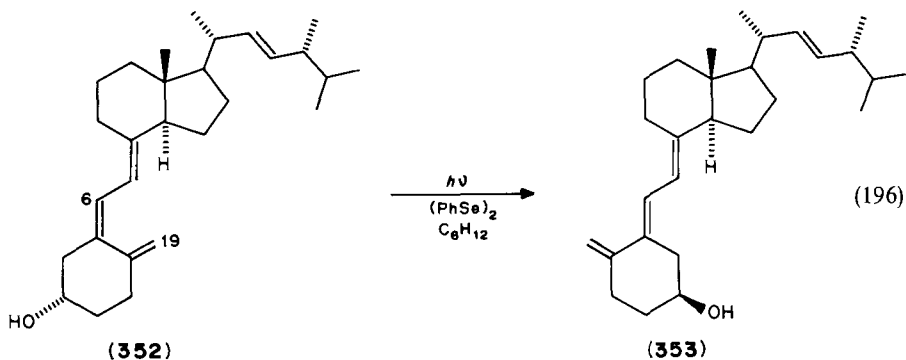
V. PHOTOOXIDATIONS

Although oxidative decompositions of organoselenium compounds by UV light were reported as early as 1974[28], only a few quantitative studies have been made since then which contain a mechanistic analysis of the results.

While the irradiation of dibenzyl diselenide (1) in the absence of oxygen leads only to the formation of dibenzyl selenide (Section II.B.1), photolysis of dilute aerated solutions of 1 in benzene at 350 nm resulted in the formation of benzaldehyde and elemental selenium in high yields (equation 197)[6,28]. It has been established[28] that the benzaldehyde oxygen arises from atmospheric oxygen and not from traces of water in the solution.

$$PhCH_2Se_2CH_2Ph \xrightarrow[PhH]{h\nu \ (350nm),\ O_2} PhCHO + Se \qquad (197)$$
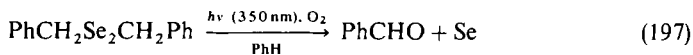
(1)

When the diselenide 1 or the ditelluride 53 was photolysed in $CDCl_3$ under limited amounts of oxygen, complex mixtures of products were obtained containing benzyl alcohol, toluene and 1,2-diphenylethylene in addition to benzaldehyde (equation 198)[30]. These were all presumably derived from incomplete oxidation of intermediate benzyl radicals formed by homolytic deselenation.

$$PhCH_2EECH_2Ph \xrightarrow[CHCl_3]{h\nu} PhCHO + PhCH_2OH + PhMe + PhCH_2CH_2Ph \qquad (198)$$
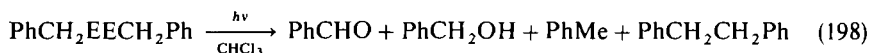
$E = Se, Te$

In the absence of oxygen, benzyl tellurocyanate (354) is photochemically stable. However, irradiation of 354 under atmospheric oxygen gave a black precipitate of elemental tellurium and the solution contained a mixture of 60% benzaldehyde and 40% benzyl alcohol (equation 199)[157]. The speculative mechanism proposed included a singlet oxygen attack on tellurium to form the 1,3-dipolar peroxide 355 followed by rearrangement to the unstable benzylperoxytellurocyanate 356. Peroxide 356 in turn decomposes to benzyloxy radicals 357, which disproportionate to the observed products.
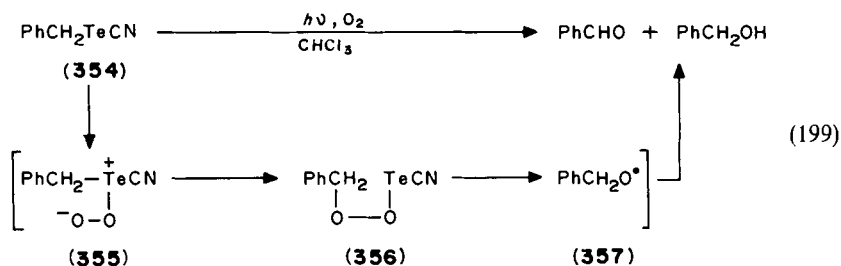
It is interesting that monoselenides are stable to photooxidation under conditions where monosulfides and monotellurides decompose. Thus, benzyl phenyl selenide (358) is reported to be stable to singlet oxygen generated by irradiation of aerated aqueous micellar solutions containing 10-methylphenothiazine sensitizer. Under these conditions benzyl sulfides are readily photooxidized to sulfoxides[158]. Dibenzyl telluride (55), the sole product of the photolysis of 53 in degassed solutions, completely photodecomposes in the presence of oxygen to give the oxidation mixture of products obtained from 53 (equation 198)[30].

$$PhCH_2SePh \qquad\qquad PhCH_2TeCH_2Ph$$
$$(358) \qquad\qquad\qquad (55)$$
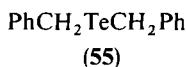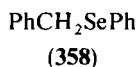
The tellurophenopyridazine 359 is photooxidized in chloroform solutions to give a 40% yield of 4,5-dibenzoylpyridazine (361). The peroxide 360 arising from a Diels–Alder reaction of singlet oxygen[159] with the tellurophene ring is suggested as the probable

intermediate, which readily decomposes thermally by loss of elemental tellurium to **361** (equation 200)[160]. Analogously, 4, 5-dibenzoyl-2, 7-diphenyltropone (**363**) was formed in 43% yield by visible light photooxidative detelluration of the tellurophene **362** (equation 201). When a high-pressure UV mercury lamp was used, only polymers and unidentified decomposition products were observed[160].

(359)   (360)   (361)

(200)

(362)   (363)

(201)
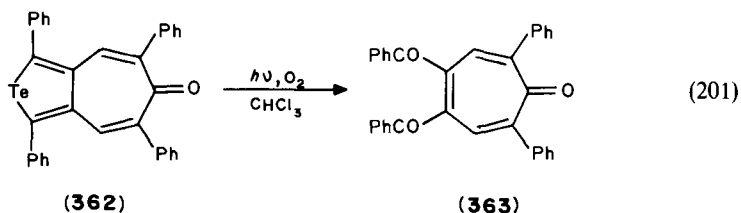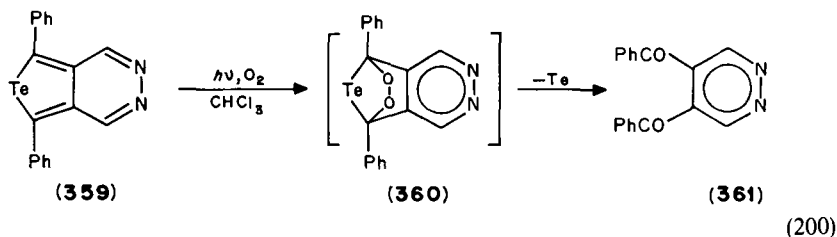
VI. PHOTOREDUCTIONS

A. Hydrogen Abstraction

In contrast to the rich literature on the photoreduction of carbonyl compounds[1,2] and the well documented photochemistry of thioketones (thiones)[4], reports on the photochemical behavior of selones are scarce[136,161]. Di-*tert*-butyl selone (**364**), first prepared in 1976[161], was found to be stable when irradiated with visible light under nitrogen. However, under UV irradiation in a variety of hydrogen-donating solvents such as hexane, dioxane and benzene, **364** was smoothly reduced to the diselenide **365** (equation 202). In solvents other than benzene, substantial amounts of unidentified compounds together with selenium metal deposition were observed[136]. The presence of a better hydrogen donor such as the selenol **366** improved the yields of **365** up to 85%.

$$(t\text{-Bu})_2 C = Se \xrightarrow[\text{RH}]{hv} (t\text{-Bu})_2 CHSeSeCH(t\text{-Bu})_2$$
(202)

(364)   (365)
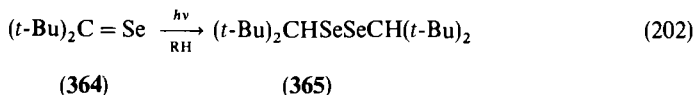
The quantum yield of disappearance of **364** in hexane increases from $\phi = 5.5 \times 10^{-3}$ in the absence of the selenol **366** to $\phi = 8 \times 10^{-2}$ in the presence of 9×10^{-2} M **366**. The photoreduction is dependent on the wavelength. Excitation into the S_1 state ($\lambda = 689$ nm) is extremely inefficient, $\phi_1 = 1.2 \times 10^{-3}$ compared with $\phi_2 = 3.2 \times 10^{-2}$ from the higher S_2 ($\lambda = 266$ nm) excited state under the same conditions. The 266 nm band tails to wavelengths beyond 300 nm and consequently irradiation of **364** in Pyrex using a medium-pressure lamp allows excitation into both S_1 and S_2 states in the same experiment. This suggests that, like the photoreduction of thiones[4], the reaction occurred from the relatively

longlived π, π^* transition state and unlike ketones for which the lower n, π^* state is reactive in hydrogen abstraction reactions[162].

When **364** was irradiated in pentane at $-110\,°C$ under conditions such that the diselenide **365** is formed, ESR signals are observed[136] which correspond to the presence of radical **368** in the solution. The intensity of the ESR signals increases 60-fold when **364** is irradiated in the S_2 excitation band compared with the S_1 band and 20-fold when **366** is present. The kinetic data are consistent with the chain mechanism shown in equation 203, in which excited **364** abstracts a hydrogen from either the solvent (route a) or the selenol (route b) to attain an equilibrium with selenyl radical **367**. This radical traps a ground-state selone molecule to give radical **368**, which abstracts hydrogen from the solvent to give **365**. If selenol **366** is added to the photolysis mixture, a chain sequence may be expected since selenyl radical is regenerated in this step.

$$(t\text{-Bu})_2C=Se \underset{(a)}{\overset{h\nu, RH}{\rightleftharpoons}} [(t\text{-Bu})_2CHSe^\bullet + R^\bullet]$$

$$\textbf{(364)} \qquad\qquad\qquad\qquad \textbf{(367)}$$

$$(b)\ \Big\downarrow\ \begin{array}{c} h\nu, \\ (t\text{-Bu})_2CHSeH \\ \textbf{(366)} \end{array} \qquad\qquad \Big\downarrow\ (t\text{-Bu})_2C=S$$

$$2(t\text{-Bu})_2CHSe^\bullet \xrightarrow{\ \textbf{364}\ } (t\text{-Bu})_2CHSe-Se\overset{\bullet}{C}(t\text{-Bu})_2 \qquad (203)$$

$$\textbf{(367)} \qquad\qquad\qquad\qquad \textbf{(368)}$$

$$\Big\downarrow\ \begin{array}{c} (a)\,RH \\ (b)\,\textbf{(366)} \end{array}$$

$$[(t\text{-Bu})_2CHSe]_2$$

$$\textbf{(365)}$$
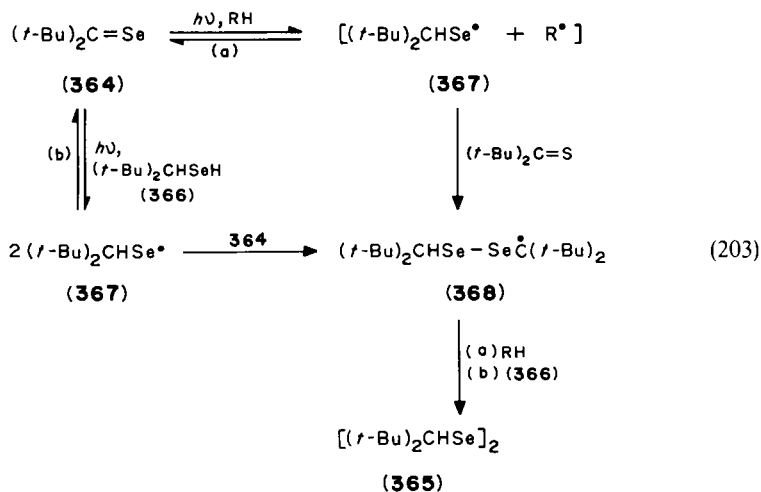
Quenching experiments with biacetyl gave Stern–Volmer plots for the quantum yields of formation of **365** and disappearance of the selone **364** as a function of the quencher concentration. Assuming $k_q = 10^{10}\,\text{l mol}^{-1}\,\text{s}^{-1}$ (hexane), the lifetime of the S_2 excited state is of the order of 10^{-10} s, which is close to the lifetime of the reactive S_2 state of thioketones[4].

Irradiation of **364** into both the S_1 and S_2 states in the presence of olefins such as acrylonitrile, ethyl vinyl ether, fumaronitrile and dimethyl maleate failed to produce detectable amounts of adducts. This is in contrast to the analogous di-*tert*-butylthione[163] and other thioketones[164]. The inertness of **364** has been attributed to steric hindrance[136].

Unlike di-*tert*-butyl selone (**364**), the photochemistry of the bicyclic selenofenchone (**321**) did not lead to reduction by intermolecular hydrogen abstraction, even in reasonably good hydrogen atom-donating solvents such as pentane. Instead, excitation of **321** into the $S_2(\pi, \pi^*)$ state gave a mixture of diselenides (see Section IV.A).

Esters of steroidal carboselenoic acids (**369–371**) undergo photoinduced reduction with tributyltin hydride to the corresponding aldehydes (**372–374**) and alkanes (**375, 376**) which are shorter by one side-chain carbon (equations 204–206)[165]. Since these reactions may also be initiated thermally with azobis(isobutyronitrile), a radical-chain mechanism is suggested, involving either hydrogen atom abstraction from the stannane by the acyl radical (**377**) intermediate to give aldehyde, or alternatively, decarbonylation of the acyl radical followed by hydrogen abstraction to give the alkane (equation 207).

(204)

(205)

(206)

$$RCOSePh \xrightarrow{Bu_3Sn^\bullet} RCO^\bullet + Bu_3SnSePh$$
(377)

$$\xrightarrow{Bu_3SnH} RCHO + Bu_3Sn^\bullet \qquad (207)$$

$$\xrightarrow{-CO} R^\bullet \xrightarrow{Bu_3SnH} RH + Bu_3Sn^\bullet$$
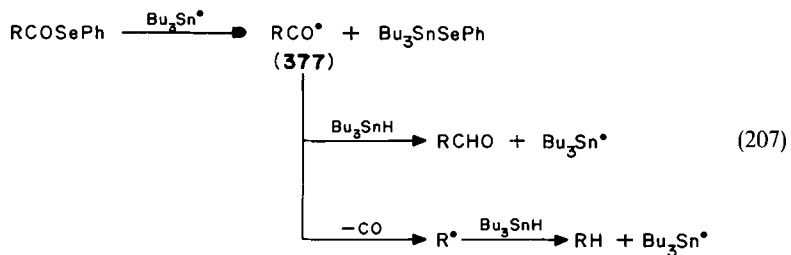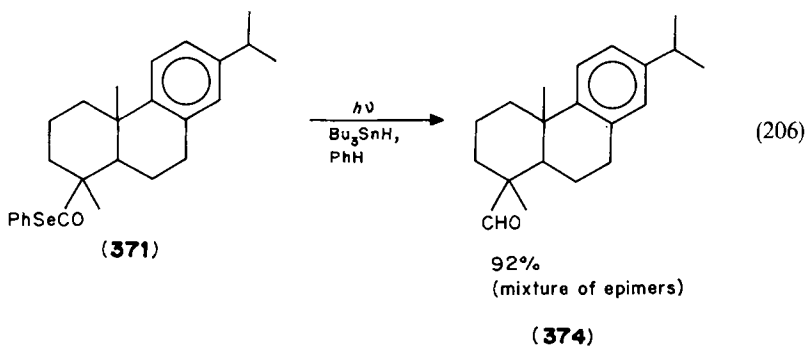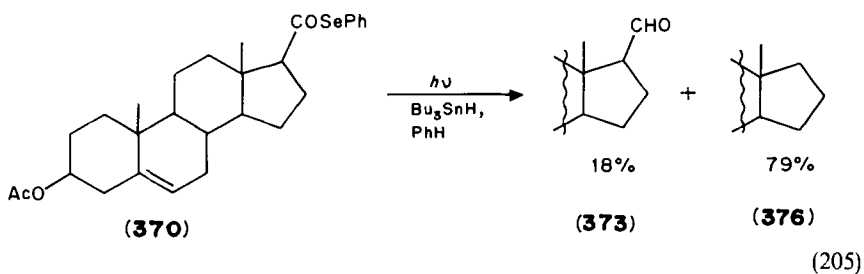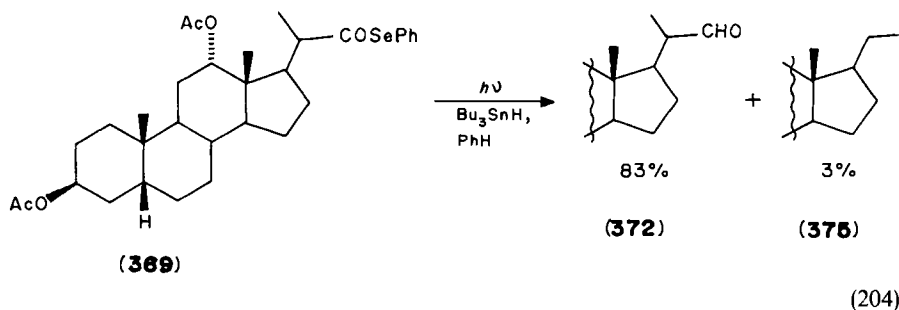
Similarly, selenocarbonates (**378** and **379**) undergo photoinduced reduction with tributyltin hydride to give a mixture containing the corresponding formates (**380** and **381**), alcohols (**382** and **383**) and alkanes (**384**) (equations 208 and 209)[165]. The series of radical-chain processes which take place in this reaction include three alternative pathways for the intermediate radical **385**: hydrogen abstraction, decarbonylation and decarboxylation, leading to the formates, alcohols and alkanes, respectively (equation 210).

(**378**)

$$\xrightarrow[\text{PhH}]{\substack{h\nu \\ \text{Bu}_3\text{SnH}}}$$

87%   1%   9%

(**380**)   (**382**)   (**384**)

(208)

(**379**)

$$\xrightarrow[\substack{h\nu, \\ \text{PhH}}]{\text{Bu}_3\text{SnH}}$$

81%   19%

(**381**)   (**383**)

(209)

$$\text{ROCOSePh} \xrightarrow{\text{Bu}_3\text{Sn}^\bullet} \text{ROCO}^\bullet + \text{Bu}_3\text{SnSePh}$$

(**385**)

$$\xrightarrow{\text{Bu}_3\text{SnH}} \text{ROCHO} + \text{Bu}_3\text{Sn}^\bullet$$

(210)

$$\xrightarrow{-\text{CO}} \text{RO}^\bullet \xrightarrow{\text{Bu}_3\text{SnH}} \text{ROH} + \text{Bu}_3\text{Sn}^\bullet$$

$$\xrightarrow{-\text{CO}_2} \text{R}^\bullet \xrightarrow{\text{Bu}_3\text{SnH}} \text{RH} + \text{Bu}_3\text{Sn}^\bullet$$
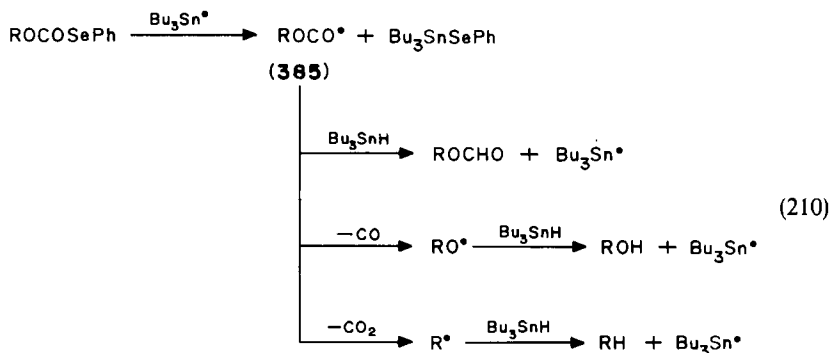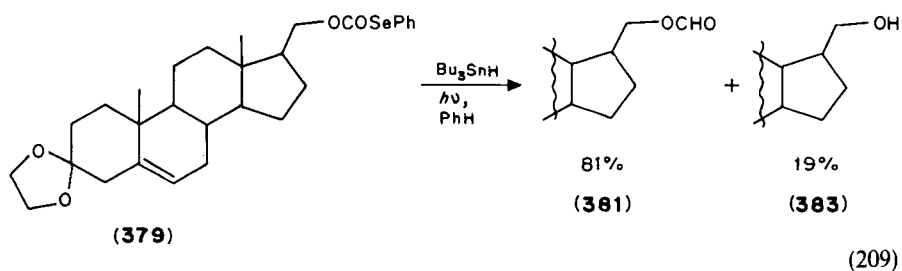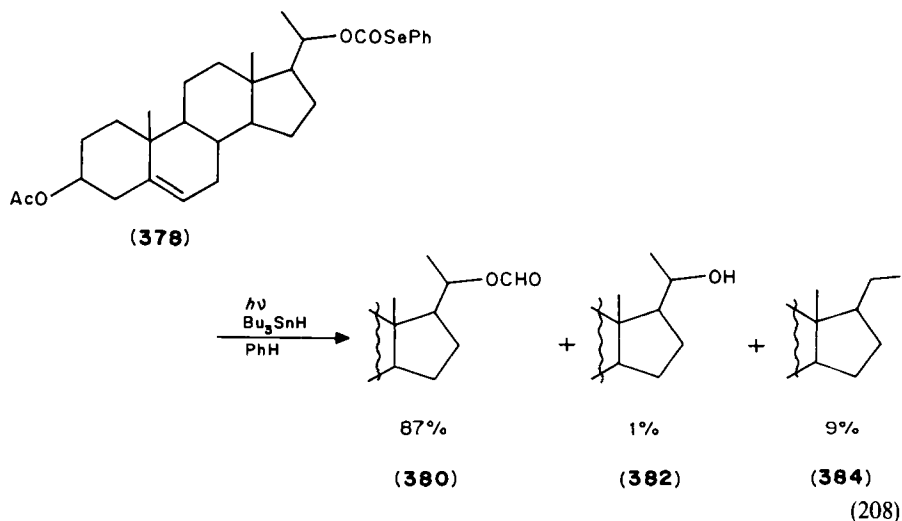
B. Oxygen Transfer

Diaryl selenoxides are photochemically reduced by sulfides to selenides and the corresponding sulfoxides. Thus, when a 3:1 mixture of dibenzoselenophene oxide (386) and the sulfide 387 in methanol (or dichloromethane) was irradiated under argon through a Pyrex filter with a high-pressure mercury lamp, dibenzoselenophene (388) was obtained in high yields together with the sulfoxide 389 (equation 211)[166]. Similarly, diphenyl selenoxide (390) is reduced by phenyl methyl sulfide to diphenyl selenide (36) in moderate yields. The mechanistic pathway for the photochemical transfer of oxygen in these reactions has been suggested to involve a bimolecular intermediate between the excited selenoxide and sulfide, which collapses to the products. Other possibilities, such as the involvement of atomic oxygen, were excluded.

$$R = Ph, R' = Me$$
$$R = R' = n\text{-}Bu$$ \hfill (211)
$$R = R' = (CH_2)_5$$

$$Ph_2Se = O + PhSMe \xrightarrow[CH_2Cl_2]{h\nu} Ph_2Se + PhSOMe \hfill (212)$$

(390)   (36)
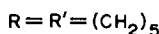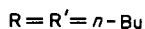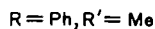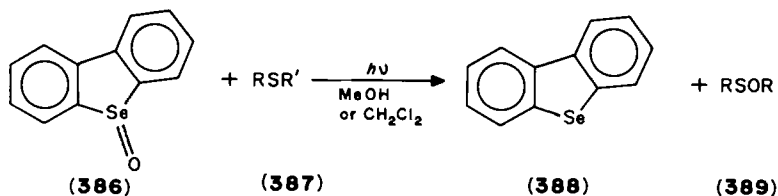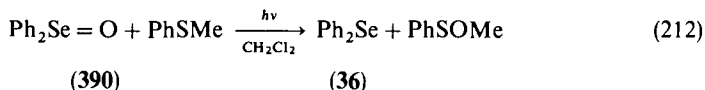
Deoxygenation has also been noted[167] when 4-methyl-2'-nitrodiphenyl selenoxide (391) was irradiated in benzene solution through quartz to give the selenide 392 (equation 213). The oxygen acceptor in this reaction was not indicated. In contrast, the analogous nitrosulfoxide 393, on irradiation into the singlet excited state, is reported[168] to undergo an intramolecular oxygen transfer from nitrogen to sulfur, forming the nitrososulfone 394 (equation 214). However, in the presence of triphenylamine as a triplet sensitizer, 393 is reduced to the corresponding sulfide in low yields (1–4%).

$$2\text{-}NO_2C_6H_4\overset{\overset{\displaystyle O}{\|}}{Se}\text{-}Tol\text{-}p \xrightarrow[PhH]{h\nu\ (quartz)} 2\text{-}NO_2C_6H_4Se\text{-}Tol\text{-}p \hfill (213)$$

(391)   (392)

$$2\text{-}NO_2C_6H_4\overset{\overset{\displaystyle O}{\|}}{S}\text{-}Tol\text{-}p \xrightarrow{h\nu} 2\text{-}NOC_6H_4\underset{\underset{\displaystyle O}{\|}}{\overset{\overset{\displaystyle O}{\|}}{S}}\text{-}Tol\text{-}p \hfill (214)$$

(393)   (394)
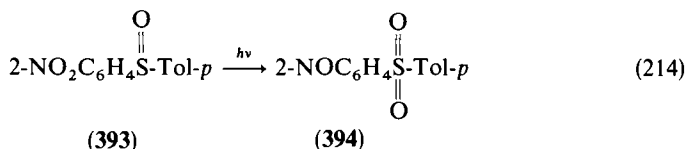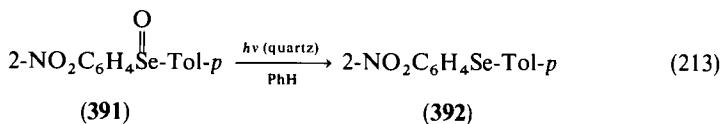
Photochemical deoxygenation was observed when 2,1,3-benzoselenadiazole 1-oxide (85) was irradiated ($\lambda > 390$ nm) in isopropanol to give a 5% isolated yield of 2,1,3-benzoselenadiazole (395)[53]. The major product in the photolysis was benzofurazan (87) (equation 215) (Section II.B.1). Irradiation (410 nm) of 85 at 100 K in methanol–ethanol glass (2:5) showed the development of both 395 and 87 in a 40:30 ratio. Interestingly, the

thermal reaction gives higher yields of **395**[140]. The oxygen is probably transferred to the solvent by an analogous mechanism to that suggested for the photo-deoxygenation of amine N-oxides[169].
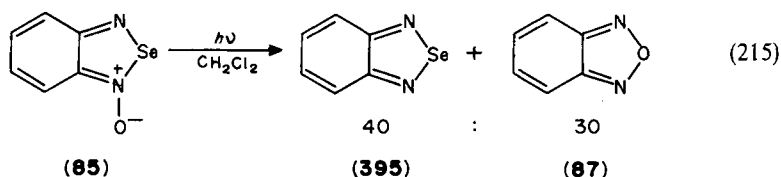
$$(215)$$

		40	:	30
(85)		**(395)**		**(87)**

VII. ACKNOWLEDGEMENTS

VIII. REFERENCES

1. P. J. Wagner, in *Triplet States III (Topics in Current Chemistry*, 66), Springer Verlag, Berlin, 1976, pp. 1–52.
2. A. Schönberger, *Preparative Organic Photochemistry*, Springer Verlag, Berlin, 1968.
3. H. Dürr, in *Houben-Weyl, Methoden der Organischen Chemie* (ed. E. Müller), Teil IV/5b, Georg Thieme Verlag, Stuttgart, 1975, pp. 1008–1076.
4. P. de Mayo, *Acc. Chem. Res.*, 9, 52 (1976).
5. C. L. Jackson, *Justus Liebigs Ann. Chem.*, 179, 1 (1875).
6. J. Y. C. Chu, D. G. Marsh and W. H. H. Gunther, *J. Am. Chem. Soc.*, 97, 4905 (1975).
7. D. L. Klayman and W. H. H. Gunther, *Organic Selenium Compounds: Their Chemistry and Biology*, Wiley, New York, 1973.
8. K. J. Irgolic, *The Organic Chemistry of Tellurium*, Gordon and Breach, New York, 1974.
9. J. Martens and K. Praefcke, *J. Organomet. Chem.*, 198, 321 (1980).
10. A. G. Schultz, *J. Org. Chem.*, 40, 3466 (1975).
11. J. Martens, K. Praefcke and H. Simon, *Z. Naturforsch., Teil B*, 31, 1717 (1976).
12. R. Ludersdorf, J. Martens, P. Pakzad and K. Praefcke, *Justus Liebigs Ann. Chem.*, 1992 (1977).
13. K. Praefcke and D. Schmidt, *J. Heterocycl. Chem.*, 16, 47 (1979).
14. K. Praefcke and U. Schulze, *J. Organomet. Chem.*, 184, 189 (1980).
15. W. Lohner, J. Martens, K. Praefcke and H. Simon, *J. Organomet. Chem.*, 154, 263 (1978).
16. G. Hohne, W. Lohner, K. Praefcke, U. Schulz and H. Simon, *Tetrahedron Lett.*, 613 (1978).
17. W. W. Lotz and J. Gosselck, *Tetrahedron*, 29, 917 (1973).
18. J. Bergman, N. Eklund, T. E. Eriksen and J. Lind, *Acta Chem. Scand., Ser. A*, 32, 455 (1978).
19. O. A. Ptitsina, M. E. Gurskii and O. A. Reutov, *Zh. Org. Khim.*, 10, 2246 (1974); *J. Org. Chem. USSR*, 10, 2262 (1974).
20. U. Schmidt, A. Muller and K. Markau, *Chem. Ber.*, 97, 405 (1964).
21. R. T. Mehdi, J. D. Miller and T. A. Tahir, *Inorg. Chim. Acta*, 90, 85 (1984).
22. R. A. Gancarz and J. L. Kice, *J. Org. Chem.*, 46, 4899 (1981).
23. N. S. Vyazankin, M. N. Bochkarev and L. P. Maiorova (Sanina), *Zh. Obshch. Khim.*, 39, 468 (1969); *J. Gen. Chem. USSR*, 39, 444 (1969).
24. A. B. Callear and W. J. R. Tyerman, *Trans. Faraday Soc.*, 61, 2395 (1965).
25. A. B. Callear and W. J. R. Tyerman, *Trans. Faraday Soc.*, 62, 371 (1966).
26. W. J. R. Tyerman, W. B. O'Callaghan, P. Kebarle, O. P. Strausz and H. E. Gunning, *J. Am. Chem. Soc.*, 88, 4277 (1966).
27. J. Connor, G. Grieg and O. P. Strausz, *J. Am. Chem. Soc.*, 91, 5695 (1969).
28. W. Stanley, M. R. VanDeMark and P. L. Kumler, *J. Chem. Soc., Chem. Commun.*, 700 (1974).
29. J. Y. C. Chu and D. G. Marsh, *J. Org. Chem.*, 41, 3204 (1976).
30. H. K. Spencer and M. P. Cava, *J. Org. Chem.*, 42, 2937 (1977).

31. D. H. Brown, R. J. Cross and D. Millington, *J. Organomet. Chem.*, **125**, 219 (1977).
32. A. Couture, A. Lablache-Combier, R. Laypouyade and G. Felix, *J. Chem. Res. (S)*, 258 (1979).
33. G. Vermeersch, N. Fabvey-Garot, S. Caplain, A. Couture and A. Lablache-Combier, *Tetrahedron Lett.*, 609 (1979).
34. R. Livingston and K. S. Wei, *J. Am. Chem. Soc.*, **89**, 3098 (1967).
35. G. Ahlgren, B. Akermark and M. Nilsson, *J. Organomet. Chem.*, **30**, 303 (1971).
36. D. G. Marsh, J. Y. C. Chu, J. W. Lewicki and J. L. Weaver, *J. Am. Chem. Soc.*, **98**, 8432 (1976).
37. S. L. N. G. Krishnamachari and T. V. Vinkitachalam, *Chem. Phys. Lett.*, **67**, 69 (1979).
38. T. A. Barton, C. R. Tully and R. W. Roth, *J. Organomet. Chem.*, **108**, 183 (1976).
39. C. L. Pedersen, *Acta Chem. Scand., Ser. B*, **30**, 675 (1976).
40. J. Bergman, *Acta Chem. Scand.*, **22**, 1883 (1968).
41. A. Krantz and J. Laureni, *J. Am. Chem. Soc.*, **99**, 4842 (1977).
42. N. Harrit, S. Rosenkilde, B. D. Larsen and A. Holm, *J. Chem. Soc., Perkin Trans. 1*, 907 (1985).
43. A. Krantz and J. Laureni, *J. Am. Chem. Soc.*, **103**, 480 (1981).
44. W. W. Sander and O. L. Chapmann, *J. Org. Chem.*, **50**, 543 (1985).
45. H. Meier and I. Menzel, *Tetrahedron Lett.*, 445 (1972).
46. F. Malek-Yazdi and M. Yalpani, unpublished results (1976), quoted in Ref. 47.
47. I. Lalezari, A. Shafiee and M. Yalpani, *Adv. Heterocycl. Chem.*, **24**, 109 (1979).
48. I. Lalezari, A. Shafiee, J. Khorrami and A. Soltani, *J. Pharm. Sci.*, **67**, 1336 (1978).
49. W. Lohner and K. Praefcke, *J. Organomet. Chem.*, **194**, 173 (1980).
50. T. Ibata, K. Ueda and M. Takebayashi, *Bull. Chem. Soc. Jpn.*, **46**, 2897 (1973).
51. C. L. Pedersen, N. Harrit, M. Poliakoff and I. Dunkin, *Acta Chem. Scand., Ser. B*, **31**, 848 (1977).
52. C. L. Pedersen and N. Hacker, *Tetrahedron Lett.*, 3981 (1977).
53. C. L. Pedersen, *Tetrahedron Lett.*, 745 (1979).
54. R. B. Woodward and R. Hoffmann, *The Conservation of Orbital Symmetry*, Verlag Chemie, Weinheim, 1970.
55. F. S. Guziec, Jr., C. J. Murphy and E. R. Cullen, *J. Chem. Soc., Perkin Trans. 1*, 107 (1985).
56. R. Hussong, H. Heydt and M. Regitz, *Phosphorus Sulfur*, **25**, 201 (1985).
57. J. F. Bunnet, *Acc. Chem. Res.*, **11**, 413 (1978).
58. R. A. Rossi, *Acc. Chem. Res.*, **15**, 164 (1982).
59. A. B. Pierini and R. A. Rossi, *J. Org. Chem.*, **44**, 4667 (1979).
60. A. B. Pierini and R. A. Rossi, *J. Organomet. Chem.*, **144**, C12 (1978).
61. A. B. Pierini and R. A. Rossi, *J. Organomet. Chem.*, **168**, 163 (1979).
62. J. F. Bunnett and X. Creary, *J. Org. Chem.*, **39**, 3173 (1974).
63. J. F. Bunnett and X. Creary, *J. Org. Chem.*, **40**, 3740 (1975).
64. R. A. Rossi, R. H. de Rossi and A. F. Lopez, *J. Am. Chem. Soc.*, **98**, 1252 (1976).
65. A. B. Pierini, A. B. Penenory and R. A. Rossi, *J. Org. Chem.*, **49**, 486 (1984).
66. S. M. Palacios, R. A. Alonso and R. A. Rossi, *Tetrahedron*, **41**, 4147 (1985).
67. A. N. Frolov, A. V. El'tsov, E. V. Smirnov and O. V. Kul'bitzkaya, *Zh. Org. Khim.*, **13**, 2007 (1977); *Chem. Abstr.*, **88**, 6482 (1978).
68. H. Okabe, *Photochemistry of Small Molecules*, Wiley–Interscience, New York, 1978.
69. L. Andrews, *Annu. Rev. Phys. Chem.*, **30**, 79 (1979).
70. G. Lodder, in *The Chemistry of Functional Groups, Supplement D* (Eds. S. Patai and Z. Rappoport), Wiley, New York, 1983, Chapt. 29, pp. 1605–1683.
71. P. G. Sammes, in *The Chemistry of the Carbon–Halogen Bond* (Ed. S. Patai), Wiley, New York, 1973, Chapt. 11.
72. J. M. Birchall, G. P. Irvin and R. A. Boyson, *J. Chem. Soc., Perkin Trans. 2*, 435 (1975).
73. M. L. Denniston and D. R. Martin, *J. Inorg. Nucl. Chem.*, **37**, 1871 (1975).
74. V. G. Voloshchuk, V. N. Bioko and L. M. Yagupol'skii, *Zh. Org. Khim.*, **13**, 2008 (1977); *Chem. Abstr.*, **88**, 6483 (1978).
75. R. C. Fort and P. v. R. Schleyer, *Adv. Alicycl. Chem.*, **1**, 283 (1966).
76. R. A. Rossi, S. M. Palacios and A. N. Santiago, *J. Org. Chem.*, **47**, 4654 (1982).
77. S. M. Palacios, A. N. Santiago and R. A. Rossi, *J. Org. Chem.*, **49**, 4609 (1984).
78. B. Pakzad, K. Praefcke and H. Simon, *Angew. Chem., Int. Ed. Engl.*, **16**, 319 (1977).
79. K. Beelitz, K. Praefcke and S. Gronowitz, *J. Organomet. Chem.*, **194**, 167 (1980).
80. J. Martens, K. Praefcke and U. Schulze, *Synthesis*, 532 (1976).
81. K. Beelitz, K. Praefcke and S. Gronowitz, *Justus Liebigs Ann. Chem.*, 1597 (1980).
82. M. F. Lappert and P. W. Lendor *Adv. Organomet. Chem.*, **14**, 345 (1976).

83. G. A. Russell and J. Hershberger, *J. Am. Chem. Soc.*, **102**, 7604 (1980).
84. J. Hershberger and G. A. Russell, *Synthesis*, 475 (1980).
85. G. A. Russell and L. L. Herold, *J. Org. Chem.*, **50**, 1037 (1985).
86. J. Deniau, K. N. V. Duong, A. Gaudemer, P. Bougeard and M. D. Johnson, *J. Chem. Soc., Perkin Trans. 2*, 393 (1981).
87. P. Mailbard, J. C. Massot and C. Giannotti, *J. Organomet. Chem.*, **159**, 219 (1978).
88. S. Pouly, G. Tainturier and B. Gautheron, *J. Organomet. Chem.*, **232**, C56 (1982).
89. B. Gautheron, G. Tainturier and S. Pouly, *J. Organomet. Chem.*, **268**, C56 (1984).
90. V. Balzani and V. Carassiti, *Photochemistry of Coordination Compounds*, Academic Press, London, 1970.
91. M. K. Chandhuri, A. Haas and A. Wensky, *J. Organomet. Chem.*, **116**, 326 (1976).
92. P. Jaitner, *J. Organomet. Chem.*, **210**, 353 (1981).
93. P. Jaitner, *J. Organomet. Chem.*, **231**, 225 (1982).
94. P. Jaitner, *J. Organomet. Chem.*, **233**, 333 (1982).
95. N. Kuhn and H. Schumann, *J. Organomet. Chem.*, **276**, 55 (1984).
96. H. Schumann, *J. Organomet. Chem.*, **293**, 75 (1985).
97. N. Kuhn, H. Schumann and G. Wolmershauser, *J. Chem. Soc., Chem. Commun.*, 1595 (1985).
98. M. Herberhold, B. Schmidkonz, U. Thewalts, A. Razavi, H. Schollhorn, W. A. Herrmann and C. Hecht, *J. Organomet. Chem.*, **299**, 213 (1986).
99. H. J. Reich, *Acc. Chem. Res.*, **12**, 22 (1979).
100. D. L. J. Clive, *Tetrahedron*, **34**, 1049 (1978).
101. B. A. Bohm and P. I. Abell, *Chem. Rev.*, **62**, 599 (1962).
102. J. L. Traynham, A. G. Lane and N. Bhacca, *J. Org. Chem.*, **34**, 1302 (1969).
103. Y.-H. Kang and J. L. Kice, *J. Org. Chem.*, **49**, 1507 (1984).
104. L. H. Gale, *J. Org. Chem.*, **33**, 3643 (1968).
105. R. Dowbenko, *Tetrahedron*, **20**, 1843 (1964); *J. Am. Chem. Soc.*, **86**, 946 (1964).
106. L. Friedman, *J. Am. Chem. Soc.*, **86**, 1885 (1964).
107. F. G. Bordwell and W. A. Hewett, *J. Am. Chem. Soc.*, **79**, 3493 (1957).
108. M. S. Alnajar and H. G. Kuivila, *J. Org. Chem.*, **46**, 1053 (1981).
109. S. J. Cristol and R. W. Gleason, *J. Org. Chem.*, **34**, 1762 (1969).
110. S. J. Cristol and D. I. Davies, *J. Org. Chem.*, **29**, 1282 (1964).
111. S. J. Cristol, J. K. Harrington and H. S. Singer, *J. Am. Chem. Soc.*, **88**, 1529 (1964).
112. R. Franzi and M. Geoffroy, *J. Organomet. Chem.*, **218**, 321 (1981).
113. O. L. Chapman, *Org. Photochem.*, **1**, 33 (1967).
114. D. R. Arnold, *Adv. Photochem.*, **6**, 301 (1968).
115. R. A. Bolivar and C. Rivas, *J. Photochem.*, **19**, 95 (1982).
116. T. J. Barton and A. J. Nelson, *Tetrahedron Lett.*, 5037 (1969).
117. C. Rivas, D. Pacheco and F. Vargas, *J. Heterocycl. Chem.*, **17**, 1151 (1980).
118. D. Pacheco, C. Rivas and F. Vargas, *J. Heterocycl. Chem.*, **20**, 1465 (1983).
119. T. Q. Minh, L. Christiaens, P. Grandclaudon and A. Lablache-Combier, *Tetrahedron*, **33**, 2225 (1977).
120. D. C. Neckers, J. H. Dopper and H. Wynberg, *J. Org. Chem.*, **35**, 1582 (1970).
121. D. C. Neckers, J. H. Dopper and H. Wynberg, *Tetrahedron Lett.*, 2913 (1969).
122. J. H. Dopper and D. C. Neckers, *J. Org. Chem.*, **36**, 3756 (1971).
123. G. R. Evanega and E. Payo, *J. Org. Chem.*, **32**, 2918 (1967).
124. R. A. Bolivar, R. Machado, L. Montero, F. Vargas and C. Rivas, *J. Photochem.*, **22**, 91 (1983).
125. R. A. Bolivar and C. Rivas, *J. Photochem.*, **17**, 91 (1981).
126. J. A. Barltrop and J. D. Coyle, *Excited States in Organic Chemistry*, Wiley, New York, 1975, p. 101.
127. C. Rivas, D. Pacheco and F. Vargas, *Acta Sud Am. Quim.*, **2**, 1 (1982); *Chem. Abstr.*, **99**, 38394 (1983).
128. C. Rivas and R. A. Bolivar, *J. Heterocycl. Chem.*, **10**, 967 (1973).
129. N. Petragnani and G. Schill, *Chem. Ber.*, **103**, 2271 (1970).
130. R. M. Kellogg, *Tetrahedron Lett.*, 1429 (1972).
131. B. S. Lukjanow, M. I. Knjazschanski, J. W. Rewinski, L. E. Niworozschkin and W. I. Minkin, *Tetrahedron Lett.*, 2007 (1973).
132. J.-L. Fourrey, G. Henry and P. Jouin, *Tetrahedron Lett.*, 455 (1980).
133. H. Suzuki, M. Usuki and T. Hanafusa, *Synthesis*, 705 (1979).

134. D. Bellus, *Adv. Photochem.*, **8**, 109 (1971).
135. J. Martens, K. Praefcke and H. Simon, *Chem. -Ztg.*, **102**, 108 (1978).
136. N. Y. M. Fung, P. de Mayo, B. Ruge, A. C. Weedon and S. K. Wong, *Can. J. Chem.*, **58**, 6 (1980).
137. D. S. L. Blackwell, K. H. Lee, P. de Mayo, G. L. R. Petrasiunas and G. Reverdy, *Nouv. J. Chim.*, **3**, 123 (1979).
138. D. H. R. Barton, D. Crich, Y. Herve, P. Potier and J. Thierry, *Tetrahedron*, **41**, 4347 (1985).
139. D. H R. Barton, D. Crich and G. Kretzschmar, *Tetrahedron Lett.*, **25**, 1055 (1984).
140. C. L. Pedersen, *J. Chem. Soc., Chem. Commun.*, 704 (1974).
141. J. Kagan, *Tetrahedron Lett.*, 6097 (1966).
142. C. Paulmier, J. Bourguignon, J. Morel and P. Pastour, *C. R. Acad. Sci., Ser. C*, **270**, 494 (1974).
143. A. G. Schultz and R. P. Lucci, *J. Org. Chem.*, **40**, 1371 (1975).
144. A. G. Schultz, *J. Org. Chem.*, **39**, 3185 (1974).
145. O. L. Chapman and G. L. Eian, *J. Am. Chem. Soc.*, **90**, 5329 (1968).
146. J.-P. Le Roux, P. L. Desbene and M. Seguin, *Tetrahedron Lett.*, 3141 (1976).
147. P. L. Desbene and N. Jehanno, *J. Heterocycl. Chem.*, **21**, 1321 (1984).
148. R. A. Abramovitch and E. P. Kyba, *The Chemistry of the Azido Group* (Ed. S. Patai), Interscience, New York, 1971, p. 306.
149. D. L. Ross, J. Blanc and F. J. Maticoli, *J. Am. Chem. Soc.*, **92**, 5750 (1970).
150. A. D. Baker, G. H. Armen, Y. Guang-di, D. Liotta, N. Flannagan, C. Barnum, M. Saindane, G. C. Zima and J. Grossman, *J. Org. Chem.*, **46**, 4127 (1981).
151. D. Betteridge, L. Hendriksen, J. Sandstrom, I. Wennerbeck and M. A. Williams, *Acta Chem. Scand., Ser. A*, **31**, 14 (1977).
152. M. V. Andreocci, M. Bossa, C. Furlani, M. N. Piancastelli, C. Cauletti and T. Tarantelli, *J. Chem. Soc., Faraday Trans. 2*, **75**, 105 (1979).
153. V. Galasso, *J. Mol. Struct.*, **86**, 231 (1982).
154. F. P. Colona and G. Distefano, *J. Electron Spectrosc.*, **18**, 75 (1980).
155. A. G. M. Barrett, D. H. R. Barton, G. Johnson and S. Nagubandi, *Synthesis*, 741 (1978).
156. K. H. Schulte and G. Ohloff, *Helv. Chim. Acta*, **51**, 548 (1968).
157. H. K. Spencer, M. V. Lakshmikantham and M. C. Cava, *J. Am. Chem. Soc.*, **99**, 1470 (1977).
158. M. C. Hovey, *J. Am. Chem. Soc.*, **104**, 4196 (1982).
159. A. A. Frimer, *Chem. Rev.*, **79**, 359 (1979).
160. E. Luppold, W. Winter and E. Muller, *Chem. Ber.*, **109**, 3886 (1976).
161. T. G. Back, D. H. R. Barton, M. R. Britten-Kelly and F. S. Guziec, *J. Chem. Soc., Perkin Trans. 1*, 2079 (1976).
162. N. J. Turro, *Modern Molecular Photochemistry*, Benjamin-Cummings, Menlo Park, CA, 1978, Chapt. 10, pp. 362–395.
163. A. Ohno, M. Uohama, K. Nakamura and S. Oka, *Tetrahedron Lett.*, 1905 (1977).
164. C. C. Liao and P. de Mayo, *J. Chem. Soc., Chem. Commun.*, 1525 (1971).
165. J. Pfenninger, C. Henberger and W. Graf, *Helv. Chim. Acta*, **63**, 2328 (1980).
166. T. Tezuka, H. Suzuki and H. Miyazaki, *Tetrahedron Lett.*, 4885 (1978).
167. J. Martens, K. Praefcke, U. Schulze, H. Schwarz and H. Simon, *Tetrahedron*, **32**, 2467 (1976).
168. R. Tanikaga and A. Kaji, *Bull. Chem. Soc. Jpn.*, **46**, 3814 (1973).
169. G. G. Spence, E. C. Taylor and O. Buchardt, *Chem. Rev.*, **70**, 231 (1970).

CHAPTER **6**

Acidity, hydrogen bonding and self-association in organic and organometallic compounds of selenium and tellurium

THOMAS B. RAUCHFUSS

School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801, USA

I. INTRODUCTION

This chapter is primarily concerned with association phenomena in the organic and organometallic chemistry of selenium and tellurium. Since the classical example of self-association involves hydrogen bonding, the review begins with this topic. However, more important examples of self-association occur in more delocalized systems and in the coordination chemistry of organotellurium compounds.

II. ACIDITY AND HYDROGEN BONDING IN SELENOLS AND TELLUROLS

The chemistry of compounds containing SeH and particularly TeH functionalities is so limited in itself that there is only meager information about their physical and structural properties. It is useful to refer to the data on the inorganic hydrides; the first acid

dissociation constants of H_2S, H_2Se and H_2Te^1 are 1×10^{-7}, 2×10^{-4} and 2.3×10^{-3}. These values indicate that selenols and tellurols should be substantially stronger acids than the corresponding thiols.

Few pK_a measurements have been made on selenols and no such measurements have been made for tellurols[2]. The simplest alkyltellurols[3] and the organometallic anions $M(CO)_5(TeH)^-$ (M = Cr, Mo, W) and $[M(CO)_5]_2(\mu\text{-}TeH)^{-4}$, are the only TeH-containing compounds known to be stable at room temperature. It is generally accepted that selenols are more acidic than the corresponding thiols by 2–3 pK_a units. Unfortunately, direct pK_a measurements of simple aryl- or alkyl-selenols have not been described although ^{13}C NMR measurements show that tertiary amines such as $(i\text{-}Pr)_2EtN$ are $> 90\%$ protonated by one equivalent of PhSeH in $CDCl_3$ solution[5]. The pK_a of $(i\text{-}Pr)_2EtNH^+$ is estimated to be 10.5.

The solution behaviour of 8-quinolineselenol indicates a pK_a of 4.94 for the non-zwitterionic form; the corresponding pK_a values for 8-quinolinethiol and 8-quinolinol are 7.68 and 9.72, respectively[6]. An equally revealing effect is also seen in the tautomeric constants shown in equation 1.

$$(1)$$
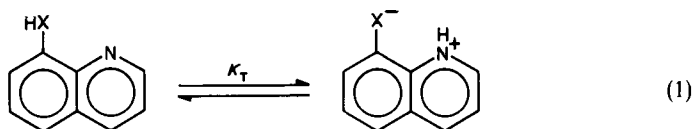
X	K_T
O	0.04
S	3.8
Se	1740

These and related measurements on selenols are hampered by their facile aerial oxidation to diselenides[7].

2-Aminoethylselenol has been studied in solution in part because of its potential as an antioxidant in nuclear medicine. Like 8-quinolineselenol, the selenium analog of cysteamine exists almost exclusively as a zwitterion at neutral pH[8]. The pK_a of selenacysteamine is 5.01 and that of cysteamine is 8.27. The pK_a of $HSeCH_2CH_2NH_2$ has been confirmed by ^{77}Se NMR spectroscopy, where the ^{77}Se chemical shift moves almost 200 ppm upfield as the pH of its aqueous solution changes from 3.5 to 6[9]. The pK_a values of MeO_2CCH_2SeH and MeO_2CCH_2SH have been determined to be 4.7 and 8.1, respectively[10].

There is little information available concerning hydrogen bonding in selenols and tellurols. Given that the strength of the $RSH \cdots SR(H)$ hydrogen bond[11] is only 1.5–2.0 kcal mol^{-1}, the corresponding selenol–selenol interaction is expected to be smaller since the strength of the hydrogen bond decreases as one descends a column in the Periodic Table. An early infrared measurement showed that ν_{SeH} in simple alkylselenols occurs in the range $2300–2380\,cm^{-1}$ and exhibits no solvent or concentration dependence[12]. On the other hand, the poor correlation of $\delta(^{77}Se)$ vs. Hammett σ constants for arylselenols has been attributed to hydrogen bonding effects[13]. Hydrogen bonding involving $Se \cdots H \cdots N$ is well documented through crystallographic studies on selenourea, 1-benzoyl-3-phenyl-2-selenourea and diselenouracil. These materials are all expected to contain very polarized $C{=}Se$ bonds which should stabilize hydrogen bonding[14].

III. SELF-ASSOCIATION OF DIORGANO-SELENIUM AND -TELLURIUM COMPOUNDS

There is considerable crystallographic evidence for intermolecular Se···Se and Te···Te interactions in organo-Se and -Te compounds. This topic has assumed great importance because of its bearing on the electrical properties of the Se- and Te-based organic metals[15]. In general it appears that Te···Te interactions are structurally more important than Se···Se interactions as judged by the overlap of van der Waals radii. Most examples of this structural effect contain the chalcogen in the divalent state.

Bis(2-naphthyl) ditelluride has been obtained in two crystalline modifications which show substantial structural differences. Polymorph A consists of a transoid Ar_2Te_2 moiety whose closest Te···Te contact is > 4.1 Å. The Ar_2Te_2 moieties are cisoid in the lattice of polymorph B and the intermolecular Te···Te contacts are 3.71 and 4.00 Å[16]. Similarly, short Te···Te contacts of 3.70 and 3.63 Å are observed in monoclinic 5,6:11,12-tetratelluro(tetracene)[16] and *trans*-2,4-dibenzylidene-1,3-ditelluretane, $(PhCHC)_2Te_2$[17], respectively. The latter is a poorly soluble compound formed in low yield from the reaction of sodium phenylacetylide and elemental Te. Although not discussed in the literature, a striking structural feature of this material is the intramolecular Te···Te contact of 3.23 Å.
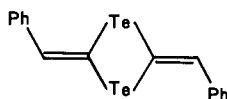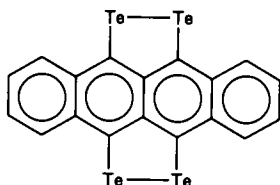
The shortest intermolecular Te···Te contact is 3.58 Å, observed in hexamethylenetetratellurafulvalene[18]. This distance is comparable to the two intramolecular Te···Te contacts of 3.65 and 3.52 Å calculated on the basis of the published data[18a]. In other words, the solid-state structure of this tetratellurafulvalene may be viewed as a Te superlattice into which are fitted organic substituents. The nearly square array of the Te atoms in this compound is reminiscent of Te_4^{2+} (see Section V).
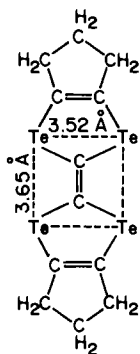
Bis(dimethylthieno)tetratellurafulvalene features Te···Te contacts of 3.66 and 3.76 Å[18b]. These intermolecular interactions may be responsible for the striking non-planarity of this molecule in the lattice where the two $Me_2SC_4Te_2$ planes are bent by 47

and 16° from the plane defined by the central C_2Te_4 core.
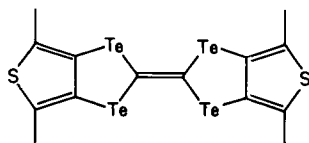
Stereochemically significant intermolecular Te···Te contacts have also been observed in 1,3-ditellurole. The intramolecular Te···Te interaction has been discussed in light of $J(^{125}Te, ^{125}Te)$ values[19].

IV. COMPLEX FORMATION

A. Selenium(II) and Tellurium(II) Compounds

The Lewis acidity of organotellurium(II) halides has been known for many years and has been briefly reviewed by Gysling[20]. Whereas many simple aryltellurium(II) halides are reported to be thermally unstable[21], derivatives containing donor substituents in the *ortho* position are robust. Examples of this type of compound are shown below [X = Cl, Br; D = CHO[22], NO$_2$[23], N$_2$Ph[24], CONH$_2$, C(O)R[25]]. The X-ray structure of 2-C$_6$H$_4$(CHO)TeBr shows a Te···O distance of 2.31 Å[26].
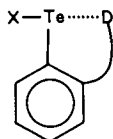
In the same way that *ortho* donor substituents stabilize aryltellurenyl halides, this class of compound has been extended to include adducts with soft donor ligands. In fact, the instability of simple organotellurenyl halides may be due to associative decomposition pathways which are suppressed by the presence of donor ligands[27]. Treatment of Ph$_2$Te$_2$ with halogens in the presence of soft Lewis bases gives the compounds PhTeLX and [PhTeL$_2$]X. In most studies thioureas and selenoureas have been employed as the Lewis bases. The structures of the adducts feature T-shaped complexes with a ligand vacancy *trans* to the phenyl group (equation 2). These compounds are also formed from the reduction of ArTeCl$_3$ by thioureas in methanol[28]. This class of compound has been the subject of several crystallographic investigations but there are few surprises and few corroborative solution studies have been described.

$$Ph_2Te_2 + Br_2 \xrightarrow{\;L\;} \begin{array}{c} X \\ | \\ Ph-Te \\ | \\ L \end{array} + \begin{bmatrix} L \\ | \\ Ph-Te \\ | \\ L \end{bmatrix}^+ \qquad (2)$$
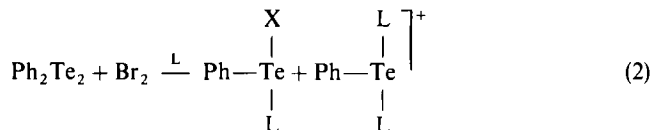
The addition of tetraorganophosphonium iodides to solutions prepared from Ar$_2$Te$_2$ and I$_2$ affords crystals of (R$_4$P)ArTeI$_2$[29], which also has the T-geometry about Te. Catenation of simple organotellurium compounds does not seem to have been studied although Ph$_3$Te$_3^-$ should be stable. Ph$_3$Te$^-$ has not been observed although it would be an electronic relative of PhTeI$_2^-$ and Ph$_3$Te$_3^-$ (Evidence has been presented for Ph$_2$I$^-$ [30]). Related salts of PhSeBr$_2^-$ have been isolated from the reaction of thioureas with PhSeBr$_3$[31].

B. Selenium(IV) and Tellurium(IV) Compounds

Monoorganotellurium(IV) halides are generally prepared via one of the routes shown below[32-34]:

$$R_2Te_2 + X_2$$
$$ArHgX + TeCl_4$$
$$ArOR + TeCl_4$$
$$RCH{=}CH_2 + TeCl_4$$
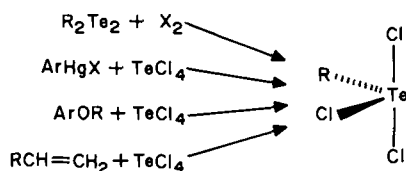
These compounds probably aggregate in solution and exist as dimers and polymers in the solid state. The majority of the most definitive work has involved the aryl derivatives.

In the solid state, the compounds $RTeCl_3$ (R = 2-$ClCH_2CH_2$[34], Ph[35], 4-$EtOPh$[33]) are polymers involving square-pyramidal Te centers interconnected by single chloride bridges. As in the aryltellurenyl systems, the coordination site *trans* to the organic substituent is vacant. The compounds $ArTeBr_3$ and $ArTeI_3$ form molecular dimers in the solid state and two isomers of $PhTeI_3$ have been characterized crystallographically[36], although it is not known if such species have significant stability in solution.
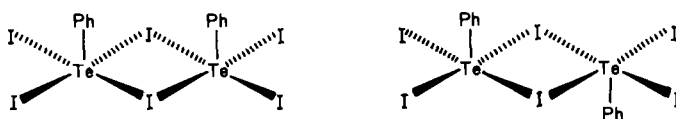
The structural differences between the trichlorides vs. the heavier trihalides have been attributed to the large size of tellurium which precludes the formation of $Te_2(\mu$-$Cl)_2$ rings. $PhTeCl_3$ is ionic in solution presumably due to the equilibrium shown in equation 3[30].

$$ArTeCl_3 \longrightarrow ArTeCl_2^+ + Cl^- \tag{3}$$
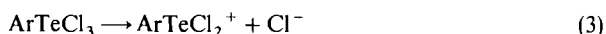
In a related way, the organotransition metal ditelluride $[(C_5H_5)Mo(CO)_2][Fe(CO)_3](Te_2)SbF_6$ is a good Lewis acid and forms adducts with pseudohalides[37] (Scheme 1). Most of the reactivity of this cation is Te-localized. The Lewis base adducts feature 4-coordinate, hypervalent Te centers.

$PhTeCl_3$ forms stable pentacoordinate adducts with thioureas[28], but reduction of the tellurium(IV) occurs when this reaction is conducted in methanolic solution[27]. Attempted complexation of $(Me_2N)_2CS$ with $PhSeBr_3$ gave $[\{(Me_2N)_2CS\}_2][PhSeBr_2]_2$[28].

The thermochromic compound $PhTe(S_2CNR_2)_3$[38] can be prepared via two routes (equation 4). In the lattice, $PhTe(S_2CNR_2)_3$ adopts a pentagonal pyramidal structure.

$$PhTeCl_3 + 3NaS_2CNR_2$$
$$PhTe(S_2CNR_2)_3 \tag{4}$$
$$Ph_2Te_2 + 3[R_2NCCS_2]_2$$
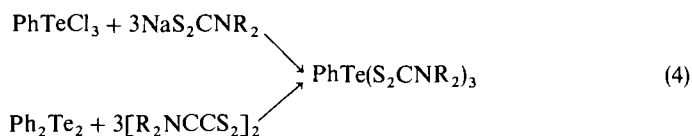
Many diorganotellurium halides have been prepared via the routes shown below[35,36].

$$Ar_2Te_2 + RCHBrCHBrR \longrightarrow Ar_2TeBr_2 + RCH{=}CHR + Te$$
$$ArTeCl_3 + Ar_2Te_2 \longrightarrow Ar_2TeCl_2 + Te$$
$$TeCl_4 + Ar_2Hg \longrightarrow Ar_2TeCl_2 + Hg$$
$$R_2Te + X_2 \longrightarrow R_2TeX_2$$
$$Ar_2TeO + 2HI \longrightarrow Ar_2TeI_2$$

$$Mo = (RC_5H_4)Mo(CO)_2; Fe = Fe(CO)_3$$
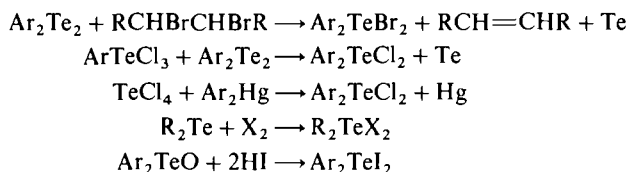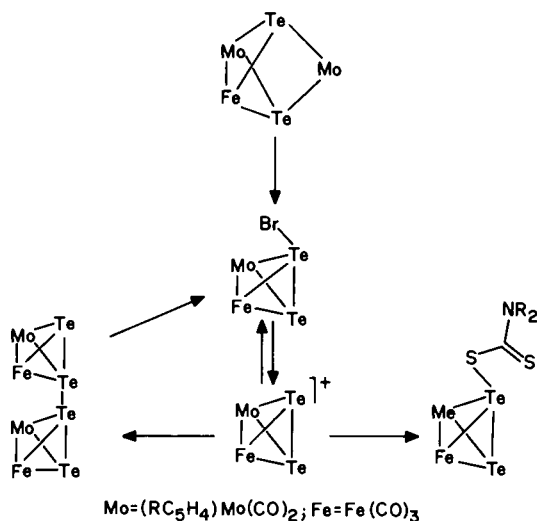
Simplest of all is Me_2TeCl_2, which, in the lattice, contains cis-Me groups, trans-Cl groups and long intermolecular $Te \cdots Cl$ interactions. The crystallographic results for Ph_2TeCl_2 show that a Cl ligand from another molecule approaches the equatorial plane but this secondary $Te \cdots Cl$ distance is 3.67 Å[35].
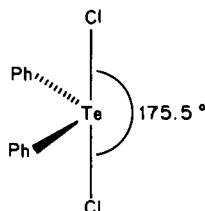
It should be noted that while the aforementioned Me_2TeCl_2 structure is general for other tellurium halides as well as Me_2SeBr_2, Me_2SeI_2 adopts a different geometry[39].

Treatment of $TeCl_4$ with acetophenones[40] and 1,3-diketones[41] gives functionalized dialkyltellurium(IV) dihalides (equations 5 and 6).

$$2ArC(O)Me + TeCl_4 \longrightarrow [ArC(O)CH_2]_2TeCl_2 + 2HCl \tag{5}$$

$$MeC(O)CH_2C(O)Me + TeCl_4 \longrightarrow Cl_2\underline{TeCH_2C(O)CH_2C(O)CH_2} + 2HCl \tag{6}$$

In contrast, certain functionalized ketones when treated with $TeCl_4$ give monoalkyl derivatives[42] (equation 7).

$$\tag{7}$$
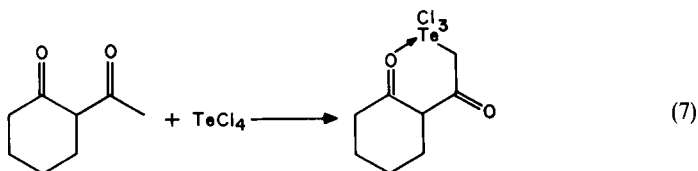
The remarkable [Ph$_3$Te][BPh$_4$] has been prepared via two routes (equation 8). In the lattice, this salt consists of well isolated Ph$_3$Te$^+$ ions of approximate C_{3v} symmetry[43].

$$
\begin{array}{c}
\text{Ph}_4\text{Te} + \text{BPh}_3 \searrow \\
\qquad\qquad\qquad \text{Ph}_3\text{Te}^+\text{BPh}_4^- \qquad\qquad (8) \\
\text{Ph}_3\text{TeCl} + \text{BPh}_4^- \nearrow
\end{array}
$$
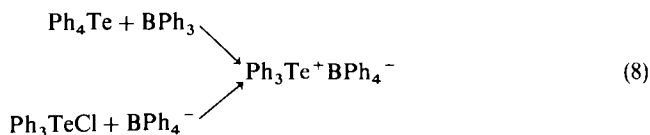
V. Se ··· Se AND Te ··· Te INTERACTIONS IN ORGANOTRANSITION METAL CHEMISTRY

The presence of short intramolecular Te–Te contacts has been demonstrated crystallographically for a number of organometallic derivatives of tellurium. Such interactions may be classified as association since, on the basis of the Te—Te distance (r_{TeTe}) they are weaker than simple two-center two-electron bonds of the type found in diphenylditelluride ($r_{\text{TeTe}} = 2.72$ Å)[44]. The variability of r_{TeTe} in related compounds is highlighted by the structural results on a series of iron–molybdenum clusters, shown below[37,45,46].

$r_{\text{TeTe}} = 3.80$ Å $r_{\text{TeTe}} = 3.14$ Å $r_{\text{TeTe}} = 2.81$ Å
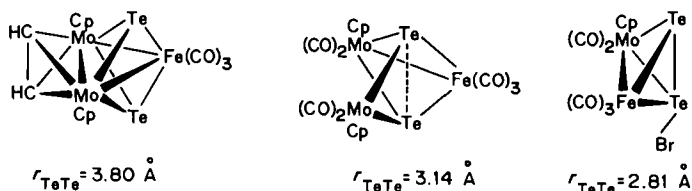
In such cases, the concept of oxidation state becomes useless and the materials must be viewed as highly delocalized systems[45]. Recall that intermolecular TeTe distances of 3.8 Å are considered short in simpler organotellurium compounds. The results for the organotransition metal tellurides lead one to examine the corresponding intramolecular Te–Te contacts in organotellurium compounds. As mentioned in Section III, hexamethylenetetratellurafulvalene[18] is an interesting standard in this regard; the four Te atoms form a rectangle with edges of 3.52 and 3.65 Å. [Te$_4$]$^{2+}$ is a square ion with Te ··· Te distances of 2.66 Å[47].
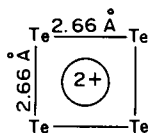
Short Te–Te contacts may be the basis of two effects in organotransition metal–Te cluster chemistry. The easily prepared compound Fe$_3$Te$_2$(CO)$_9$ forms stable adducts with a variety of Lewis bases such as phosphines, amines, isocyanides and carbon monoxide[48]. In contrast, Fe$_3$S$_2$(CO)$_9$ and Fe$_3$Se$_2$(CO)$_9$, which are nearly isostructural with the ditelluride, show no Lewis acidity although they do undergo CO substitution[49]. It has been hypothesized that the facility of the adduct forming reaction of Fe$_3$Te$_2$(CO)$_9$ derives in part from an attractive Te ··· Te interaction[45] (equation 9).

Even more striking is the conversion of octahedral Co$_4$Te$_2$(CO)$_{10}$ ($r_{\text{TeTe}} = 3.3$ Å) into Co$_4$Te$_2$(CO)$_{11}$ ($r_{\text{TeTe}} = 3.06$ Å)[50]; in the latter the r_{TeTe} is elongated by only 10% relative to elemental tellurium[51].

$$\delta_{Te} = 1123$$
$$r_{TeTe} = 3.36 \text{ Å}$$

$$\delta_{Te} = -887, -938$$
$$r_{TeTe} = 3.13 \text{ Å}$$
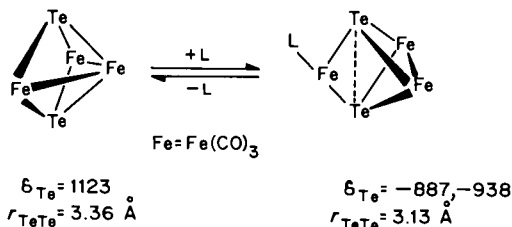
The ^{125}Te chemical shifts for clusters of the type $M_3Te_2L_n$ (L = ligand) vary in a highly systematic way over a 2000 ppm range[52]. Those clusters with short Te $\cdots$ Te distances (3.15–2.8 Å) exhibit δ_{Te} 1000 ± 100 ppm upfield of neat Me_2Te, whereas those clusters with Te $\cdots$ Te distances in the range 3.3–3.8 Å have δ_{Te} of 1000 ± 100 ppm downfield of Me_2Te. The large upfield shifts apparently arise because of magnetic anisotropy due to the short Te—Te distances.

Associative phenomena are prevalent in the chemistry of the polychalcogen cations[47]. Because of their very high reactivity[53], this chemistry has only recently been extended to the organometallic realm. The ion $[W_2(CO)_{10}Se_4]^{2+}$, prepared from $W(CO)_5THF$ and $[Se_4]^{2+}$, may be considered as a dimer of two $[W(CO)_5Se_2]^+$ radical cations[54]. In support of this view, r_{SeSe} for the coordinated Se_2 moieties is 2.21 Å and the 'intermolecular' r_{SeSe} is 3.02 Å.

VI. REFERENCES

1. N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Pergamon Press, Oxford, 1984, p. 900.
2. (a) K. Hamada and M. Morishita, *Synth. React. Inorg. Met.-Org. Chem.*, 7, 355 (1970); (b) C. W. Sink and A. B. Harvey, *Chem. Commun.*, 1023 (1969); (c) J. E. Drake and R. T. Hemmings, *Inorg. Chem.*, 19, 1879 (1980).
3. K. J. Irgolic, *The Organic Chemistry of Tellurium*, Gordon and Breach, New York, 1974.
4. H. Hausmann, M. Höfler, T. Kruck and H. W. Zimmermann, *Chem. Ber.*, 114, 975 (1983); V. Küllmer, E. Röttinger and H. Vahrenkamp, *Z. Naturforsch., Teil B*, 34, 217 (1979). For a more recent example, see W. A. Herrmann, J. Rohrmann, M. L. Ziegler and T. Zahn, *J. Organomet. Chem.*, 273, 221 (1984).
5. H. J. Reich and M. L. Cohen, *J. Org. Chem.*, 44, 3149 (1979).
6. N. Nakamura and E. Sekido, *Talanta*, 17, 515 (1970).
7. D. G. Foster, *Org. Synth.*, Coll. Vol. III, 771 (1951).
8. H. Tanaka, H. Sakurai and A. Yokohama, *Chem. Pharm. Bull.*, 18, 1015 (1970).
9. J. D. Odom, W. H. Dawson and P. D. Ellis, *J. Am. Chem. Soc.*, 101, 5815 (1979).
10. J. H. Kurz and J. C. Harris, *J. Org. Chem.*, 35, 3086 (1970).
11. M. D. Joesten and L. J. Schaad, *Hydrogen Bonding*, Marcel Dekker, New York, 1974.
12. N. Sharghi and I. Lalezari, *Spectrochim. Acta*, 20, 237 (1964).
13. W. McFarlane and R. J. Wood, *J. Chem. Soc., Dalton Trans.*, 1397 (1972).
14. I. L. Karle and J. Karle, in *Organic Selenium Compounds: Their Chemistry and Biology* (Eds. D. L. Klayman and W. H. H. Günther), Wiley, New York 1973, p. 67.
15. M.-H. Whangbo, J. M. Williams, M. A. Beno and J. R. Dorfman, *J. Am. Chem. Soc.*, 105, 645 (1983).
16. D. J. Sandman, J. C. Stark, M. Rubner, L. A. Acampora and L. A. Samuelson *Mol. Cryst. Liq. Cryst.*, 93, 293 (1983); D. J. Sandman, J. C. Stark and B. M. Foxman, *Organometallics*, 1, 739 (1982).
17. S. L. Bender, N. F. Haley and H. R. Loss, *Tetrahedron Lett.*, 22, 1495 (1981); M. V. Lakshmikantham, M. P. Cava, M. Albeck, L. Engman, P. Carroll, J. Bergman and F. Wudl, *Tetrahedron Lett.*, 22, 4199 (1981); for related work see S. L. Bender, M. R. Detty, M. W. Fichtner and N. F. Haley, *Tetrahedron Lett.*, 24, 237 (1983); see also S. L. Bender, M. R. Detty and N. F. Haley, *Tetrahedron Lett.*, 23, 1531 (1982).

18a. P. J. Carroll, M. V. Lakshmikantham, M. P. Cava, F. Wudl, E. Aharon-Shalom and S. D. Cox, *J. Chem. Soc., Chem. Commun.*, 1316 (1982).

18b. K. Lerstrup, D. O. Cowan and T. J. Kistenmacher, *J. Am. Chem. Soc.*, **106**, 8303 (1984).

19. M. R. Detty, P. M. Henrichs and J. A. Whitefield, *Organometallics*, **5**, 1544 (1986); M. R. Detty, N. F. Haley, R. S. Eachus, J. W. Hassett, H. R. Luss, J. M. McKelvey and A. A. Wernberg, *J. Am. Chem. Soc.*, **107**, 6298 (1985).

20. H. J. Gysling, *Coord. Chem. Rev.*, **42**, 133 (1982).

21. N. Petragnani and M. de Moura Campos, *Chem. Ber.*, **94**, 1759 (1961).

22. J. L. Piette, R. Lysy and M. Renson, *Bull. Soc. Chim. Fr.*, 3559 (1972).

23. P. Wiriyachitra, S. J. Falcone and M. P. Cava, *J. Org. Chem.*, **44**, 3957 (1979); J. L. Piette, P. Thibaut and M. Renson, *Tetrahedron Lett.*, 655 (1978).

24. R. E. Cobbledick, F. W. B. Einstein, W. R. McWhinnie and F. H. Musa, *J. Chem. Res. (S)*, 145 (1979).

25. J. L. Piette and M. Renson, *Bull. Soc. Chim. Belg.*, **80**, 669 (1971).

26. M. Baiwir, G. Llabres, O. Dideberg, L. DuPont and J. L. Piette, *Acta Crystallogr., Sect. B*, **30**, 139 (1974).

27. (a) O. Foss, S. Husebye and K. Maroy, *Acta Chem. Scand.*, **17**, 1806 (1963); (b) O. Foss and K. Maroy, *Acta Chem. Scand.*, **20**, 123 (1966). (c) O. Foss and S. Husebye, *Acta Chem. Scand.*, **20**, 132 (1966). (d) S. Hauge and O. Vikane, *Acta Chem. Scand.*, **27**, 3596 (1973). (e) O. Vikane, *Acta Chem. Scand., Ser. A*, **29**, 738, 763, 787 (1975). (f) S. Hauge, O. Johannesen and O. Vikane, *Acta Chem. Scand., Ser. A*, **32**, 901 (1978). (g) O. Foss and S. Hauge, *Acta Chem. Scand.*, **13**, 2155 (1959). (h) P. Klaeboe and O. Vikane, *Acta Chem. Scand., Ser. A*, **31**, 120 (1977).

28. K. J. Wynne and P. S. Pearson, *Inorg. Chem.*, **10**, 2735 (1971).

29. (a) P. Klaeboe, C. J. Nielson, R. Suchi and O. Vikane, *Acta Chem. Scand., Ser. A*, **32**, 565 (1978); (b) S. Hauge and O. Vikane, *Acta Chem. Scand., Ser. A*, **29**, 755 (1975). (c) K. Maartmann-Moe and J. Songstad, *Acta Chem. Scand., Ser. A*, **36**, 829 (1982).

30. H. J. Reich, N. H. Phillips and I. L. Reich, *J. Am. Chem. Soc.*, **107**, 4104 (1985).

31. K. J. Wynne and P. S. Pearson, *Inorg. Chem.*, **11**, 1192, 1197 (1972).

32. N. Petragnani, *Tetrahedron*, **11**, 15 (1960).

33. P. H. Bird, V. Kumar and B. C. Paul, *Inorg. Chem.*, **19**, 2487 (1980).

34. D. Kobelt and E. F. Paulus, *Angew. Chem., Int. Ed. Engl.*, **10**, 73, 74 (1971).

35. N. W. Alcock and W. D. Harrison, *J. Chem. Soc., Dalton Trans.*, 251 (1982).

36. (a) N. W. Alcock and W. D. Harrison, *J. Chem. Soc., Dalton Trans.*, 869 (1984); (b) A. C. Hazell *Acta Chem. Scand.*, **26**, 1510 (1972).

37. L. E. Bogan, Jr., T. B. Rauchfuss and A. L. Rheingold, *Inorg. Chem.*, **24**, 3720 (1985).

38. S. Esperas and S. Husebye, *Acta Chem. Scand.*, **26**, 3293 (1972).

39. (a) G. D. Cristofferson, R. A. Sparks and J. D. McCullough, *Acta Crystallogr.*, **11**, 782, 249 (1958); (b) G. C. Hayward and P. J. Hendra, *J. Chem. Soc. A*, 1760 (1969).

40. D. G. Marsh, J. Y. C. Chu, J. W. Lewicki and J. L. Weaver, *J. Am. Chem. Soc.*, **98**, 8432 (1976).

41. C. L. Raston, R. J. Secomb and A. H. White, *J. Chem. Soc., Dalton Trans.*, 2307 (1976).

42. H. J. Gysling, H. R. Luss and S. A. Gardner, *J. Organomet. Chem.*, **184**, 417 (1980).

43. R. F. Ziolo and J. Troup, *Inorg. Chem.*, **18**, 2271 (1979).

44. G. Llabres, O. Dideberg, and L. Dupont, *Acta Crystallogr., Sect. B*, **28**, 2438 (1972).

45. L. E. Bogan, Jr., T. B. Rauchfuss and A. L. Rheingold, *J. Am. Chem. Soc.*, **106**, 3843 (1985).

46. L. E. Bogan, Jr., G. R. Clark and T. B. Rauchfuss, *Inorg. Chem.*, **25**, 4050 (1986).

47. R. J. Gillespie, *Chem. Soc. Rev.*, **8**, 315 (1979).

48. D. A. Lesch and T. B. Rauchfuss, *Organometallics*, **1**, 494 (1982).

49. S. Aime, L. Milone, R. Rossetti and P. L. Stanghellini, *J. Chem. Soc., Dalton Trans.* 500 (1980).

50. R. C. Ryan and L. F. Dahl, *J. Am. Chem. Soc.*, **97**, 6904 (1975).

51. J. Donohue, *The Structures of the Elements*, Wiley, New York, 1971.

52. D. A. Lesch and T. B. Rauchfuss, *Inorg. Chem.*, **22**, 1854 (1983).

53. A. M. Rosan, *J. Chem. Soc., Chem. Commun.*, 377 (1985).

54. C. Belin, T. Makani and J. Roziere, *J. Chem. Soc., Chem. Commun.*, 118 (1985).

CHAPTER **7**

Biochemistry of physiologically active selenium compounds

KENJI SODA, HIDEHIKO TANAKA AND NOBUYOSHI ESAKI

Institute for Chemical Research, Kyoto University, Uji, Kyoto-Fu 611, Japan

I. SELENIUM AMINO ACIDS AND SELENOENZYMES

A. Introduction

Selenium is recognized as an essential micronutrient for mammals, birds, fish and several bacteria. The physiological functions of selenium in mammals and birds can be attributed mostly to the action of glutathione peroxidase, which contains the essential selenocysteine residue in the polypeptide chain. Several microbial enzymes have also been demonstrated to contain in their polypeptide chains selenocysteine residues which play an

integral role in catalysis. Various other natural selenium amino acids occur in the free state and have been reported to give protection to mammals from radiation injury and carcinogenesis, as described in Masukawa's chapter in this volume.

In this section we describe enzymological aspects of selenium-containing enzymes and the metabolism of selenium amino acids. The mechanism of the enzymatic synthesis of selenium amino acids is also described here.

B. Selenium Enzymes

Enzymes that contain selenium as an essential component are called selenoenzymes. Table 1 summarizes the selenoenzymes so far studied.

Glutathione peroxidase (E.C. 1.11.1.9) catalyses the decomposition of hydrogen peroxide or organic peroxides by reduction with glutathione as shown in the equation

$$2GSH + H_2O_2 \text{ (or ROOH)} \rightarrow GSSG + H_2O \text{ (or ROH} + H_2O) \tag{1}$$
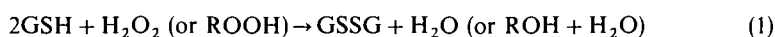
The enzyme is distributed widely in mammalian tissues, and is responsible for the protection of erythrocyte membrane and other tissues from oxidation damage. The crystalline enzyme has been prepared from bovine erythrocytes to study its three-dimensional structure by X-ray analysis at 2.0 Å resolution[1]. The partial amino acid sequence of rat liver enzyme determined by Edman degradation coincides with the corresponding part of the bovine erythrocyte enzyme deduced by X-ray analysis[1].

Several molecular weights (76000–92000) have been reported for the native enzyme from various sources. The enzyme is composed of four identical subunits (M_r 19000–23000), each of which contains a selenocysteine residue. The selenol group of selenocysteine has lower redox potential and higher nucleophilicity than the thiol group of cysteine. The high reactivity of selenol substantially contributes to the specific catalytic function of glutathione peroxidase. The selenium-containing moiety of xanthine dehydrogenase and nicotinic acid hydroxylase has not been elucidated. Recently, Sliwkowski and

TABLE 1. Selenium enzymes

Enzyme	Chemical form of selenium	Other components	Molecular weight	Source
Glutathione peroxidase	Selenocysteine	–	76000–92000	Rat liver Bovine erythrocytes
Glycine reductase	Selenocysteine	Fe	462000	*Clostridium sticklandii*
Formate dehydrogenase	Selenocysteine	Mo, Fe/S	500000	*Methanococcus vannielii*
	Selenocysteine	W, Mo, Fe/S	300000	*Clostridium thermoaceticum*
	N.d.[a]	Mo, Fe/S, haeme	590000	*E. coli*
Hydrogenase	Selenocysteine	Ni	340000	*Methanococcus vannielii*
Nicotinate hydroxylase	N.d.[a]	Fe/S	300000	*Clostridium barkeri*
Xanthine dehydrogenase	N.d.[a]	Fe, Mo	N.d.[a]	*Clostridium cylindrosporum*

[a] Not determined

Stadtman[2] showed that selenomethionine residues are distributed throughout the primary structure of thiolase; methionine is replaced by selenomethionine non-specifically. Therefore, they suggested that no specific function of selenomethionine is required for the enzyme. All the other selenoenzymes contain a selenocysteine residue. The properties and catalytic functions of these selenoenzymes have been reviewed in detail by Stadtman[3].

C. Enzymological Aspects of Selenium Amino Acid Metabolism

Selenium amino acids are thought to be synthesized through an analogous pathway to the sulphur counterparts. Various enzymes acting on sulphur amino acids (e.g. mammalian cystathionine γ-lyase and bacterial methionine γ-lyase) work on the selenium analogues, although enzymes that act specifically on selenium compounds have been considered[4]. The indiscriminate catalytic action of enzymes on sulphur and selenium compounds is probably involved at least partly in the toxicity of selenium compounds. Provided that the selenium compounds are present at high concentrations, indiscriminate substitution of selenium for sulphur in proteins, nucleic acids and complex carbohydrates could occur and cause various toxic effects on organisms. The metabolism of selenium amino acids was discussed in detail in earlier reviews by Stadtman[4] and Shrift[5], and is not treated here. We shall discuss mainly the metabolism of selenocysteine recently elucidated in our laboratory.

1. Synthesis of selenocysteine

Selenomethionine has been shown to occur in wheat and some other grains, but there are few reports of the occurrence of selenocysteine and selenocystine[6]. In mammalian tissues, selenocysteine synthesis was assumed to be analogous to that of cysteine. Selenomethionine serves as a better substrate than methionine for ATP:L-methionine S-adenosyltransferase of rabbit liver and other sources[7,8]. Se-Adenosylselenomethionine was shown to be an efficient methyl donor in various methylation systems[9]. Evidence for the enzymatic synthesis of selenocysteine has been reported[10]. Cystathionine β-synthase of rat liver catalyses the formation of selenocystathionine (equation 2) in addition to the cystathionine synthesis (equation 3), as summarized in Table 2.

$$\text{L-serine} + \text{L-selenohomocysteine} \rightarrow \text{L-selenocystathionine} + H_2O \qquad (2)$$

$$\text{L-serine} + \text{L-homocysteine} \rightarrow \text{L-cystathionine} + H_2O \qquad (3)$$
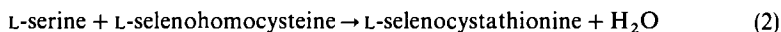
Selenohomocysteine is as susceptible as homocysteine; the relative V_{max} value is about 0.7. L-Homocysteine inhibits the selenocystathionine synthesis in the presence of 5 mM L-serine as a competitive inhibitor for L-selenohomocysteine, and L-selenohomocysteine also inhibits the cystathionine synthesis in the same manner. The K_i values are substantially consistent with the K_m values (Table 2), indicating that both reactions 2 and 3 are carried out at the same active site.

Cystathionine γ-lyase can catalyse α, β-elimination of L-cystine in addition to α, γ-elimination of L-cystathionine, as described by Cavallini et al.[11]. Esaki et al.[10] have found that the α, β-elimination of L-cystathionine (equation 4) proceeds much more slowly (> 3%) than the α, γ-elimination (equation 5).

$$\text{L-cystathionine} + H_2O \rightarrow \text{pyruvate} + \text{L-homocysteine} + NH_3 \qquad (4)$$

$$\text{L-cystathionine} + H_2O \rightarrow \alpha\text{-ketobutyrate} + \text{L-cysteine} + NH_3 \qquad (5)$$

$$\text{L-selenocystathionine} + H_2O \rightarrow \text{pyruvate} + \text{L-selenohomocysteine} + NH_3 \qquad (6)$$

$$\text{L-selenocystathionine} + H_2O \rightarrow \alpha\text{-ketobutyrate} + \text{L-selenocysteine} + NH_3 \qquad (7)$$
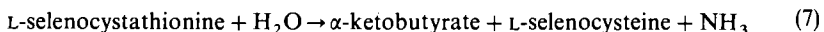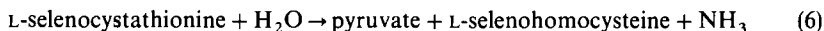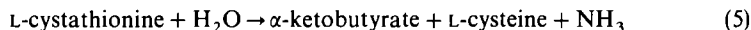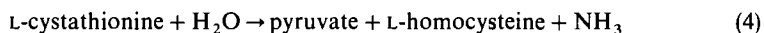
TABLE 2. Kinetic parameters for cystathionine β-synthase

	V_{max} (μmol mg^{-1} min^{-1})	K_m (mM)	K_i (mM)
Selenocystathionine synthesis			
(reaction 2)	0.11		
L-Serine		0.3	
L-Selenohomocysteine		2.5	3.4
Cystathionine synthesis			
(reaction 3)	0.16		
L-Serine		1.2	
L-Homocysteine		1.2	0.85

TABLE 3. Kinetic parameters for cystathionine γ-lyase

	Type of reaction	K_m (mM)	V_{max} (μmol mg^{-1} min^{-1})
L-Selenocystathionine	α, γ-Elimination (reaction 7)	1.7	19
	α, β-Elimination (reaction 6)		9.5
L-Cystathionine	α, γ-Elimination (reaction 5)	1.3	6.2
	α, β-Elimination (reaction 4)		0.18
L-Selenohomocysteine	α, γ-elimination	1.4	0.62
L-Homocysteine	α, γ-Elimination	2.9	0.25
DL-Selenocysteine	α, β-Elimination	1.2	0.51
L-Cysteine	α, β-Elimination	1.1	0.17

However, the α, β-elimination of selenocystathionine proceeds at a comparable rate to the α,γ-elimination of the same substrate (Table 3). Cystathionine γ-lyase can eliminate further both the amino acids formed from selenocystathionine and cystathionine by elimination reactions, although slowly. All the selenium amino acids are decomposed 2.5–3 times more rapidly than the corresponding sulphur analogues (Table 3). Braunstein et al.[12] reported that cystathionine β-synthase of chicken liver catalyses synthesis of cysteine from serine and H_2S (equation 8). The rat liver enzyme also catalyses the reaction at a rate of 12% of cystathionine synthesis (equation 3), but selenocysteine cannot be synthesized directly from L-serine and H_2Se (equation 9)[10]. This is probably due to the low reactivity of selenide as a substituting agent in the replacement reaction.

$$\text{L-serine} + H_2S \rightarrow \text{L-cysteine} + H_2O \qquad (8)$$
$$\text{L-serine} + H_2Se \rightarrow \text{L-selenocysteine} + H_2O \qquad (9)$$
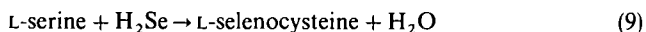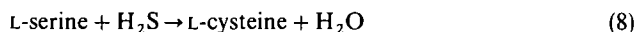
2. Occurrence of selenocysteine β-lyase and its enzymological properties

Selenocysteine is synthesized by the coupled reactions with cystathionine β-synthase (E.C. 4.2.1.22) and cystathionine γ-lyase (E.C. 4.4.1.1) purified from rat liver, and also by

reaction with a rat liver homogenate[10], with which the synthesis proceeds far less efficiently. This is due to the presence of a novel enzyme in the homogenate that decomposes selenocysteine specifically into alanine and H_2Se[13]. The enzyme catalyses the removal of elemental selenium from L-selenocysteine; the formation of H_2Se is due to reduction of the elemental selenium by the unreacted selenocysteine. Thus, the enzyme has been termed selenocysteine β-lyase, or systematically selenocysteine selenium-lyase (alanine-forming)[13].

Selenocysteine β-lyase is distributed widely in mammalian tissues (Table 4)[13]. The enzyme activities of livers and kidneys are higher than those of other tissues in several animals. Significant activity is found in pancreas and adrenal, but none in blood and fat. The enzyme has also been demonstrated in various bacterial strains such as *Citrobacter freundii*, *Alcaligenes viscolactis* and *Pseudomonas alkanolytica*. However, no significant activity was found in yeasts and fungi (Table 5)[14].

Selenocysteine β-lyase has been purified to homogeneity from pig liver and *Citrobacter freundii* and characterized[13,15]. The bacterial enzyme is remarkably different from the mammalian enzyme in its physicochemical properties (Table 6) and amino acid composition (Table 7). In contrast, both the enzymes are very similar in their enzymological properties: both contain pyridoxal 5'-phosphate (pyridoxal-P) as a coenzyme, exhibit strict specificity for L-selenocysteine and have similar K_m values for the substrates. L-Cysteine behaves as a competitive inhibitor against L-selenocysteine for both the enzymes. Based on the K_m value for L-selenocysteine and the K_i value for L-cysteine, the enzyme probably acts on selenocysteine very slowly *in vivo*, because the concentration of selenocysteine in the tissues is lower than the K_m value. However, the total activity of enzyme is probably sufficient to metabolize a small amount of selenocysteine in the tissues (Table 4). The localization and compartmentation of the enzyme, the substrate and the inhibitors probably affect the enzyme activity *in vivo*.

Selenomethionine and selenocysteine are toxic to animals, and H_2Se is the most toxic selenium compound studied so far[16]. Selenocysteine can be synthesized from selenomethionine derived from a diet[6] as described above. H_2Se is produced from selenomethionine through selenocysteine by catalysis of selenocysteine β-lyase. The lack of specificity of the enzymes acting on the biosynthetic pathway of cysteine from methionine (e.g. cysta-

TABLE 4. Distribution of selenocysteine β-lyase in tissues

Tissue	Specific activity ($\times 10^3$)								
	Rat	Dog	Mouse	Guinea pig	Pig	Cat	Rabbit	Bovine	Monkey
Liver	5.5	10	9.7	15	8.2	1.6	17	3.5	9.9
Kidney	4.9	4.5	8.9	14	3.6	1.9	17		
Pancreas	8.0	3.0	0.21	0.34					
Adrenal	3.5								
Heart	0.90	0.81							
Lung	2.0	1.2							
Testis	0.83								
Brain	0.93	0.96							
Thymus	1.7	6.0							
Spleen	1.4	1.8							
Muscle	0.57								
Fat	0								
Blood	0								

TABLE 5. Distribution of selenocysteine β-lyase in microorganisms

Microorganism	Activity (nmol min^{-1} mg^{-1}) determined by		
	H$_2$Se formed	Alanine formed	Selenocysteine consumed
Alcaligenes viscolactis	32.0	28.5	33.9
Citrobacter freundii	17.5	20.5	31.3
Corynebacterium pseudodiphtheriticum	15.0	19.5	12.8
Pseudomonas alkanolytica	16.7	17.9	17.2
Brevibacterium leucinophagum	22.5	28.3	29.2
Escherichia coli	1.90	1.31	
Erwinia carotovora	2.80	2.10	
Serratia marcescens	2.70	1.54	
Alcaligenes bookeri	5.40	5.24	
Aspergillus ficuum	3.80	1.33	
Aspergillus sojae	0.70	0.00	
Absidia corymbifera	1.40	0.94	
Neurospora crassa	0.56	0.26	
Penicillium expansum	1.00	0.48	
Saccharomyces cerevisiae	2.60	1.30	
Kluyveromyces fragilis	5.60	2.52	
Candida albicans	8.10	1.13	
Hansenula beckii	0.70	0.55	
Schwanniomyces occidentalis	2.90	1.62	

TABLE 6. Properties of selenocysteine β-lyase

Property	Pig liver enzyme	*Citrobacter freundii* enzyme
Molecular weight	93000	63000
Subunit structure	Dimer	Monomer
Isoelectric point	5.9	6.6
Absorption maxima	280, 420	280, 420
Pyridoxal-P content (mol per mol of enzyme)	1	1
Optimum pH	8.4	7.0
Substrate (K_m)	L-Seleno-cysteine (0.8 mM)	L-Selenocysteine (0.95 mM)
Competitive inhibitor (K_i)	L-Cysteine (1.0 mM)	L-Cysteine (0.65 mM)
Inactivation by abortive transamination	Yes	Yes
Irreversible inactivation by β-chloroalanine	Yes	Yes

TABLE 7. Amino acid composition of selenocysteine β-lyase

Amino acid	*Citrobacter freundii* enzyme		Pig liver enzyme	
	mol-%	mol per mol of subunit	mol-%	mol per mol of subunit
Aspartic acid	14.12	82	8.15	36
Threonine	7.53	43	5.55	25
Serine	12.44	72	5.45	24
Glutamic acid	6.30	36	11.84	52
Proline	3.82	22	5.68	25
Glycine	9.99	58	9.06	40
Alanine	5.93	34	10.66	47
Cysteine	1.05	6	0.84	4
Valine	2.47	14	7.58	33
Methionine	1.63	9	2.26	10
Isoleucine	2.03	12	3.30	15
Leucine	4.05	23	9.48	42
Tyrosine	4.53	26	1.72	8
Phenylalanine	2.69	16	2.82	13
Lysine	7.30	42	3.20	14
Histidine	4.51	26	2.95	13
Arginine	7.89	46	7.19	32
Tryptophan	1.73	10	2.98	7

thionine γ-lyase and cystathionine β-synthase) and the presence of selenocysteine β-lyase may contribute in part to the selenium toxicity.

The mechanism of incorporation of selenium into the enzymes that contain selenocysteine residues has been studied. Sunde and Hoekstra[17] suggested that serine or cysteine residues in polypeptide chains are converted, for example, into dehydroalanine residues, and then H_2Se is added to the α, β-unsaturated bond to give the selenocysteine residues. In contrast, Hawkes et al.[18] proposed a direct incorporation mechanism, according to which a tRNA and a codon specific for selenocysteine are present, and selenocysteine is directly incorporated into the protein in the stage of translation. According to the post-translational selenium incorporation hypothesis[17], selenocysteine β-lyase can function to give the direct selenium precursor that is incorporated into the proenzyme to form the selenocysteine residue. Alternatively, according to the direct incorporation hypothesis, selenocysteine β-lyase functions to decompose an excess of selenocysteine to give H_2Se, which can be detoxified through methylation or some other reactions[18].

3. Reaction mechanism of selenocysteine β-lyase

The selenocysteine β-lyase reaction is exceptional among those of the pyridoxal-P enzymes studied so far. The enzyme resembles bacterial aspartate β-decarboxylase (E.C. 4.1.1.12)[19] and kynureninase (E.C. 3.7.1.3)[20] in the reaction mechanism where a moiety binding to $C_{(3)}$ of the substrate is cleaved to produce alanine. Esaki et al.[21] and Chocat et al.[15] have proposed mechanisms for the reactions catalysed by selenocysteine β-lyase. The selenohydryl group of selenocysteine is substantially in an anionic form under physiological conditions because its pK_a is 5.28[22]. Cysteine is not a substrate of selenocysteine β-lyase, but it inhibits the enzyme reaction competitively with selenocysteine between pH 7.0 and 9.0. In this pH range, a thiol group of cysteine is dissociated at

least partially since its pK_a is about 8.8. Thus, the difference in the enzymatic reactivities of selenol and thiol is not derived from differences in their dissociation states. The deuterium isotope effect at the α position determined by Esaki et al.[21] and Chocat et al.[15] indicates that an α-hydrogen release occurs in the enzyme reaction and is rate limiting. The α-hydrogen of selenocysteine is abstracted by a base at the enzyme active site, and then selenium is removed in an elemental form. L-Cysteine can bind the enzyme active site, but elemental sulphur is not removed from a cysteine–pyridoxal-P aldimine complex owing to the strong bond between the β-carbon and the sulphur of cysteine, which is stronger than that between the β-carbon and selenium of selenocysteine (the dissociation energies are 272 kJ mol^{-1} for C—S and 243 kJ mol^{-1} for C—Se)[23]. The situation is similar in various organic reactions, such as the reactions of episulphides and episelenides[24].

The selenocysteine β-lyase reactions have been studied in deuterium oxide by Esaki et al.[21] and Chocat et al.[15] to show deuterium incorporation into alanine. The ^{1}H and ^{13}C NMR spectra of the alanine produced indicate the formation of [β-^{1}H$_1$]- and [β-^{1}H$_2$]-alanines. Therefore, in addition to the incorporation of one deuterium atom into the β-position of alanine after removal of elemental selenium, one of the two β-hydrogen atoms of selenocysteine is exchanged with a solvent deuterium atom at a frequency of 0.5. The enzyme catalyses no hydrogen exchange at the α- and β-positions of alanine with a solvent deuterium atom, and the α-hydrogen of selenocysteine is fully retained at the α-position of alanine. Thus, a two-base mechanism has been proposed for the enzyme reaction: the α-protonation and deprotonation are performed by one base, and the other base mediates the β-protonation. A similar mechanism has been proposed by Chang et al.[25] for the reactions catalysed by aspartate β-decarboxylase.

Selenocysteine β-lyase is inactivated through transamination between selenocysteine and the bound pyridoxal-P to produce pyridoxamine 5'-phosphate (pyridoxamine-P) and a keto analogue of selenocysteine when the enzyme is incubated with L-selenocysteine in the absence of added pyridoxal-P, as reported by Esaki et al.[21] and Chocat et al.[15]. Analogous transaminations catalysed by pyridoxal-P enzymes have been reported involving serine hydroxymethyltransferase[26], arginine racemase[27], tryptophan synthase[28], aspartate β-decarboxylase[25] and kynureninase[20]. All three enzymes catalysing β-elimination (kynureninase, aspartate β-decarboxylase and selenocysteine β-lyase) also catalyse the transamination, although very slowly.

Chocat et al.[15] reported that selenocysteine β-lyase catalyses the α,β-elimination of β-chloro-L-alanine to form NH$_3$, pyruvate and Cl$^-$, and is irreversibly inactivated during the reaction in a suicide fashion. The relatively low partition ratio (825) of the α,β-elimination to the inactivation is similar to that reported for alanine racemase[29] and amino acid racemase with low substrate specificity[30], and indicates highly efficient inactivation.

D. Enzymatic Synthesis of Selenium Amino Acids

The biological role of optically active selenium amino acids has received considerable attention, but studies of their metabolism have been hampered by difficulties in their synthesis. Recently, facile synthetic procedures giving optically active Se-substituted selenocysteines and Se-substituted selenohomocysteines were developed by Soda and coworkers[31–33,39–41] by means of the microbial pyridoxal-P enzymes methionine γ-lyase, tryptophan synthase and O-acetylhomoserine sulphydrylase.

1. Methionine γ-lyase

L-Methionine γ-lyase (E.C.4.4.1.11) is a pyridoxal-P enzyme catalysing the conversion of L-methionine into α-ketobutyrate, methanethiol and ammonia, and plays an impor-

tant role in the bacterial metabolism of methionine. The enzyme is widely distributed in psuedomonads. The enzyme is inducibly produced by addition of L-methionine to the medium, and was purified to homogeneity from the crude extract of *Pseudomonas putida* ICR 3460, the best producer of the enzyme[31]. Recently, *Aeromonas* sp. isolated from a lake was also found to produce L-methionine γ-lyase abundantly, and the *Aeromonas* enzyme was purified to homogeneity by a similar procedure to that for the *Pseudomonas* enzyme[32]. Table 8 summarizes the physicochemical properties of the enzyme purified from both strains. The enzyme has multiple catalytic functions: it catalyses α, γ-elimination and γ-replacement reactions of L-methionine and its analogues and α, β-elimination and β-replacement reactions of L-cysteine and its analogues. The enzyme also catalyses the α, γ-elimination of selenomethionine to yield α-ketobutyrate, ammonia and methaneselenol, and also γ-replacement reactions with various thiols to produce S-substituted homocysteines[33]. Selenomethionine is a better substrate than methionine for α, γ-elimination based on the V_{max} and K_m values, but is less effective for γ-replacement. In addition, L-methionine and its derivatives, which are substrates for the α, γ-elimination, react with selenols to form the corresponding Se-substituted selenohomocysteines, although selenols are less efficient substituent donors than thiols. The enzymatic β-replacement reaction also occurs between S-substituted cysteines or O-substituted serines and selenols.

Davis and Metzler[34] have proposed that a ketimine intermediate of pyridoxal-P and vinylglycine (2-amino-3-butenoate) is the key intermediate of α, γ-elimination and γ-replacement reactions catalysed by pyridoxal-P enzymes. Vinylglycine has been reported to inactivate several transaminases as a suicide substrate[35]. This is not the case with methionine γ-lyase. It catalyzes the deamination reaction of vinylglycine to produce α-ketobutyrate and ammonia (equation 10), but is not inactivated by vinylglycine[36]. The enzyme also catalyses the γ-addition reaction of various thiols or selenols to yield the corresponding S- or Se-substituted homocysteines (equation 11). The relative activities of the enzyme for a variety of thiols and selenols in the γ-addition reaction of vinylglycine are close to those in the γ-replacement reaction of methionine. Incubation of the enzyme with vinylglycine results in the appearance of a new absorption band at 480 nm, which is also observed with substrates such as methionine, O-acetylhomoserine and selenomethionine

TABLE 8. Properties of methionine γ-lyase

Property	Source	
	Pseudomonas putida	*Aeromonas* sp.
$S^0{}_{20,w}$	8.3S	–
Molecular weight:		
Sedimentation equilibrium	165000	–
Gel permeation chromatography	–	149000
Low-angle light scattering	174000	159000
Absorption maxima	278 nm ($\varepsilon = 134000$)	278 nm ($\varepsilon = 159000$)
	420 nm ($\varepsilon = 38900$)	423 nm ($\varepsilon = 31300$)
Number of subunits	4	4
Molecular weight of subunits	43000	41000
Pyridoxal-P content (mol per mol of enzyme)	4	4

for α,γ-elimination, but not with α,β-elimination substrates. These findings support the mechanism through a vinylglycine–pyridoxal-P quinonoid intermediate proposed by Davis and Metzler[34].

$$CH_2 = CHCH(NH_2)COOH + H_2O \longrightarrow EtCOCOOH + NH_3 \qquad (10)$$

$$CH_2 = CHCH(NH_2)COOH + RXH \longrightarrow RXCH_2CH_2CH(NH_2)COOH \qquad (11)$$

$$(X = S \text{ or } Se)$$
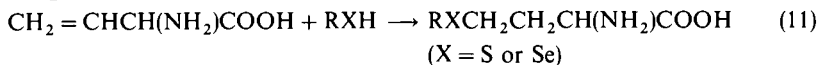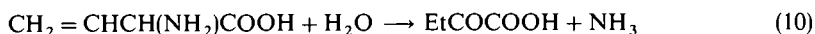
2. Tryptophan synthase

Tryptophan synthase (E.C. 4.2.1.20) is a pyridoxal-P enzyme with a variety of catalytic functions (Table 9, reactions 12–17), among which reaction 12, the synthesis of tryptophan from indole glycerol phosphate, is of physiological importance. Reactions 13 and 14 are regarded as partial reactions of reaction 12 (Table 9). Tryptophan synthase is found widely in various bacteria, yeasts, moulds and plants. The enzyme of $E.\ coli$ is composed of two kinds of proteins, α ($M_r 29000$) and β ($M_r 44200$). Pyridoxal-P is bound to the β-subunit through a Schiff base. Two α-subunits combine with one β_2-dimer to form an $\alpha_2\beta_2$-complex ($M_r 147000$) that catalyses the physiological reaction. Each of the subunits also catalyses its own specific reaction (Table 9). The crystalline $\alpha_2\beta_2$-complex is obtained after a six-fold purification from $E.\ coli$ trp R$^-$ ΔtrpED102/F'ΔtrpED102. About 16% of the intracellular soluble protein of this mutant is the tryptophan synthase complex. Goldberg and Baldwin[37] and Miles $et\ al.$[38] have shown that methanethiol and β-mercaptoethanol serve as S-substituent donors to serine to yield S-methyl-L-cysteine and S-(β-hydroxyethyl)-L-cysteine, respectively, by the $\alpha_2\beta_2$- and β_2-complexes (Table 9, reaction 16).

Esaki $et\ al.$[39] have studied the enzymatic synthesis of various S-substituted-L-cysteines from L-serine and its derivatives (e.g. β-chloro-L-alanine and O-methyl-L-serine) with the $\alpha_2\beta_2$-complex. Thiols such as α-toluenethiol, 1-propanethiol and 1-butanethiol are efficient S-substituent donors. When L-threonine and L-vinylglycine are used as S-substituent acceptors of thiols, the corresponding S-substituted β-methyl-L-cysteines are synthesized[39]. The enzyme also catalyses the β-replacement reactions of L-serine with selenols to produce the corresponding Se-substituted L-selenocysteines[40]. Se-Benzyl-L-selenocysteine and Se-methyl-L-selenocysteine are synthesized from L-serine and α-tolueneselenol and methaneselenol in a similar way with yields of 44 and 16%, respectively,

TABLE 9. Reactions catalysed by tryptophan synthase

No.	Reaction	Catalysed by
12	Indole-3-glycerol phosphate + L-serine → L-tryptophan + D-glyceraldehyde 3-phosphate + H_2O	$\alpha_2\beta_2$
13	Indole-3-glycerol phosphate → indole + D-glyceraldehyde 3-phosphate	$\alpha; \alpha_2\beta_2$
14	Indole + L-serine → L-tryptophan + H_2O	$\beta_2; \alpha_2\beta_2$
15	L-Serine → pyruvate + ammonia	β_2
16	β-Mercaptoethanol + L-serine → S-(β-hydroxyethyl-L-cysteine + H_2O	$\beta_2; \alpha_2\beta_2$
17	β-Mercaptoethanol + L-serine + pyridoxal-P → S-pyruvylmercaptoethanol + pyridoxamine-P + H_2O	β_2

based on L-serine. The relative activity of indole to methanethiol (100) is approximately 150. Those of methaneselenol and α-tolueneselenol are 24 and 30%, respectively. The production of Se-methyl- and Se-benzyl-L-selenocysteines proceeds much more rapidly than tryptophan synthesis, the inherent reaction of the enzyme. L-Serine can be replaced with a variety of β-substituted L-alanines such as β-chloroalanine and O-acetylserine in the reaction system containing these selenols.

According to the general mechanism for the β-replacement reaction catalysed by pyridoxal-P enzymes[34], nucleophilic addition of selenols occurs in an intermediate derived from the substrate. Although selenols are more nucleophilic than thiols, selenols are less reactive substituent donors than thiols in the enzymatic β-replacement reactions catalysed by tryptophan synthase. This is compatible with the reactivities of α-tolueneselenol and α-toluenethiol, although methaneselenol is a slightly more efficient substituent donor than methanethiol. Some physicochemical properties of methaneselenol and methanethiol, such as volatility and solubility, may affect their reactivity in the enzyme reaction.

3. O-Acetylhomoserine sulphydrylase

O-Acetylhomoserine sulphydrylase [O-acetylhomoserine (thiol)-lyase, E.C. 4.2.99.10] is a pyridoxal-P enzyme that catalyses the synthesis of cysteine and homocysteine from H_2S with O-acetyl-L-serine (OAS) and O-acetyl-L-homoserine (OAH), respectively. The enzyme of baker's yeast has been purified and characterized. It is involved in the synthesis in vivo of cysteine.

Chocat et al.[41] have shown that OAH sulphydrylase catalyses the β- and γ-replacement reactions between the O-acetyl groups of OAS and OAH and Na_2Se_2. Serine O-sulphate also serves as a substrate of the β-replacement reaction, although its reactivity is lower than that of OAS (Table 10). The selenium amino acids produced have been isolated and identified as L-selenocystine and L-selenohomocystine, but this does not necessarily mean that the primary enzymatic product is the diselenide. The initial products of the enzyme reaction are probably Se-(selenohydryl) derivatives, i.e. $^-SeSeCH_2CH(NH_2)COOH$ and $^-SeSeCH_2CH_2CH(NH_2)COOH$, which are non-enzymatically oxidized to the corresponding diselenides.

TABLE 10. Kinetic parameters of reactions catalysed by O-acetylhomoserine sulphydrylase

Substituent acceptor	Substituent donor	Relative V_{max}	K_m (mM) substituent	
			Acceptor	Donor
O-Acetylhomoserine	NaHS	100	4.1	0.52
O-Acetylhomoserine	Na_2Se_2	17	5.3	8.9
O-Acetylserine	NaHS	14	2.5	0.70
O-Acetylserine	Na_2Se_2	8.4	5.0	N.d.[a]
Serine O-sulphate	NaHS	5.1	4.0	0.70
Serine O-sulphate	Na_2Se_2	1.4	4.0	10
Serine O-sulphate	NaHSe	1.3	N.d.[a]	1.2

[a]Not determined

4. Comparison between pyridoxal-P enzymes catalysing sulphur and selenium amino acid synthesis

Methionine γ-lyase is useful for the production of various sulphur and selenium amino acids. However, the enzyme catalyses not only replacements but also eliminations; the yield depends mainly on the concentrations of the substrates, thiols or selenols. The amino acids produced may be decomposed by the elimination reactions, which constitutes a weak point of the enzyme from the point of view of amino acid production. Therefore, an excess of thiols or selenols have to be added to prevent the elimination reaction.

Tryptophan synthase surpasses methionine γ-lyase with regard to reaction specificity: it does not catalyse the elimination reaction that leads to a decrease in a yield of sulphur and selenium amino acids. However, tryptophan synthase is inferior to methionine γ-lyase in substrate specificity: it does not catalyse the synthesis of S-substituted homocysteines and Se-substituted selenohomocysteines by the γ-replacement reactions.

O-Acetylhomoserine (thiol)-lyase catalyses both the β- and γ-replacement reactions between O-acetylhomoserine or O-acetylserine and various thiols or selenols, but does not catalyse the elimination reactions. Therefore, the enzyme is also useful for the synthesis of optically active sulphur and selenium amino acids. However, O-acetylhomoserine (thiol)-lyase is poorly produced by yeasts, and shows a high substrate specificity with respect to substituent acceptors. Hence we have to use expensive substrates such as O-acetylhomoserine and O-acetylserine for the desired amino acid syntheses.

II. SELENIUM NUCLEIC ACIDS

A. Introduction

Amino acid transfer ribonucleic acids (tRNAs) undergo a variety of modifications after transcription from deoxyribonucleic acid. More than 50 modified nucleosides including sulphur-containing derivatives of uridine, cytidine and adenosine have been identified in tRNA to date. Recently, it was discovered that certain tRNAs also contain selenium nucleosides as a specific constituent. The selenium is incorporated through a highly specific process. Selenium tRNAs are the second groups of biologically active selenium-containing macromolecules, selenium enzymes described in Section I being the first. The selenium nucleic acids have been studied mainly by Stadtman and coworkers. In the following we describe the occurrence, structure and function of the selenium tRNAs.

B. Natural Occurrence of Selenium-containing tRNA

In 1972, Saelinger et al.[42] reported that growth of Escherichia coli in a medium containing [75Se]selenite results in incorporation of 75Se into tRNA bases. One of the nucleosides isolated by enzymatic digestion of 75Se-labelled tRNAs was identified as 4-selenouridine. The authors assumed that selenium incorporation results from the non-specific substitution through the pathway of sulphur transfer to a uracil residue of E. coli tRNA. However, incorporation of selenium into the tRNA of E. coli B grown in the presence of 0.08 μM selenite was not affected by the addition of 1 mM sulphate[43]. Chen and Stadtman found that in Clostridium sticklandii, selenium is incorporated into tRNAs and also into selenoprotein A, one of the components of glycine reductase, in the presence of a large excess of sulphate[44]. Selenium incorporation was shown to be specific for selenium; no dilution effects of varying ratios of the concentrations of sulphur to that of selenium in the medium were observed. Selenium occurs in at least four different tRNA species. The lability of the incorporated selenium in these species towards CNBr, KBH₄ and iodoacetate and its stability under conditions in which aminoacylated tRNA is de-

esterified indicate that the selenium is located in the polynucleotide portion of the molecules, but not in esterified amino acids. The most prominent seleno-tRNA corresponding to 80% of the total seleno-tRNAs is the major glutamate-accepting species, which contains one selenium atom per tRNA molecule[45]. The seleno-tRNA^{Glu} has been purified in its acylated form by repeated reversed-phase chromatography from an enriched sample prepared with an organomercurial affinity column[46]. A proline isoacceptor[44] and a valine isoacceptor[47] are also seleno-tRNAs.

Synthesis of seleno-tRNA by a highly specific process, which is distinct from the mechanism of sulphur incorporation, was also found in bacteria such as *E. coli*[48] and *Methanococcus vannielii*[49], in cultured mammalian cells[50] and in plants[51]. In *E. coli*, the amount of selenium incorporated is unchanged by 10–20-fold variations in selenium or sulphate concentrations or by the addition of excess of cysteine, sulphide and sulphite. Further *E. coli* mutants that do not synthesize an abundant sulphur-modified base, 4-thiouracil, produce normal levels of selenium-modified tRNAs. Two major *E. coli* tRNA species modified with selenium (over 50% of the total seleno-tRNAs) have been identified as a lysyl-tRNA and a glutamyl-tRNA, but they are minor isoacceptors for lysine and glutamate[48]. In *M. vannielii*, 13–20% of the total tRNA population is modified with selenium[49]. The amount of seleno-tRNA in *M. vannielli*, a strict anaerobe, is higher than those in *C. sticklandii* (5–8%), a less strictly anaerobic bacterium and in *E. coli* (up to 6%), a facultative anaerobe[49]. No seleno-tRNA is detected in *Bacillus subtilis*, a strict aerobe[52]. Hence the biosynthesis of seleno-tRNA may be associated with the concentration of oxygen. The amino acid-accepting activities of *M. vannielii* seleno-tRNA have not been determined exactly, although the possibility of a glutamyl-tRNA is presumed.

The tRNA of mouse leukaemia cells has a low concentration of selenium, and the chemical properties of the seleno-tRNA are different from those of the bacterial species described above[50]. In plants, the occurrence of seleno-tRNA in *Astragalus bisulcatus*, a selenium accumulator plant[43], and wild carrot cells, *Daucus carota* L.[51], has been demonstrated.

C. Structure of Selenium Nucleosides

The most abundant selenium nucleoside found in cells of three bacterial species has been identified as 5-[(methylamino)methyl]-2-selenouridine (mnm^{5}se^{2}U), and was compared with the authentic compound (Fig. 1). The latter was chemically synthesized from selenourea and characterized by its UV and ^{1}H NMR spectral properties[52]. The authentic
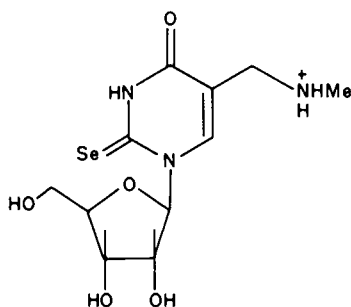
FIGURE 1. Structure of 5-methylamino-methyl-2-selenouridine (mnm^{5}se^{2}U).

and natural compounds show identical UV spectra and chromatographic behaviour, and are decomposed by anaerobic treatment with HCl to the same products[52]. All the ^{75}Se label in the bulk tRNA in *E. coli* and about half of the ^{75}Se found in [^{75}Se]tRNA from *C. sticklandii* and *M. vannielii* are present as mnm^{5}se^{2}U[49,52]. Each of the latter two bacterial species contains an additional uncharacterized 2-selenouridine derivative. 4-Selenouridine, which was initially reported to be a constituent of *E. coli* tRNAs[43,53,54], has not been detected in the tRNA populations of *E. coli*, *C. sticklandii* or *M. vannielii*, which produce about the same amount of 4-thiouridine[52]. 4-Selenouridine may be synthesized only when ratio of the concentration of selenium to that of sulphur in the growth medium is abnormally high.

The structure of the selenonucleoside of the major seleno-tRNA found in cultured mouse leukaemia cells has not been determined. It exhibits strong hydrophobic character, and resembles chromatographically highly modified thioadenosine derivatives such as 2-methyl-N^6-isopentyladenosine, 2-methylthioribosylzeatin and N-[(9-β-D-ribofuranosyl-2-methylthiopurine-6-yl)carbamoyl]threonine[50]. Therefore, selenium analogues of these or related thioadenosines are probably found in mammalian cells.

The mechanism of the incorporation of selenium into tRNA and the biosynthesis of the 5-methylaminomethyl side-chain of mnm^{5}se^{2}U residue on seleno-tRNA^{Glu} described above are unknown. Presumably, the nucleoside of the precursor tRNA is modified post-transcriptionally by enzymes.

D. Biological Function of seleno-tRNA

Modified tRNA bases have been shown to play an important role in codon recognition, and some show a regulatory function. Removal of selenium from seleno-tRNA^{Glu} of *C. sticklandii* by exposure to alkali[45] or by treatment with CNBr[46] results in a loss of glutamate-accepting activity. The glutamate-accepting activity of a partially purified *M. vannielii* tRNA preparation also disappears on release of the selenium[49]. These results suggest that the presence of selenium in tRNA^{Glu} species is essential for aminoacylation by its cognate glutamyl-tRNA synthetase. Similar findings have been reported for the removal of sulphur from *E. coli* sulphur modified tRNA$_2^{Glu}$, which contains 5-methylaminomethyl-2-thiouridine (mnm^{5}s^{2}U) in the first position of the anticodon[55]. Nucleoside sequence analysis of the seleno-tRNA^{Glu} from *C. sticklandii* indicates that the mnm^{5}se^{2}U residue is also located at this site (the 'wobble position')[56]. The sequence containing the anticodon (25 bases long) is homologous with that of *E. coli* sulphur-modified tRNA$_2^{Glu}$ from residues 27 to 50, except that mnm^{5}se^{2}U replaces mnm^{5}s^{2}U in the first position of the anticodon (Fig. 2)[56]. Similar results have been shown for the relationship between seleno-tRNA^{Lys} and non-seleno-tRNA^{Lys}[57].

The codon recognition by seleno-tRNA^{Glu} from *C. sticklandii* was studied with the standard trinucleotide-ribosome assay[46]. The seleno-tRNA^{Glu} recognizes both glutamate codons (GAA and GAG) equally well, and does not interact with the termination codons (UAA and UAG) at a non-physiological high Mg^{2+} concentration (20 mM). However, at a near-physiological Mg^{2+} concentration (10 mM), the GAA codon is only slightly favored over GAG (ca. 15%). In contrast, *E. coli* sulphur-modified tRNA$_2^{Glu}$ shows a four-fold preference for GAA[46]. Several reports have shown that sulphur-modified tRNAs such as tRNA^{Glu} and tRNA^{Lys}, which contain 5-alkyl-2-thiouridine at the wobble position, recognize preferentially codons ending in A (i.e. glutamate GAA and lysine AAA) rather than those ending in G (GAG and AAG)[58]. This codon preference has been explained on the basis of the weaker hydrogen bond between the 2-thio group and G compared with the standard U–A base pair; in U–A pairing, the $C_{(4)}$ oxygen and $N_{(3)}$ nitrogen of U participate, whereas, according to the wobble hypothesis, the $C_{(2)}$ oxygen and $N_{(3)}$ nitrogen of U participate in U–G pairing[58]. This explanation, however, conflicts

FIGURE 2. Comparison of *E. coli* tRNA$_2^{Glu}$ sequence with the sequence of seleno-tRNA^{Glu} from *C. sticklandii*. Total sequence of *E. coli* tRNA$_2^{Glu}$ is shown in a cloverleaf structure. Bold line indicates region of homology between the two bacterial tRNAs. N represents mnm^{5}s^{2}U in *E. coli* tRNA$_2^{Glu}$ and mnm^{5}se^{2}U in *C. sticklandii* seleno-trRNA^{Glu} [56].

with the results of the nearly equal recognition of GAA and GAG by seleno-tRNA^{Glu} described above, because the hydrogen bond involving a seleno group is expected to be even weaker than that with a thio group (i.e. mnm^{5}se^{2}U should show a stronger preference of GAA over GAG). Ching[46] have shown that the mnm^{5}se^{2}U residue is significantly ionized at neutral pH, whereas the sulphur analogue is not ionized under the same conditions[46]. However, it has also been found that the ionization of the mnm^{5}se^{2}U residue is not relevant to the difference in codon preference between the seleno-tRNA^{Glu} and sulphur-containing tRNA^{Glu}[46]. Some other factors such as the interaction of the 5-methylaminomethyl side-chain with the ribosome site and the different atomic radii of selenium and sulphur may cause the difference[46].

[^{3}H]Glutamylseleno-tRNA^{Glu} from *C. sticklandii* is effectively utilized for protein synthesis in a wheat germ extract *in vitro* translation system[46].

III. REFERENCES

1. D. Epp, R. Ladenstein and A. Wendel, *Eur. J. Biochem.*, **133**, 51 (1983).
2. M. Sliwkowski & T. C. Stadtman, *J. Biol. Chem.*, **260**, 3140 (1985).
3. T. C. Stadtman, *Annu. Rev. Biochem.*, **49**, 93 (1980).
4. T. C. Stadtman, *Adv. Enzymol.*, **48**, 1 (1979).

5. A. Shrift, in *Organic Selenium Compounds: Their Chemistry and Biology* (Eds. D. L. Klayman and W. H. H. Gunther), Wiley, New York, 1973 pp. 763–814.
6. O. E. Olson, E. J. Novacek, E. I. Whitehead and I. S. Palmer, *Phytochemistry*, **9**, 1181 (1970).
7. S. H. Mudd and G. L. Cantoni, *Nature (London)*, **180**, 1052 (1957).
8. R. C. Greene, *Biochemistry*, **8**, 2255 (1969).
9. E. H. Coch and R. C. Greene, *Biochim. Biophys. Acta*, **230**, 223 (1971).
10. N. Esaki, T. Nakamura, H. Tanaka, T. Suzuki, Y. Morino and K. Soda, *Biochemistry*, **20**, 4492 (1981).
11. D. Cavallini, B. Mondovi, C. DeMarco and S. Sciscia-Santoro, *Arch. Biochem. Biophys.*, **96**, 456 (1962).
12. A. E. Braunstein, E. V. Goryachenkova, E. A. Tolosa, 1. H. Willhardt and L. L. Yefremova, *Biochim. Biophys. Acta*, **242**, 247 (1971).
13. N. Esaki, T. Nakamura, H. Tanaka and K. Soda, *J. Biol. Chem.*, **257**, 4386 (1982).
14. P. Chocat, N. Esaki, T. Nakamura, H. Tanaka and K. Soda, *J. Bacteriol.*, **156**, 455 (1983).
15. P. Chocat, N. Esaki, K. Tanizawa, K. Nakamura, H. Tanaka and K. Soda, *J. Bacteriol.*, **163**, 669 (1985).
16. J. L. Martin, in *Organic Selenium Compounds: Their Chemistry and Biology* (Eds. D. L. Klayman and W. H. H. Gunther), Wiley, New York, 1973, p. 663.
17. R. A. Sunde and W. G. Hoekstra, *Biochem. Biophys. Res. Commun.*, **93**, 1181 (1980).
18. W. C. Hawkes, D. E. Lyons and A. L. Tappel, *Biochim. Biophys. Acta*, **699**, 183 (1982).
19. S. S. Tate and A. Meister, *Biochemistry*, **8**, 1660 (1969).
20. K. Tanizawa and K. Soda, *J. Biochem.*, **86**, 1199 (1979).
21. N. Esaki, T. Nakamura, H. Tanaka and K. Soda, *J. Biol. Chem.*, **257**, 4386 (1982).
22. R. E. Huber and R. S. Criddle, *Arch. Biochem. Biophys.*, **122**, 164 (1967).
23. F. A. Cotton and G. Wilkinson, *Basic Inorganic Chemistry*, Wiley, New York, 1976, p. 10.
24. D. L. J. Clive, *Tetrahedron*, **34**, 1049 (1978).
25. C. C. Chang, A. Laghai, M. H. O'Leary and H. G. Floss, *J. Biol. Chem.*, **257**, 3564 (1982).
26. J. G. Voet, D. M. Hindenlag, T. J. J. Blanck, R. J. Ulevitch and R. G. Kallen, *J. Biol. Chem.*, **248**, 841 (1973).
27. T. Yorifuji and K. Soda, *J. Biol. Chem.*, **246**, 5093 (1971).
28. H. C. Dunathan and J. G. Voet, *Proc. Natl. Acad. Sci. USA*, **71**, 3888 (1974).
29. B. Badet, D. Roise and C. T. Walsh, *Biochemistry*, **23**, 5188 (1984).
30. D. Roise, K. Soda, T. Yagi and C. T. Walsh, *Biochemistry*, **23**, 5195 (1984).
31. T. Nakayama, N. Esaki, K. Sugie, T. T. Berezov, H. Tanaka and K. Soda, *Anal. Biochem.*, **138**, 421 (1984).
32. T. Nakayama, N. Esaki, W.-J. Lee, I. Tanaka, H. Tanaka and K. Soda, *Agric. Biol. Chem.*, **48**, 1991 (1984).
33. N. Esaki, H. Tanaka, S. Uemura, T. Suzuki and K. Soda, *Biochemistry*, **18**, 407 (1979).
34. L. Davis and D. E. Metzler, *Enzymes*, 3rd ed., Vol. 7, Academic Press, New York, 1972, p. 33.
35. C. Walsh, *Tetrahedron*, **38**, 871 (1982).
36. N. Esaki, T. Suzuki, H. Tanaka, K. Soda and R. R. Rando, *FEBS Lett.*, **84**, 309 (1977).
37. M. E. Goldberg and R. L. Baldwin, *Biochemistry*, **6**, 2113 (1967).
38. E. W. Miles, M. Hatanaka and I. P. Crawford, *Biochemistry*, **7**, 2742 (1968).
39. N. Esaki, H. Tanaka, E. W. Miles and K. Soda, *Agric. Biol. Chem.*, **47**, 2861 (1983).
40. N. Esaki, H. Tanaka, E. W. Miles and K. Soda, *FEBS Lett.*, **161**, 207 (1983).
41. P. Chocat, N. Esaki, H. Tanaka and K. Soda, *Agric. Biol. Chem.*, **49**, 1143 (1985).
42. D. A. Saelinger, J. L. Hoffman and K. P. McConnell, *J. Mol. Biol.*, **69**, 9 (1972).
43. P. A. Young and I. I. Kaiser, *Plant Physiol.*, **63**, 511 (1979).
44. C.-S. Chen and T. C. Stadtman, *Proc. Natl. Acad. Sci. USA*, **77**, 1403 (1980).
45. W.-M. Ching and T. C. Stadtman, *Proc. Natl. Acad. Sci. USA*, **79**, 347 (1982).
46. W.-M. Ching, *Arch. Biochem. Biophys.*, **244**, 137 (1986).
47. C.-S. Chen, T. N. Wen and H. M. Tuan, *Biochim. Biophys. Acta*, **699**, 92 (1982).
48. A. J. Wittwer, *J. Biol. Chem.*, **258**, 8637 (1983).
49. W.-M. Ching, A. J. Wittwer, L. Tsai and T. C. Stadtman, *Proc. Natl. Acad. Sci. USA*, **81**, 57 (1984).
50. W.-M. Ching, *Proc. Natl. Acad. Sci. USA*, **81**, 3010 (1984).
51. C.-S. Chen, N. W. Tuan and J.-H. Chang, *Curr. Top. Cell. Regul.*, **27**, 509 (1985).
52. A. J. Wittwer, L. Tsai, W.-M. Ching and T. C. Stadtman, *Biochemistry*, **23**, 4650 (1984).

53. J. L. Hoffman and K. P. McConnell, *Biochim. Biophys. Acta*, **366**, 109 (1974).
54. Y. S. Prasada Rao and J. D. Cherayil, *Life Sci.*, **14**, 2051 (1974).
55. P. F. Agris, D. Soll and T. Sens, *Biochemistry*, **12**, 4331 (1973).
56. W.-M. Ching, B. Alzner-DeWeerd and T. C. Stadtman, *Proc. Natl. Acad. Sci. USA*, **82**, 347 (1985).
57. W.-M. Ching, L. Tsai and A. J. Wittwer, *Curr. Top. Cell. Regul.*, **27**, 497 (1985).
58. S. Nishimura, in *Transfer-RNA: Structure, Properties and Recognition* (eds. P. R. Schimmel, I. Soll and J. N. A. Belson), Cold Spring Harbor Laboratory, Cold Spring Harbor, NY 1979, p. 59.

CHAPTER **8**

Biological and biochemical aspects of tellurium derivatives

TSVI SADEH*

Institute of Chemical Research, University of Kyoto, Uji, Kyoto-Fu 611, Japan

I. INTRODUCTION

Within the context of biologically oriented research on Group VI elements, tellurium can be regarded as the biological Cinderella of the group. The position of oxygen and sulphur is, of course, incontestable with respect to their biological importance, and the last few years have seen the emergence of selenium as a major factor in biochemistry, playing a

*On Sabbatical leave from the Soreq Nuclear Research Center, 70600 Yavneh, Israel.

specific role as a key component in certain vitally important enzymes and being regarded, therefore, as an essential trace element. In comparison, no similar functions have yet been discovered in the case of tellurium. However, the available facts point to a so far unexplored territory in tellurium research, involving its biological interactions with livings systems, which may require a different approach to its problems compared with sulphur and selenium. The underlying reasons can be sought in the specificity of its chemical interactions, which differ in many ways from those of sulphur and selenium. The causes can be found in the more metallic properties of the tellurium, which are expressed by a distinct weakening of its covalent bonds with hydrogen and carbon in comparison with sulphur and selenium. Also, the larger covalent, electrovalent and coordination sphere radii of tellurium must be considered in its chemical interactions, and will inevitably influence its biochemical behaviour.

Tellurium has an extensive organic chemistry with distinctive reaction patterns[1], but its biochemistry lags behind that of selenium and can be regarded as having reached a state of development comparable to that of selenium 30 years ago. However, the toxicology of tellurium has been the subject of investigations which might lend themselves as a suitable starting point for more fundamental biochemical research. The very fact that tellurium compounds are toxic points to their biological interactions with metabolic processes of major importance to cell life and indicates the involvement of tellurium-containing molecular species with vital cell components, possibly enzymes, in a so far unknown manner. Whereas selenium can be found incorporated into numerous kinds of biomolecules, the list of such tellurium compounds is very short. This does not necessarily prove that none are formed in living systems; very possibly the methods applied for their isolation were not adequate and did not take sufficient account of their great sensitivity to air and light.

II. TE COMPOUNDS IN BIOLOGY AND BIOCHEMISTRY

We shall divide the discussion of tellurium in biological and biochemical research into three sections: (a) toxicity of tellurium; (b) biological interactions of tellurium, including those with other elements encountered in the environment; and (c) the occurrence of tellurium and its compounds in nature and tellurium-containing analogues of naturally occurring compounds.

A. Toxicology

The toxicology of tellurium has received less attention than that of selenium, partly because contact between tellurium compounds and humans or animals in industry or agriculture is less frequent, leading to fewer accidental poisonings. Possibly the toxicity of tellurium in general may be lower than that of selenium. One of the reasons for the smaller potential hazards from tellurium compounds may be their lower solubility at physiological pH. For instance, elemental tellurium is less oxidizable than elemental selenium, and the tellurium dioxide formed is almost insoluble in water at physiological pH. Also, hydrogen telluride, a potential industrial pollutant, is even more easily decomposed than hydrogen selenide by light and oxygen, yielding relatively harmless elemental tellurium, before the H_2Te can do any damage. The toxicology of tellurium has been reviewed[2], experimental toxicity studies have been conducted[2-6] and accidental tellurium poisoning has been described[7,8], but it may safely be stated that the danger from occupational or environmental tellurium poisoning does not constitute one of the major hazards of human existence[9].

B. Biological Interactions

Clearly, tellurium and its compounds are not biologically inert; they interact with living systems in specific ways. Toxicity is caused only if the detoxification mechanism available to living organisms is overwhelmed by excessive amounts of tellurium compounds. Living organisms have various methods of ridding themselves of unrequired tellurium compounds. Bacteria, for instance, deal with them by a reductive pathway leading to elemental black tellurium, which is biologically inert[10], and which forms a black precipitate within the bacterial cell. The capability for tellurite reduction varies with different kinds of microorganisms and can be employed for their identification[11], such as for *Vibrio* species[12]. Fungi and animals can carry the reduction of tellurites and tellurates further. The tellurium is reduced to the telluride stage, Te^{2-}, and subsequently methylated[19,13-15]. The dimethyl telluride produced is volatile and is thus removed from the organisms. The production of methylated compounds from Group V and V_I elements and also from certain metals in other groups has been well documented[14,15]. Not only fungi, but also mammals, including humans, are able to methylate tellurium compounds and to produce dimethyl telluride[16], which imparts a characteristic smell to persons who come into contact with inorganic tellurium compounds[9]. The biological interaction of microorganisms with tellurium is not confined to biological methylation.

Certain microorganisms are able to decompose metallic ores oxidatively and liberate anionic Group VI elements, including tellurium, as water-soluble salts[17-19]. It seems that sulphur bacteria are implicated in these oxidative reactions, leading to mineral breakdown and solubilization. However, it was found that the sulphur bacterium *Thiobacillus thiooxidans* is sensitive to relatively moderate tellurium concentrations[20]. In its interactions with higher animals, it was found that tellurium acts as an antagonist to selenium, and is able to cause the symptoms of selenium deficiency[21]. The animals undergoing these tests were fed tellurium compounds and subsequently showed the characteristic lesions of the internal organs associated with selenium deficiency. In the case of pigs fed tellurium, a marked decrease in glutathione peroxidase activity of the blood was noted[22]. This can be taken as an indication that tellurium interferes in an unknown manner with the selenium-incorporating mechanism of mammalian protein synthesis.

In living systems, tellurium tends to become attached to proteins in a manner yet to be established[23], and has a special affinity for nervous tissue. Prolonged treatment with tellurium will cause degeneration of the nervous system and demyelinization of nerve strands[24].

An effect typical of tellurium was found in rats. In animals fed tellurium for prolonged periods, lipofuscin pigment developed in their brains in the form of granules, interspersed with elemental tellurium particles[25]. Tellurium has been found to affect adversely the learning ability of rats[26]. If administered to pregnant animals, it acts as a teratogen[27] and in particular may cause hydrocephalus of foetuses. It acts in the same manner towards embryos in birds' eggs[28].

Additional biological effects of tellurium have been noted. Tellurium salts administered to rats influence the development of experimental caries, which in turn can be manipulated by administration of additional chemicals, such as glutathione[29], cysteine, ascorbic acid, thioctic acid[30] and dimercaptosuccinic acid[31]. Also, a change in the oral streptococcal flora was observed on administration of tellurite[32].

Continuing with the evaluation of the interaction of tellurium salts with rat tissues, or rat tissue components, the influence of tellurite and related chemicals on the respiration and oxidative phosphorylation of rat liver mitochondria was investigated[33]. At relatively high concentrations, tellurite was found to be an inhibitor of substrate oxidation, whereas at lower concentrations it proved to be an uncoupler for oxidative phosphorylation. Rats exposed to drinking water contaminated with tellurium tetrachloride showed that

tellurium is a cumulative contaminant, but that typical tellurium neurochemical effect was revealed only after a threshold concentration in the brain was exceeded[34]. By employing radioactive [127m]Te, Duckett[35] was able to demonstrate a physiological difference in the penetration rate of blood vessels by tellurium in rats which had been exposed previously to tellurium, in comparison with rats not previously exposed to tellurium[35]. Blood vessels of rats to whom tellurium had been administered previously permitted a more rapid penetration of radiotellurium into the sciatic nerve than in rats without prior exposure.

The specific damage to the nervous tissue of rats fed tellurium was also demonstrated[36]. Tellurium tetrachloride fed to ducklings caused the symptoms of selenium–vitamin E deficiency, which became evident as myocardial ultrastructural alterations. However, some kind of repair mechanism for the damaged heart muscle seems to come into play also[37]. Bacteria have also been the subject of studies concerning tellurium. Resistance to tellurium poisoning in *Salmonella*[38] and certain strains of *Escherichia coli*[39] is carried by IncH plasmids, which also confer resistance to other toxic agents. In other bacterial strains, resistance to tellurite is carried in IncP plasmids[40]. Reistance to heavy metals and drugs, colicin production and the biochemical characteristics of selected bovine and porcine strains of *E. coli* all seem to depend on belonging to certain O serogroups, with corresponding resistance to tellurium toxicity[41]. Autotrophic, photosynthetic cyanobacteria species also show patterns of resistance to groups of toxic substances, including tellurium[42]. This also seems to indicate genetic control of these properties.

Aspects of environmental pollution seemed to be the reason for investigating the binding of tellurium and heavy metals by the proteins contained in isolated gill preparations of certain mussels[43]. Likewise, the determination of tellurium in cereal crops[44] could conceivably have a bearing on the problem of Keshan desease[45], since tellurium is known to act as an antagonist to selenium, and can cause the symptoms of selenium deficiency[22].

Tellurium can show certain heavy metal binding properties resembling those of selenium if administered to various animal species. For instance, tellurium administered to mice will cause enhanced accumulation of inhaled mercury, particularly in living tissue[46].

Some physiological effects of tellurium have been discovered that point to potentially significant functions in relation to the chemistry of cell membranes. Tellurite and also selenite caused the haemolysis of sheep erythrocytes[47]. This haemolysis seems to depend on an interaction with reduced glutathione, since sheep erythrocytes depleted of reduced glutathione showed increased resistance to haemolysis. This effect was independent of biochemical lesions responsible for reduced glutathione deficiency. Another approach to the problem of the causes of the interaction of tellurium compounds with erythrocyte cell membranes was made by De Meio and Doughty[48], who also found a dependence of erythrocyte haemolysis on reduced glutathione concentration. This reduced glutathione-induced haemolysis was inhibited by disodium 4-acetamido-4″-isothiocyanatostilbene 2,2′-disulphonate. The inhibition could be abolished by excess of reduced glutathione. Anaerobic incubation of tellurite with reduced glutathione produced a haemolytic agent, but air prevented its formation. Mercury-containing haemolytic agents, such as *p*-hydroxymercuribenzoate or *p*-hydroxymercuriphenyl sulphonate, caused haemolysis which did not involve reduced glutathione.

An effect of considerable significance involving tellurite was discovered recently. Tellurite prevents sickling of erythrocytes, and it was found to be a potent membrane-acting agent *in vitro*[49]. Tellurite is effective in low doses, and the anti-sickling effect depends on the incubation time. Tellurite causes swelling of erythrocytes and the anti-sickling effect can be attributed to a decreased mean cell haemoglobin concentration[49]. The problem which remains to be solved is the mechanism of this interesting effect, and to establish what can be learned from it in relation to blood diseases such as sickle-cell anaemia.

An *in vitro* effect of tellurite which closely resembles that of selenite is represented by its catalytic action on the reduction of methaemoglobin by glutathione (GSH). The catalytic action is explained by the possible formation of selenol groups attached to sulphur if excess of GSH acts on selenite. It must therefore be postulated, if indeed the explanation is correct, that excess of GSH would form tellurol groups attached to sulphur if acting on tellurite[50,51]. Support for this suggestion can be inferred from the fact that heavy metals and other sulphydryl inhibitors are able to block this catalytic reaction by both selenite and tellurite.

C. Organotellurium Compounds in Nature and Their Synthetic Analogues

Unlike organosulphur and organoselenium compounds, no organotellurium derivatives more complicated than dimethyl telluride seem to have been isolated so far from natural sources. This does not necessarily indicate that they are not produced by various organisms that have to deal with tellurium absorbed from the environment, but rather that suitable isolation methods have not been employed so far. Every chemist who has worked with organotellurium compounds, particularly of the aliphatic kind, has experienced their sensitivity towards light and air. Isolation procedures for organotellurium species in materials derived from living matter must take account of these factors and be adapted accordingly. Analogously, it took many years for techniques to be developed sufficiently to enable organoselenium compounds to be isolated from natural sources. However, synthetic tellurium analogues of naturally occurring compounds have been prepared, and are described below.

1. Carbohydrate derivatives

Sugar complexes with hexavalent telluric acid have been described[52]. It could well be that the primary reaction of hexavalent tellurium freshly absorbed by plants, microorganisms or animals could be with carbohydrate derivatives, such as glucose. These complexes might well be an intermediate stage of tellurium metabolism, before the element undergoes further biochemical reactions and incorporation into compounds with carbon—tellurium bonds. True telluro-carbohydrates have also been synthesized recently[53]. The compounds concerned are essentially 1-β-D-telluroglucosides made from acetobromoglucose.

The synthesis of the telluroglucoside described involves a novel method of introducing the tellurium atom by means of 2-tellurido-2-oxo-1, 3, 2-dioxaphosphorinane. This method might be applied with advantage also to other syntheses with tellurium not involving carbohydrate chemistry. The sensitivity of the telluroglucosides described towards oxygen and moisture, and presumably towards light, show again the necessity to take this into account when attempting to isolate tellurium-containing natural products from living systems fed tellurium salts. It should be noted in passing that naturally occurring carbohydrates containing selenium have been found and identified[54].

2. Fatty acid analogues

A group of organotellurium compounds which have found use in biomedical research are tellura-fatty acids. These are long-chain fatty acid analogues in which a methylene group has been replaced with a bivalent tellurium atom, which thus forms a telluro-ether linkage between two carbon chains constituting the molecule[55].

Tellura-fatty acids have been synthesized with γ-ray-emitting tellurium isotopes for organ-imaging purposes in nuclear medicine, and have been designed specifically for the investigation of cardiac disorders[55-69].

It was also found that a tellurium atom enhances retention of the fatty acid analogue in

heart muscle tissue. The reason for this is assumed to be connected with oxidation of the tellurium atom *in vivo* to a hydrated telluroxide moiety, which interacts with the carboxy group of the fatty acid molecule to form a cyclic hemiketal ester-like entity, which probably prevents β-oxidative breakdown of the fatty acid analogue molecule. It could be demonstrated that the analogous selena-fatty acid analogues do not form a similarly hydrated selenoxide moiety, and evidently a cyclic hemiketal ester structure cannot be expected to be formed[62]. It seems, therefore, that tellurium as a labelling atom has potential advantages, because of its specific chemical reactivity, over selenium, and future work along these lines might well reveal additional features of interest to biomedicine.

The utility of double labelling has been demonstrated[58], the tellurium atom employed being non-radioactive natural tellurium, with the radioactivity being carried by one of the γ-ray-emitting radioisotopes of bromine[67] or iodine[61]. The radiohalogens are attached preferentially to an aromatic[60] or vinylic[64] moiety forming the end of the carbon chain of the fatty acid analogue. The reason for this is the superior stability of a halogen atom bound to an aromatic or vinylic structure to loss by hydrolysis or exchange compared with a halogen bound to an aliphatic moiety.

3. Tellura-steroids

In addition to fatty acid analogues containing tellurium, other lipids have also been synthesized with an included tellurium atom[55,70-74]. Whereas Wolff and Zanati[70] prepared a telluro-steroid derivative as a potential androgen analogue, Knapp and coworkers[55,71-75] synthesized their compounds for intended use as adrenal imaging agents by employing the γ-ray-emitting radioisotope ^{123m}Te.

4. Telluro-amino acids

Telluro-α-amino acids including telluro-methionine have been described[75]. In the case of telluro-methionine, the difficulty of working with functionalized aliphatic tellurium derivatives was again demonstrated. Although the method used to synthesize telluro-methionine was essentially identical with one of the established methods for preparing ordinary 'sulphur' methionine, the compound failed to crystallize during the final isolation step, despite various approaches. No such difficulties were encountered during the crystallization of the analogous selenomethionine[76] from its mother liquor. However, various analytical methods (e.g. NMR, TLC and mass spectometry) confirmed the presence of telluromethionine. Telluro-α-amino acids with a telluro-ether link between the aliphatic moiety of the functional part of the amino acid and an aromatic ring were found to be more stable and could be isolated[77]. For some of them, anticarcinogenic and antileukaemic properties have been claimed[78]. Heterocyclic ring-derived α-amino acids have also been prepared. Thus a benzo[b]tellurophene derivative of glycine, with the α-carbon of the amino acid linked to one of the carbon atoms of the heterocyclic part of the benzo[b]tellurophene moiety, has recently been prepared[79].

5. Porphyrin analogues

Macro-ring nitrogen-, sulphur- and tellurium-containing heterocycles as analogues of porphyrins have also been prepared. These compounds show strong interactions between the internal heteroatoms, in particular between the heterocyclic tellurium and sulphur atoms situated opposite each other at the apexes of the five-membered rings which form part of the porphyrin system[80].

6. Analogues of drugs and antibiotics

Tellurium-containing analogues of drugs and antibiotics have also been prepared. Examples are tellurium-substituted barbiturates[81] and a tellurium-containing analogue of the antibiotic chloromycetin[82].

Various organotellurium compounds synthesized in the past have been tested for antimicrobial activity and have been listed by Irgolic[83]. More recent work seems to indicate a renewal of interest in the antibacterial properties of tellurium compounds[84,85].

Tellurium-containing chelates of organic metal complexes have also been investigated as potential antimicrobial derivatives. They include tellurium sulphonamide Schiff base complexes[86], aromatic imine complexes of selenium and tellurium[87], tellurium complexes with substituted chalcones[88] and bimetallic complexes of 2,4-diketonates[89], in addition to selenium and tellurium complexes with 2-substituted benzimidazoles[90] and thiopicolinamide complexes of selenium and tellurium[91].

III. A LOOK AT THE FUTURE

In the field of bioscience-oriented tellurium work, the following research topics might well be rewarding.

A. Teratogenicity

Nothing is really known about the mechanism by which simple inorganic tellurium compounds cause teratogenicity. The reason is the absence of knowledge concerning the molecular basis of the interaction of tellurium compounds with biological systems. For instance, the fate of simple inorganic tellurium compounds inside various organisms has not been adequately investigated. It is not known whether organisms are able to synthesize organotellurium compounds more complicated than dimethyl telluride, nor has the exact manner in which tellurium binds to biopolymers such as proteins, nucleic acids and polysaccharides been determined.

B. Tellurium and the Nervous System

Tellurium is known to have an affinity for the nervous system and cerebral tissue and has been found to cause hydrocephalus in foetuses. Here, too, no research in depth has been carried out to determine the underlying metabolic interactions which might throw light on the biochemical processes responsible for the influence of tellurium on the nervous system.

C. Tellurium Bio-organic Chemistry

Whereas with selenium an area of life science-oriented bio-organic chemistry has evolved, selenium-specific and independent of that of sulphur, little has been achieved yet in the parallel field of organotellurium chemistry. Much needs to be done in the identification and synthesis of tellurium containing amino acids, peptides and carbohydrates. Whereas selenium compounds in these categories have been found in nature and have also been synthesized, no such organotellurium analogues have been mentioned in the literature, with the exception of the few tellura-fatty acids, tellura-steroids, telluro-amino acids and a lone telluro-carbohydrate, covered in this review. Whereas with organoselenium compounds numerous selenoanalogues of sulphur derivatives have been prepared and tested for biological activity, no such efforts seem to have been made to prepare the corresponding tellurium analogues.

D. Application of Organotellurium Compounds in Biology and Medicine

Certain specific properties of the tellurium atom of potential usefulness to biomedicine have already been discovered[62]. Further efforts in this direction may lead to new developments which may lend themselves to possible applications to pharmacology. As examples, recent developments in selenium pharmacology may be cited, such as that of ebselen[92-95] and the anti-viral drug selenazofurin[96-99].

E. Tellurium as an Essential Trace Element

Selenium has been proved to be an essential trace element, but the possible role played by tellurium in biological systems has not been evaluated sufficiently. One possible reason for this might be the difficulty of removing completely the tellurium content from the nutrients supplied to the living organisms to be tested, because only if nutrients free from traces of tellurium are available will it be possible to assess its potential role as an essential trace element.

IV. ACKNOWLEDGEMENT

V. REFERENCES

1. K. J. Irgolic, *The Organic Chemistry of Tellurium*, Gordon and Breach, New York, 1974.
2. L. Fishbein in *Advances in Modern Toxicology, Vol. 2, Toxicology of Trace Elements, Selenium and Tellurium* (Eds. R. A. Goyer and M. A. Mehlman), Wiley, New York, 1977, pp. 191–240.
3. R. H. De Meio, *J. Ind. Hyg. Toxicol.*, **29**, 393 (1946).
4. R. H. De Meio and F. C. Henriques, Jr., *J. Biol. Chem.*, **169**, 609 (1947).
5. R. H. De Meio and W. W. Jetter, *J. Ind. Hyg. Toxicol.*, **30**, 53 (1948).
6. M. L. Amdur, *Arch. Ind. Health*, 17, 665 (1958).
7. J. H. H. Keall, N. H. Martin and R. E. Tunbridge, *Br. J. Ind. Med.*, 3, 175 (1946).
8. E. S. Blackadder and W. G. Manderson, *Br. J. Ind. Med.*, **32**, 5961 (1975).
9. H. J. Einbrodt and S. Michels, in *Metalle in der Umwelt* (Ed. E. Merian), Verlag Chemie. Weinheim, 1984, Chapt. II.21, pp. 561, 564, 566, 567.
10. W. A. Konetzka, in *Microbiol. Series, 1977, 3, Review: Microbiology of Metal Transformations, Selenium and Tellurium*, Chapt. 8, pp. 323, 338, 339.
11. F. J. Baker, in *Handbook of Bacteriological Techniques*, Butterworth, London, 1967, p. 98.
12. M. O'Brien and R. Colwell, *J. Clin. Microbiol.*, **22**, 1011 (1985).
13. F. Challenger, in *Organometals and Organometalloids* (Eds. F. E. Brinckman and J. M. Bellama), ACS Symp. Ser. No. 82, American Chemical Society, Washington, DC, 1978, p. 1.
14. Y. K. Chau, and P. T. S. Wong, 1978, in *Organometals and Organometalloids* (Eds. F. E. Brinckman and J. M. Bellama), ACS Symp. Ser. No. 82, American Chemical Society, Washington, DC, 1978, p. 39.
15. N. R. Bottino, E. R. Cox, K. J. Irgolic, S. Maeda, W. J. McShane, R. A. Stockton and R. A. Zingaro, in *Organometals and Organometalloids* (Eds. F. E. Brinckman and J. M. Bellama), ACS Symp. Ser. No. 82, American Chemical Society, Washington, DC 1978, p. 116.
16. R. W. Fleming and M. Alexander *Appl. Microbiol.*, 24, 424 (1972).
17. N. N. Lyalikova, M. F. Kulikova and N. Z. Kurbanova, *Geokhim. Deyat. Mikroorg. Vodooemakh. Mestorozhz. Polezn. Inskop.*, 293 (1973).
18. M. Miskey and T. Lakatos, *Banyasz. Kohasz. Lapok Kohasz.*, **108**, 35 (1975); *Chem. Abstr.*, **83**, 118974n (1975).

19. J. F. Spisak, in *Biotechnology and Minerals: Legitimate Challenge or Myth?* (Eds. J. F. Spisak and G. Jergensen, II), AIME, New York, 1985, pp. 3–12.
20. O. H. Tuovinen, S. I. Niemala and H. G. Gyllenberg, *Antonie van Leeuwenhoek J. Microbiol Serol.*, **37**, 489 (1971).
21. R. J. Shamberger, in *Biochemistry of Selenium, Biochemistry of the Elements Series* (Ed. E. Frieden) Vol. 2, Plenum, New York, 1983, Chapt. 5, pp. 154–155.
22. J. F. Van Vleet, G. D. Boon and V. J. Ferrans, *Am. J. Vet. Res.*, **42**, 789 (1981).
23. W. F. Agnew and J. T. Cheng, *Toxicol. Appl. Pharmacol.*, **20**, 346 (1971).
24. G. Said and S. Duckett, *Muscle Nerve*, **4**, 319 (1981).
25. S. Duckett and R. White, *Brain Res.*, **73**, 205 (1974).
26. D. Dru, W. F. Agnew and E. Greene, *Psychopharmacologia*, **24**, 508 (1972).
27. S. Duckett, *Ann. N. Y. Acad. Sci.*, **192**, 220 (1972).
28. W. W. Carlton and W. A. Kelly *Toxicol. Appl. Pharmacol.*, **2**, 203 (1967).
29. Y. Matsumoto, T. Saruta, T. Higa, N. Fujimoto and S. Tamura, *Shika Gakuho*, **81**, 797 (1981).
30. T. Saruta, T. Higa, N. Fujimoto and Y. Matsumoto, *Shika Gakuho*, **82**, 447 (1982).
31. S. Tamura, Y. Matsumoto, T. Saruta, E. Nakayasu, T. Kano and N. Haseda, *Bull. Tokyo Dent. Coll.*, **26**, 95 (1985).
32. H. Baba and Y. Matsumoto, *Bull. Tokyo Dent. Coll.*, **26**, 103 (1985).
33. T. Watanabe, Y. Osawa and S. Horie, *Kitasato Igaku*, **15**, 35 (1985).
34. S. Valkonen and H. Savolainen, *Bull. Environ. Contam. Toxicol.*, **34**, 170 (1985).
35. S. Duckett, *Neurotoxicology*, **3**, 63 (1982).
36. G. Said and S. Duckett, *Muscle Nerve*, **4**, 319 (1981).
37. J. F. Van Vleet and V. J. Ferrans, *Am. J. Vet. Res.*, **43**, 2000 (1983).
38. P. Pohl, P. Lintermans, B. Corbio, J. Gledel, L. Le Minor, M.-L. Chasseur and G. Ghysels *Ann. Microbiol. (Paris)*, **132B**, 399 (1981).
39. E. Chaslus-Dancla and J.-P. Lafont *Appl. Environ. Microbiol.*, **49**, 1016 (1985).
40. D. E. Bradley, *J. Gen. Microbiol.*, **131**, 3135 (1985).
41. N. M. Harnett and G. L. Gyles, *Appl. Environ. Microbiol.*, **48**, 930 (1984).
42. M. G. Lorenz and W. E. Krumbein, *Appl. Microbiol. Biotechnol.*, **20**, 422 (1984).
43. C. Nolan, E. Duke, G. Lorenzon, E. Sabbioni and E. Marafante, *Sci. Total. Environ.*, **40**, 83 (1984).
44. S. Tang, X. Chen and J. Li, *Huanjing Huaxne*, **2**, 35 (1983).
45. X. Chen, G. Yang, J. Chen, X. Chen, Z. Wen and K. Ge, *Biol. Trace Elem. Res.*, **2**, 91 (1980); *Chem. Abstr.*, **93**, 237390k (1980).
46. A. I. Y. Khayat, *Acta Pharm. Suec.*, **22**, 301 (1985).
47. J. D. Young, C. Crowley and E. M. Tucker, *Biochem. Pharamacol.*, **30** 2527 (1981).
48. R. H. De Meio and P. F. Doughty, *Biol. Trace Elem. Res.*, **1**, 131 (1979).
49. T. Asakura, Y. Shibutani, M. P. Reilly and R. H. De Meio, *Blood*, **64**, 305 (1984).
50. T. Masukawa and H. Iwata, *Life Sci.*, **21**, 695 (1977).
51. H. Iwata, T. Masukawa. S. Kasamatsu, K. Inoue and H. Okamoto, *Experientia*, **33**, 678 (1977).
52. M. Jolocam, *Carbohydr. Res.*, **140**, 151 (1985).
53. J. Czyzewska-Chlebny and M. Michalska, *J. Chem. Soc., Chem. Commun.*, 693 (1985).
54. R. A. Zingaro, J. Ekelund-Price and C. R. Benedict, *J. Carbohydr. Nucleos. Nucleot.*, **4**, 271 (1977).
55. F. F. Knapp, Jr., in *Radiopharmaceuticals, Structure–Activity Relationships* (Ed. R. P. Spencer), Grune and Stratton, New York, 1981, Chapt. 16, pp. 345–391.
56. J. A. Bianco, L. A. Pape, J. S. Alpert, M. Zheng, D. Hnatowich, M. M. Goodman and F. F. Knapp, Jr., *J. Am. Coll. Cardiol.*, **4**, 80 (1984).
57. D. R. Elmaleh, F. F. Knapp, Jr., T. Yasuda, S. Kopiwoda, K. A. McKusick and H. W. Strauss, *J. Nucl. Med., Proc. 27th Annu. Meet.*, **21**, 58 (1980).
58. M. M. Goodman, F. F. Knapp, Jr., A. P. Callahan and L. A. Ferren, *J. Med. Chem.*, **25**, 613 (1982).
59. M. M. Goodman F. F. Knapp, Jr., A. P. Callaher and L. A. Ferren, *J. Nucl. Med.*, **23**, 904 (1982).
60. M. M. Goodman and F. F. Knapp, Jr., *J. Org. Chem.*, **47**, 3004 (1982).
61. M. M. Goodman, A. P. Callahan, F. F. Knapp, Jr., M. D. Strauss, D. Elmaleh, P. Richards and L. F. Mausner, in *Proceedings of Symposium on Single-Photon, Ultra-Short-Lived Radionuclides*, DOE Symp. Ser., 1985, 56; *Nucl. Med. Pract.*, 488; *Chem. Abstr.*, **103**, 156525f (1985).
62. G. Kirsch, M. M. Goodman and F. F. Knapp, Jr., *Organometallics*, **2**, 357 (1983).
63. F. F. Knapp, Jr., K. R. Ambrose, A. P. Callahan, L. A. Ferren R. A. Grigsby and K. J. Irgolic, *J. Nucl. Med.*, **22**, 988 (1981).

64. F. F. Knapp, Jr., M. M. Goodman, A. P. Callahan, L. A. Ferren, G. W. Kabalka and K. A. R. Sastry, *J. Med. Chem.*, **26**, 1293 (1983).
65. F. F. Knapp, Jr., P. C. Srivastava, A. P. Callahan, E. B. Cunningham, G. W. Kabalka and K. A. R. Sastry, *J. Med. Chem.*, **27**, 57 (1984).
66. R. D. Okada, F. F. Knapp, Jr., D. R. Elmaleh, D. Yasuda, C. A. Boucher and H. W. Strauss, *Circulation*, **65**, 305 (1982).
67. P. C. Srivastava, F. F. Knapp, Jr., A. P. Callahan, B. A. Owen, G. W. Kabalka and K. A. R. Sastry, *J. Med. Chem.*, **28**, 408 (1985).
68. T. Yasuda, F. F. Knapp, Jr., D. R. Elmaleh, S. Kopiwoda, K. A. McKusick and H. W. Strauss, *J. Nucl. Med., Proc. 27th Annu. Meet.*, **21**, 58 (1980).
69. Y. Yonekura, P. Som, S. C. Srivastava, K. Yamamoto, G. E. Meineken, A. B. Brill, D. R. Elmaleh, H. W. Strauss, M. M. Goodman and F. F. Knapp, Jr., *J. Nucl. Med., Proc. 30th Annu. Meet.*, **24**, 125 (1983).
70. M. E. Wolff and G. Zanati, *Experientia*, **26**, 1115 (1970).
71. F. F. Knapp, Jr., *J. Labelled Compd. Radiopharm.*, **17**, 81 (1979).
72. F. F. Knapp, Jr., K. R. Ambrose and A. P. Callahan, *J. Nucl. Med.*, **21**, 251 (1980).
73. F. F. Knapp, Jr., K. R. Ambrose and A. P. Callahan, *J. Nucl. Med.*, **21**, 258 (1980).
74. D. V. Woo F. F. Knapp, Jr., K. R. Ambrose, A.·P. Callahan and J. L. Coffey, *J. Nucl. Med.*, **21**, 454 (1980).
75. F. F. Knapp, Jr., *J. Org. Chem.*, **44**, 1007 (1979).
76. G. Zdansky, in *Organic Selenium Compounds. Their Chemistry and Biology* (Eds. D. L. Klayman and W. H. H. Günther), Wiley, New York, 1973, Chapt. XII, p. 593.
77. F. F. Knapp, Jr., K. R. Ambrose and A. P. Callahan, *J. Med. Chem.*, **24**, 794 (1981).
78. Ajinomoto Co. Inc., *Japan Kokai Tokkyo Koho*, JP 59216868 (84216868), 1984; *Chem. Abstr.*, **102**, 185497h (1985).
79. T. Sadeh, L. Christiaens, J. L. Piette, M. Guillaume and K. Soda, *Abstr. Jpn. Agric. Biochemi. Soc. Meet., April 2, 1986*, 1986, p. 80, 2G-10.
80. A. Ulman, J. Menassen, F. Frolow and D. Rabinovich, *Tetrahedron Lett.*, 1885 (1978).
81. R. A. Grigsby, F. F. Knapp, Jr., A. P. Callahan, L. A. Ferren and K. J. Irgolic, *J. Nucl. Med., Proc. 28th Annu. Meet.*, **22**, 12 (1981).
82. F. Rogoz, *Diss. Pharm.*, **16**, 157 (1962).
83. K. J. Irgolic, *The Organic Chemistry of Tellurium*, Gordon and Breach, New York, 1974, Chapt. XVI, pp. 369–379.
84. T. N. Srivastava, P. C. Srivastava and R. Kumar, *Bokin Bobai*, **10**, 523 (1982).
85. Y. D. Kulkarni and S. Srivastava, *Indian J. Chem., Sect. A*, **24**, 429 (1985).
86. W. E. Rudzinski, T. M. Aminabhavi, N. S, Biradar and C. S. Patil, *Inorg. Chim. Acta*, **67**, 177 (1982).
87. W. E. Rudzinski, T. M. Aminabhavi, N. S. Biradar and C. S. Patil, *Inorg. Chim. Acta*, **69**, 83 (1983).
88. W. E. Rudzinski, T. M. Aminabhavi, N. S. Biradar and C. S. Patil, *Inorg. Chim. Acta*, **70**, 175 (1983).
89. N. S. Biradar, M. C. Divakar and G. V. Karajagi, *J. Karnatak Univ. Sci.*, **28**, 89 (1983).
90. N. S. Biradar, T. M. Aminabhavi, C. S. Patil and W. E. Rudzinski, *Inorg. Chim. Acta*, **78**, 47 (1983).
91. T. M. Aminabhavi, W. E. Rudzinski, N. S. Biradar and C. S. Patil, *Inorg. Chim. Acta*, **78**, 51 (1983).
92. A. Mueller, E. Cadenas, P. Graf and H. Sies, *Biochem. Pharmacol.*, **33**, 3235 (1984).
93. A. Wendel, M. Fausel, H. Safayhi, G. Tiegs and R. Otter, *Biochem. Pharmacol.*, **33**, 3241 (1984).
94. M. J. Parnham and S. Kindt, *Biochem. Pharmacol.*, **33**, 3247 (1984).
95. A. Mueller, H. Gabriel and H. Sies, *Biochem. Pharmacol.*, **34**, 1185 (1985).
96. J. J. Kirsi, J. A. North, P. A. McKernan, B. K. Murray, P. G. Canonico, J. W. Huggins, P. C. Srivastava and R. K. Robins, *Antimicrob. Agents Chemother.*, **24**, 353 (1983).
97. J. L. Huey, K. Pawlak, B. T. Nguyen, R. K. Robins and W. Sadee, *Cancer Res.*, **45**, 5512 (1985).
98. R. W. Sidwell, J. H. Huffman, E. W. Call, H. Alaghamandan, P. D. Cook and R. K. Robins, *Antimicrob. Agents Chemother.*, **28**, 375 (1985).
99. R. K. Robins, *Chem. Eng. News*, **64**, No. 4, 29 (1986).

CHAPTER **9**

Pharmacological and toxicological aspects of inorganic and organic selenium compounds

TOHRU MASUKAWA

Department of Pharmacology, Faculty of Pharmaceutical Sciences, Setsunan University, 45-1, Nagaotoge-cho, Hirakata, Osaka 573-01, Japan

I. INTRODUCTION

Since selenium intoxication such as alkali disease and blind staggers and its deficiency syndromes such as white muscle disease and cardiac myopathy have long been known in animals, the toxicological and nutritional aspects of selenium in farm animals have become major subjects of selenium research. During the early period of these investigations, carcinogenic properties of selenium were reported. Later, the opposite effect was observed and selenium has been demonstrated to exhibit anticarcinogenic activity in experiments with animals and in epidemiological studies with humans. Even so, confusion and controversy over the relationship between selenium and cancer has continued for a long time. On the other hand, selenium deficiency syndrome was recognized in animals and humans, and selenium was found to be an important element in human nutrition.

Most of the investigations on the biological activity of selenium have employed nutritional methods using physiological doses of selenium. One of the possible reasons for this is the narrow safety margin between an effective and a toxic dose and a lingering doubt as to the carcinogenicity of selenium. The pharmacological effects of selenium remain obscure. Recently, considering that selenium exhibits various beneficial effects as described below, attempts have been made to synthesize organic selenium compounds with lower toxicity than inorganic selenium compounds and to apply them in human medication.

This review is mainly concerned with the physiological and pharmacological aspects of selenium.

II. BIOLOGICAL EFFECTS ON ORGANS

A. Cardiovascular System

The cardiac effects of selenium vary with the amount of selenium administered or ingested. Heinrich and MacCanon[1] demonstrated that a decrease in systemic blood pressure and a rise in pulmonary artery pressure were produced by a toxic dose of selenite (2.0 mg kg^{-1} i.v.) in dogs, accompanied by increased heart rate, arrhythmic bradycardia and occasionally tachycardia and fibrillation. Lower doses produced moderate elevations of both systemic and pulmonary pressure. However, according to Aviado et al.[2], selenite ($0.04-20$ mg kg^{-1} i.v.) did not elicit any signs of cardiac depression in dogs. Selenite caused a positive inotropic effect in isolated dog ventricular strip perfused with either blood or a krebs–hydrogen carbonate solution that was deficient in oxygen. They thought that this effect may relate to the protective action of selenite against the lethal effects of oxygen deficiency, ouabain and 2,4-dinitrophenol in mice. However, in an isolated and perfused guinea-pig heart, selenite showed a negative inotropic effect, accompanied by mitochondrial alterations[3].

In animals fed on a low selenium diet, it has been demonstrated that abnormal electrocardiograms (ECGs) accompanied by blood pressure changes appear. Histological changes in the cardiac muscle of rats reveal that the abnormal ECG pattern is related to a change in the properties of the muscle fibres rather than to electrolyte disturbances or other changes in plasma constituents[4]. In lambs, ECG showed the progressive development of a characteristic abnormality. Just before death, the ECG pattern became grossly abnormal in some cases, a rise in the T-wave giving way to an elevated S–T segment, similar to that seen frequently in myocardial infarction in humans. From a comparison of the histopathological pictures, entirely different syndromes appear to develop in the rat and the lamb, but the ECG changes in both species are similar[5]. These abnormalities can be prevented by the administration of adequate amounts of selenium. Similar myocardial disease is frequently seen in other species, e.g. pigs, sheep, calves and ducklings, with selenium–vitamin E deficiency[6].

In humans, associations between selenium intake and cardiovascular diseases have been suggested from numerous epidemiological studies[6]. According to Shamberger[6], both the male and female mortalities due to cardiovascular, renal, cerebrovascular, coronary and hypertensive heart diseases were significantly lower in a high than in a low selenium area. In another study on the relationship between trace element intakes and cardiovascular diseases in 25 countries, a significant negative correlation was seen between selenium and ischemic heart disease, and a positive correlation was observed with cadmium and ischaemic heart disease. An even more significant correlation existed between the ratio of cadmium/selenium intake and ischemic heart disease[6]. An association between mode rate exposure to cadmium and hypertension in experimental animals has also been reported[7],

but cadmium-induced hypertension in rats could be alleviated by feeding selenium. The preventive effect of selenium can be explained by its antagonistic action towards cadmium[8]. Further, prophylactic application of selenite ($1.0 \, \text{mgkg}^{-1}$ s.c. per day) was shown to lower the blood pressure of rats with renal hypertension and to suppress a rise in blood pressure following infusion of angiotensin II[9].

Another epidemiological study showed that low serum selenium resulting from low dietary selenium intake is associated with an excess risk of death from acute coronary heart disease and myocardial infarction. Salonen et al.[10] investigated case-control pairs coming from a population of 11 000 persons in eastern Finland. The subjects were aged 35–59 years and had either died of acute coronary heart disease or other atherosclerotic cardiovascular diseases or had a non-fatal myocardial infarction during a 7-year follow-up. Controls were matched for sex, age, tobacco consumption, serum cholesterol, diastolic blood pressure and history of angina pectoris. The mean serum selenium levels in all cases and all controls were 51.8 and 55.3 μg l^{-1}, respectively. Since there was no significant relationship between serum selenium and the risk of death of the diseases studied at Se levels above 45 μg l^{-1}, this level was used as a reference. The relative risk of death markedly increased with the decrease of serum selenium. Regarding the relationship between the development of coronary heart diseases and selenium intake, the following mechanisms of action were proposed: Firstly, the decrease in glutathione peroxidase activity due to selenium deficiency may lead to an accumulation of lipid peroxides with subsequent injury to various tissues including arterial vessels. Secondly, thrombus formation in the coronary artery may be involved in the development of the diseases. In fact, platelet aggregatability was enhanced in selenium-deficient animals, as evidenced by the aggravation of arachidonate-induced respiratory distress in mice and enhanced platelet aggregation by arachidonate, ADP and collagen in vitro[11]. Selenium-deficient platelets have been observed to be associated with a marked alteration in the lipoxygenase metabolism of arachidonate[12]. The platelets of patients with acute myocardial infarction had significantly lower activity of glutathione peroxidase[13]. Additionally, the formation of PGI_2 with a potent antiaggregatory and vasodilating activity was suppressed in the aorta from selenium-deficient rats[11]. These findings suggest that dietary selenium may function in vascular haemostasis and thrombosis by maintaining the metabolism of arachidonate.

It was recently reported that Keshan disease with cardiomyopathy developed in some areas of China is a selenium deficiency syndrome[14]. Keshan disease could be prevented by selenium supplementation[15], but its mechanism remains obscure. Other cases of cardiomyopathy similar to Keshan disease have been observed in patients given long-term parenteral alimentation without selenium supplementation[16].

Experimental cardiomyopathy related to dietary selenium has also been investigated. Long-term administration of adriamycin, an antineoplastic agent, resulted in the development of cardiomyopathy in various animals, including humans. The toxic effect may be the result of membrane lipid peroxidation. Revis and Marusic[17] demonstrated that a marked decrease in glutathione peroxidase activity and selenium content occurred in the hearts of adriamycin-treated rabbits. They suggested that the increase in lipid peroxides in the heart may be the result of a decrease in glutathione peroxidase activity, in turn caused by an alteration in the selenium flux in the myocardial cells. The protective effects of vitamin E and selenium supplementation on cardiomyopathy were reported to be found in rabbits[18] but not in dogs[19] and rats[20]. Cadmium also caused cardiomyopathy in rats. In cadmium-treated rats fed a low selenium diet, an increase in heart weight with histopathological changes was produced, accompanied by a decrease in glutathione peroxidase activity and a rise in the lipid peroxide level in the heart. Increased dietary selenium markedly decreased the level of lipid peroxide. Since the cardiotoxic effect of cadmium was observed without concomitant peroxidative damage to the kidney and liver, the heart is the most susceptible organ to cadmium-induced damage[21].

B. Pulmonary System

The injection of selenite (0.1–2.0 mg kg^{-1} i.v.) to anaesthetized dogs produced respiratory stimulation, increased minute volume and decreased tidal volume, which appear to result from reflexes originating in the thorax. The early elevation of oxygen consumption after selenite may be due to the release of epinephrine. From the results, Heinrich and MacCanon[22] thought that the primary cause of death in acute selenium poisoning is not respiratory failure.

The lung is directly exposed to oxidizing pollutants in the atmosphere. Inhalation of oxygen, ozone and nitrogen dioxide causes pulmonary tissue injury in animals, including humans. These oxidants readily attack unsaturated lipids in cell membranes, and the resulting lipid peroxidation is an important process in lung injury. After 3 days of exposure to 80% O_2, 35% of selenium-deficient rats died in respiratory distress, but no respiratory damages were observed in selenium-supplemented rats[23]. This indicates that dietary selenium reduces the susceptibility of pulmonary tissue to oxidant-induced damage as a nutritional factor. Glutathione peroxidase activity in the lung after exposure to various oxidant gases was shown to increase in selenium-supplemented[23–25] but not in selenium-deficient animals[23,24]. According to Elsayed et al.[24], since the selenium content in the lung increased with exposure to ozone, selenium might be mobilized to the lung from other body sites under oxidant stress. However, considering that other antioxidative defence factors such as superoxide dismutase, catalase, non-selenium glutathione peroxidase(glutathione S-transferases) and vitamin E also play an important role in the protective effect of oxidant-induced injury, the effect of dietary selenium could not be explained merely by the alteration of glutathione peroxidase activity alone.

Compounds that undergo redox cycling have been shown to produce the superoxide anion ($O_2^{-\cdot}$) in the process. Injury by paraquat, a herbicide, is thought to be due to the peroxidative damage of membrane lipids by $O_2^{-\cdot}$ formed during the redox cycling of the parent compound. Lung injury developed because paraquat was selectively retained in the lungs. Both dietary selenium and vitamin E provided protection against the toxicity of paraquat[26,27]. The acute toxicity of paraquat in the chick was especially highly responsive to selenium status but not to vitamin E status[28]. A similar redox cycling mechanism underlies the pulmonary injury caused by nitrofuranotoin, a urinary tract antibiotic. In protecting against the acute toxicity of nitrofurantoin in the chick, selenium status was shown to be more important than vitamin E status[29]. These findings suggest that the toxicity of redox cycling compounds may be enhanced by selenium deficiency.

C. Liver

The main effects of chronic excess selenium poisoning are depressed growth, decreased survival and damage to the liver and other organs. Although the detailed mechanism still remains unknown, perturbations of hepatic glutathione status or resulting impairment of the redox state of the cells may be involved, since the liver is the main organ involved in the reduction of excess selenium[30].

The relationship between liver necrosis and lipid peroxidation has been demonstrated under various experimental conditions. Dietary deficiency of selenium and vitamin E in growing rats caused massive liver necrosis[31]. Rats with nutritional liver necrosis exhaled large amounts of ethane as an index of in vivo lipid peroxidation, suggesting that liver necrosis is the result of lipid peroxidation[32]. Concerning liver necrosis as a result of drug toxicity, Gallagher[33] first reported that the injection of selenite and also vitamin E and other antioxidants protects mice from the lethal toxicity of carbon tetrachloride. According to Hafeman and Hoekstra[34], dietary selenium inhibited carbon tetrachloride-

induced evolution of ethane from rats. This is also true of paraquat- and diquat-induced liver necrosis in selenium-deficient animals[35,36]. The protective effect of selenium against liver necrosis is considered to be due to the decomposition of lipid peroxides via glutathione peroxidase. However, in the case of diquat toxicity, selenium injection provided significant protection against lipid peroxidation and mortality within 10 h, even though this treatment did not result in a rise in tissue glutathione peroxidase activity. Thus, a selenium-dependent factor in addition to glutathione peroxidase is thought to exist that protects against lipid peroxidation[36].

Lipid peroxidation does not always correlate with liver necrosis. Both iodipamide and acetaminophen were shown to cause liver necrosis but only minor ethane production. The hepatic toxicity of these drugs was diminished by selenium deficiency[37]. Since the detoxification of these drugs was carried out either by binding to glutathione S-transferases or by conjugation with glutathione catalysed by the enzymes, an increased activity of hepatic glutathione S-transferases in selenium deficiency may result in enhanced detoxification of these drugs, leading to reduced toxic effects. The hepatotoxicity of aflatoxin B_1 was also markedly attenuated in a selenium-deficient status[38]. Since aflatoxin B_1 is detoxified by glutathione conjugation, a similar mechanism may be involved. Bromobenzene-induced hepatic damage was prevented by the acute injection of selenite (12.5, $30 \mu g \, kg^{-1}$ i.p.), but the mechanism remains obscure[39].

Selenium is known to influence microsomal drug metabolizing systems via alterations of the haeme metabolism. Pharmacological or toxicological doses of selenite (10–$100 \mu mol \, kg^{-1}$ s.c.) in rats with a normal selenium status caused the induction of δ-aminolevulinate synthase and haeme oxygenase in the liver. The effect of selenium was rapid; the cellular content of haeme was significantly increased 30 min after injection and subsequently returned to normal levels. The alteration of the haeme metabolism with excess of selenium resulted in the marked inhibition of the microsomal drug metabolism[40]. Nutritional doses of selenium play an important role in the maintenance of drug metabolism. The effect of selenium deficiency on the microsomal drug metabolism was investigated by Burk and Masters[41]. Selenium deficiency impaired the induction of cytochrome P-450 by phenobarbital, but had no effect on basal levels of the haemoprotein.

Ethylmorphine demethylase activity was affected by selenium deficiency, but NADPH–cytochrome c reductase activity and biphenyl-4-hydroxylase activity were not. When 3-methylcholanthrene was used in place of phenobarbital, selenium deficiency had no effect on the system. In addition, aminopyrine N-demethylation, monocrotane metabolism and aniline hydroxylation were depressed by selenium deficiency. The depression was greater in second generation rats with severe selenium deficiency[42].

From a comparison of hepatic haeme metabolisms in selenium-deficient rats and in control rats, Burk and Correia[43] showed that phenobarbital increased the hepatic microsomal haeme oxygenase activity in selenium-deficient rats. After phenobarbital administration, the haeme synthesis and catabolism increased strikingly in selenium-deficient liver, whereas haeme utilization in the formation of cytochrome P-450 was impaired in selenium deficiency. The resulting abnormal excess of haeme induced microsomal haeme oxygenase. These findings may be related to the finding that the induction of cytochrome P-450 system in rats and chicks was accompanied by an increased requirement for selenium[44,45]. Thus, selenium may play a key role in the homeostasis of microsomal haeme through normalization of haeme synthesis and/or its utilization. Concerning the mode of action of selenium involved in haeme metabolism, injection of selenite corrected the abnormality in haeme metabolism within 12 h, although there was not detectable recovery of glutathione peroxidase activity in this period. Therefore, the improvement of the abnormality in haeme metabolism is considered to be due to an unrecognized function of selenium other than glutathione peroxidase[43].

D. Gastrointestinal System

Selenoamino acids are thought to be absorbed from the gastrointestinal tract in the same way as other amino acids[46], and inorganic selenium such as selenite and selenate to be likewise absorbed from the intestine as are selenoamino acids[47]. In the ligated intestinal segments of rats, the absorption of selenite and selenomethionine occurred from the duodenum rather than from the jejunum or ileum[47]. As a mechanism of absorption, McConnell and Cho[48] demonstrated that selenite is absorbed by diffusion, but not by active transport. According to Wolffram et al.[49], selenate was absorbed markedly faster than selenite and its absorption showed a saturable process, indicating that the absorption of selenate may occur by a carrier-mediated mechanism.

Hadjimarkos[50] has reported that dental caries is more prevalent in seleniferous areas than non-seleniferous areas.

Prevention of the formation and detoxification of lipid peroxides may be especially important in the gastrointestinal tract because the tissue is frequently exposed to such substances. Oral administration of hydrogen peroxide in the chick could have a detrimental effect on the intestinal mucosa, resulting in a decreased rate of selenium absorption and reduced glutathione peroxidase activity[51]. On the other hand, Vilas et al.[52], observing that dietary peroxides increased glutathione peroxidase activity in the gastric mucosa, suggested that glutathione peroxidase may be involved in protecting the gastric mucosa from damage caused by dietary peroxides. Further, according to Negishi et al.[53], when mice were orally given autoxidized methyl linoleate with a low vitamin E diet, an increase in glutathione peroxidase activity in the gastrointestinal tract occurred in proportion to the peroxide value of the oil, but the activity in the liver remained unchanged. With intraperitoneal injection of the oil, an increase in enzyme activity was observed in the liver, but not in the gastrointestinal tract. From the results, they suggested that most of the orally administered oil is reduced in the mucosa of the gastrointestinal tract.

Dietary selenium deficiency produced an increase in glutathione S-transferase activity in the duodenal mucosa in addition to the liver and kidney[54]. The enhanced activity was restored to the control value 48 h after injection of selenite ($1.0 \mu g\, kg^{-1}$ s.c.), but the total glutathione peroxidase activity, including non-selenium glutathione peroxidase (glutathione S-transferases), remained unchanged owing to an increase in selenium-dependent glutathione peroxidase activity. This suggests that glutathione S-transferases with non-selenium glutathione peroxidase activity may function as a substitute for selenium-dependent glutathione peroxidase in the duodenal mucosa in addition to the liver and kidney of selenium-deficient rats. Further, selenium deficiency caused a decrease in the cytochrome P-450 level in the small intestinal mucosa of rats, resulting in profound decreases in aryl hydrocarbon hydroxylase and ethoxyresorufin O-deethylase activities[55]. These findings indicate that selenium is necessary for the metabolism in the gastrointestinal tract of ingested xenobiotics.

E. Haematological System

Anaemia is known to occur in animals as a result of selenium intoxication and also selenium deficiency. Rats fed a diet containing a high concentration of selenium developed anaemia, which was attributed to haemolysis rather than to a defect in erythrocyte synthesis[56]. In contrast, in experiments with erythrocytes from selenium-deficient rats, dietary selenium was shown to reduce ascorbic acid-induced haemolysis, oxidation of haemoglobin and the proportion of cells with Heinz bodies in the presence of glucose[57]. The effects of dietary selenium were explained by a defect of the antioxidative system due to a deficiency of glutathione peroxidase[58]. In contrast to the above in vitro findings, Hu

et al.[59] reported that haemolytic anaemia or oxidation of haemoglobin does not occur in rats fed a selenium-deficient diet for 7 months. They thought that the above effect of dietary selenium may not have an important physiological significance *in vivo* under normal conditions. However, an anaemia associated with the presence of Heinz bodies and selenium deficiency was recently reported to develop in cattle grazing in the Florida Everglades[60].

On the other hand, according to Iwata *et al.*[61], when injected at high levels with aniline or phenylhydrazine, pharmacological doses of selenite (0.5, 2.0 mg kg^{-1} s.c.) was shown to suppress drug-induced methaemoglobinaemia in rats. The effect of selenite was not attributed to the activity of glutathione peroxidase but to the selenite-induced catalytic reduction of methaemoglobin by glutathione[62,63]. The catalytic action was highly specific to selenium.

F. Others

A deficient detoxification of peroxides may be associated with the pathogenic mechanism of neuronal ceroid lipofuscinosis (NCL), characterized by visual failure and progressive cerebral injury. As a result, ceroid and lipofuscin pigments as an endoproduct of lipid peroxidation were accumulated in the nerve cells and other cells. A decreased plasma selenium content and erythrocyte glutathione peroxidase activity in NCL patients in Finland were corrected by prolonged administration of selenite[64,65]. The symptoms of the disease were also improved by this treatment. In other neurological degenerative diseases associated with increased oxidative damage, e.g. Down's syndrome and geriatric disease, antioxidant therapy with selenium and vitamin E seems to be effective[66].

The skeletal muscle injury in patients with myotonic dystrophy, Duchenne muscular dystrophy and long-term parenteral alimentation therapy was also associated with selenium deficiency[66]. The symptoms due to this injury were shown to be alleviated by selenium supplementation.

Kaschin–Beck disease in China, characterized by a disorder of cartilage development, was demonstrated to be associated with selenium deficiency and to be prevented by oral selenite supplementation[67,68].

Selenium is recognized as a constituent of sperm and to be essential for spermatogenesis. The effect on spermatogenesis was specific to selenium and could not be replaced by vitamin E[69].

III. RELATION TO INFLAMMATION AND IMMUNITY

In 1963, an inorganic substance with anti-inflammatory effects was isolated and reported to be selenium[70]. The effectiveness of various organic selenium compounds tested varied with the organic group attached to the selenium atom. Selenite was also shown to exhibit a stabilizing action against heat-induced protein denaturation[71] and lysosomal labilization[72], the action of which was correlated with anti-inflammatory activity.

Macrophages and neutrophils involved in the inflammatory process are both capable of releasing large amounts of reactive oxygen species at sites of inflammation. According to Parnham *et al.*[73], reduced glutathione peroxidase activity in macrophages from selenium-deficient mice was associated with enhanced macrophage hydrogen peroxide release on zymosan stimulation. Hydrogen peroxide-mediated cell injury may account for the reduction in lymphocyte mitogenesis and enhancement of adjuvant arthritis in selenium-deficient animals. Thus, enhancement of glutathione peroxidase activity is thought to be beneficial in improving inflammatory and immune diseases. Recently, an organic selenium compound, 2-phenyl-1,2-benzoisoselenazole-3(2*H*)-one (ebselen), with very low toxicity

was reported to have anti-inflammatory activity in various inflammatory models, e.g. cobra venom factor- or carrageenin-induced paw oedema (ID_{50} 60–100 mg kg^{-1}, oral), cotton pellet granuloma (ID_{30} 4 mg kg^{-1}, oral) and adjuvant arthritis (ID_{30} 2 mg kg^{-1}, oral)[74]. Ebselen itself exhibited glutathione peroxidase-like activity *in vitro* and antioxidant activity independent of exogenous glutathione[75,76]. Additionally, both the generation of chemiluminescence by macrophages (an index of reactive oxygen species) and the formation of leukotriene B_4 as a potent mediator of chemotaxis and aggregation of neutrophils were inhibited dose dependently by ebselen[77]. Parnham and Kindt[77] thought that scavenging of peroxides at inflamed sites by oral ebselen is a possible new approach to anti-inflammatory therapy. Further, they suggested the possibility of the therapeutic usefulness of this type of selenium compounds in treating various diseases associated with overproduction of hydrogen peroxide or lipid peroxides. Rudzinski and coworkers[78–80] synthesized various chelate complexes of selenium with sulphonamide Schiff bases, 2-substituted benzimidazoles and thiopicolinamide, which exhibited a variety of biological effects, and examined their pharmacological activities. Some of these complexes exhibited mild anti-inflammatory activity in addition to antibacterial and hypoglycaemic activities.

Selenium acted as immunoadjuvant when it was fed to animals in amounts in nutritional excess[81] or when administered by injection[82]. Dietary selenium at levels above that generally accepted as nutritionally adequate (0.1 ppm) enhanced the primary immune response in mice as measured by the plaque-forming cell test and by haemaggulutination[81]. The enhancement of the primary immune response by selenite administration (3, 5 μg of Se) was greatest when selenium was administered prior to or simultaneously with sheep red blood cells[82]. Mice fed selenium (1–3 ppm) supplemented diets showed a markedly increased formation of IgG and IgM antibody to the sheep red blood cell antigen[83].

Selenium may possibly be involved in both cellular and humoral immunity. The involvement of selenium in cellular immunity was supported by impaired microbicidal activity, increased dinitrochlorobenzene (DNCB) hypersensitivity and the insensitivity of lymphocytes to selenium depletion. Serfass and Ganther[84] reported that phargocytic cells of selenium-deficient rats, although capable of ingestion of yeast cells *in vitro*, are unable to kill them. The finding was supported in other animal species deficient in selenium[85]. Guinea-pigs fed diets with 1–3 ppm selenium supplements appeared more sensitive than controls to DNCB, showing that selenium enhances the delayed type hypersensitivity[86]. The mitogenesis of lymphocytes to various mitogens was suppressed in selenium-deficient animals[73,87]. Recently, it was demonstrated that the supplementation of selenium (0.5, 2.0 ppm) in drinking water enhances the cytotoxic response of rat splenic natural killer cells, which are considered to play a part in immunosurveillance against tumours[88].

IV. RELATION TO CANCER

In 1943, Nelson *et al.*[89] reported the development of hepatic cell adenoma and low-grade carcinoma in rat liver, beginning 18 months after the rats had been fed on a seleniferous diet. Later, several reports supporting the carcinogenicity of selenium appeared[90,91]. In contrast, in 1949, Clayton and Baumann[92] presented the first evidence that selenium may have an anticarcinogenic effect; dietary selenium reduced liver tumours caused by 3-methyl-4-dimethylaminoazobenzene. Owing to the apparently conflicting reports, confusion and controversy about the relationship between selenium and cancer continued for a long time.

In the numerous epidemiological studies in humans that have subsequently been reported, selenium has been demonstrated to exhibit an anticarcinogenic effect. There was an inverse relationship between human cancer incidence and the selenium content of plants in the local area and between blood selenium levels and cancer deaths, as

demonstrated by the studies of Shamberger and coworkers[93,94]. Further, Schrauzer *et al.*[95] showed significant inverse correlations between selenium intake, estimated from food consumption data in 27 countries, and the incidence of cancers of the large intestine, rectum, prostate, breast, ovary and lung. Similar results were obtained in the relationship between cancer and selenium[96]. However, since there is no higher incidence of cancer in low-selenium districts such as Finland, New Zealand and China, other factors must be considered[97,98]. In this respect, Schrauzer[99] thought that selenium deficiency does not cause cancer but merely increases the susceptibility to cancer induction.

In recent years, evidence has accumulated that selenium can prevent or retard the growth of chemically induced, viral-induced and transplantable tumours in experimental animals[98,100,101]. Table 1 summarizes the anticarcinogenic effects of selenium in various cancer models. Selenium is effective against carcinogenesis by a number of chemical carcinogens. Most of these studies involved the use of inorganic selenium (mainly selenite) supplemented either in the drinking water or in the diet. Selenium intake was for the entire duration of the experiments and the doses were subtoxic, ranging from 0.5 to 6 ppm. To establish the time at which selenium is most effective against chemically induced

TABLE 1. Anticarcinogenic effects of selenium in various cancer models

Carcinogenesis	Species	Tissue of tumours	Ref.
Chemically induced:			
3-Methyl-4-dimethylaminoazobenzene	Rat	Liver	92
2-Acetylaminofluorene	Rat	Liver	104
Aflatoxin B_1	Rat	Liver	128
Dimethylnitrosamine	Rat	Liver	129
3-Methylcholanthrene	Mouse	Skin	130
Benzopyrene	Mouse	Skin	130
7, 12-Dimethylbenz[*a*]anthracene	Mouse	Skin	130
	Mouse	Mammary gland	131, 132
	Rat	Mammary gland	102, 133, 134
1-Methyl-1-nitrosourea	Rat	Mammary gland	135
Estrone, progesterone	Mouse	Mammary gland	136
1, 2-Dimethylhydrazine	Rat	Colon	103, 105
Methylazoxymethanol	Rat	Colon	137
Bis(2-oxopropyl)nitrosamine	Rat	Colon	138
	Rat	Lung	138
Azoxymethane	Rat	Intestine	139
Virus-induced:			
	Mouse (C₃H/St)	Mammary gland	106
	Mouse (BALB/cf. C₃H)	Mammary gland	107
Transplantable:			
Ehrlich ascites cells	Mouse		108
L1210 leukaemic cells	Mouse		109

carcinogenesis, Ip[102] designed an experiment in which rats were given selenium either before, during or after various combinations of exposure to 7,12-dimethyl[a]anthracene. The results indicated that selenium can inhibit both the initiation and promotion phases of carcinogenesis. The inhibitory effect of selenium in the early promotion phase was probably reversible, but a continuous intake of selenium was necessary in order to achieve maximal effect. Similar results were found for the effects of selenium against 1,2-dimethylhydrazine-induced colon tumour[103]. Since selenium is effective in inhibiting tumours induced by a variety of carcinogens, the primary action of selenium is probably not through interference with the carcinogen metabolism. However, in the case of 2-acetylaminofluorene, increased ring hydroxylation and decreased N-hydroxylation of the carcinogen may be involved in the protection by selenium against the carcinogen-induced tumour[104]. With 1,2-dimethylhydrazine-induced tumours, the protection by selenium may be partly attributed to enhanced detoxification due to an increase in glutathione S-transferase activity[105].

Selenium exhibits an anticarcinogenic effect against spontaneous or virally induced tumours[98,101]. Subtoxic amounts of selenium (1–15 ppm) were shown to prevent the genesis of spontaneous mammary tumours in C_3H/St mice[106]. Additionally, mammary carcinogenesis in $BALB/cfC_3H$ mice, containing the highly oncogenic exogenic murine mammary tumour virus, was also prevented by selenium (2,6 ppm) in the drinking water[107]. Since the tumour models may be related to human breast cancer development, these results are of considerable interest.

With regard to transplantable tumours, the injection of selenium was reported to prevent the development of tumours in Ehrlich ascites tumour cell-inoculated mice[108]. Of various selenium compounds used (0.25–2.0 mg kg^{-1} i.p.), selenite was the most effective. Similar results were also obtained with L1210 leukaemic cell-inoculated mice[109]. These results clearly indicate that selenium may have both preventive and therapeutic benefits in the etiology of cancer.

When comparing the activities of various selenium compounds, selenomethionine or selenocystine as organic selenium compounds are exclusively used, whereas their anticarcinogenic effect was less effective[108–110]. In general, the degree to which the biological activity of drugs can be altered by replacing sulphur or other atoms with selenium has received considerable attention. In developmental research on antitumour agents, a number of organic selnium compounds have been synthesized with the purpose of enhancing or improving antitumour activity by modifications to parent compounds. For example, various selenium analogues of nucleoside- and nucleotide-related compounds[111–117], aromatic seleno lactones[118], retinyl phenyl selenoether[119] and the analogues of amino acids and steroids bearing the —SeAsMe$_2$ group[120] have been shown to possess antitumour activity. In particular, 2-β-D-ribofuranosylselenazole-4-carboxamide (selenazofurin), derived from the corresponding 2-β-D-ribofuranosylthiazole-4-carboxamide (tiazofurin) synthesized as a novel potential antitumour and antiviral agent[121], exhibited remarkable effects in doses of 6–24 mg kg^{-1} i.p. against Lewis lung carcinoma in mice and was about 10 times more cytotoxic than tiazofurin towards L-1210 and P-388 cells in culture[111,122]. Selenazofurin was metabolized into ribonucleoside monophosphate and subsequently into an analogue of NAD in which the nicotinamide portion of the molecule was replaced with selenazofurin. The resulting NAD analogue stopped the proliferation of tumour cells by depressing guanosine nucleotide synthesis as a result of the inhibition of IMP dehydrogenase, similarly to tiazofurin[123,124]. Further, selenazofurin also possessed a broad-spectrum antiviral activity against DNA and RNA viruses[125]. Since both activities of selenazofurin were noticeably better than those of tiazofurin, selenazofurin may be expected to be useful as a new antitumour and antiviral agent. However, in these studies, the activity of the organic selenium compounds was exclusively compared with that of the corresponding

parent compounds, while their mechanism of action may be different from that of inorganic selenium.

Little information is available on the mode of action of selenium, but there is some support for its anticarcinogenic properties: exposure to a high concentration of selenium inhibited DNA synthesis[126], and modulation of mitochondria function by selenium was involved in one of the early effects of growth inhibition[127]. Further, the doses of selenium required for anticarcinogenic activity agree with the doses for potentiating the immune response[88].

V. INTERACTION WITH HEAVY METALS

There have been many reports on the biological interaction between selenium and a number of heavy metals. The first report of such an interaction was presented in 1938, arsenic counteracting the toxic effects of seleniferous grain[140,141]. So far, the metals which alleviate selenium toxicity are known to be arsenic[140,141], silver[142], tin[143], copper[142], lead[143], mercury[144], cadmium[144], thallium[143] and tungsten[141]. Conversely, the toxicities of mercury[145-147], cadmium[148], silver[149], lead[150], tin[151], thallium[152] and platinum[153] were suppressed by selenium. The detoxification of heavy metals by selenium is thought to be one of its important roles.

Inorganic selenium compounds such as selenite may be reduced in the body to selenide (Se^{2-}), which may subsequently react with heavy metals. Examples of the direct interaction are the formation of inactive complexes or compounds such as HgSe and CdSe detected after coadministration of selenium with these metals[154-156]. The direct interactions may result in changes in the distribution of the metals in various organs, which may be relevant to the mechanisms of the metal detoxification. Heavy metals administered alone may react with endogenous Se^{2-} to cause the status of selenium deficiency, including a decrease in glutathione peroxidase activity, resulting in damage of physiological functions dependent on selenium[149,157]. In the case of methylmercury intoxication, bismethylmercury(II) selenide(BMS) was formed temporarily soon after injection of selenite[158,159]. Since BMS is a non-ionic, lipid-soluble substance, it may function as a diffusible form in the process of selenite-induced redistribution of methylmercury[160]. However, it remains obscure whether this phenomenon may be responsible for the protective action of selenium against methylmercury toxicity. The mechanisms underlying the interaction of selenium with heavy metals are unknown, although suggestions for the mechanisms have been provided by many investigators.

The side effects of drugs undergoing redox cycling have already been described to be suppressed by selenium supplementation, and the same is true for the platinum-containing drug cis-diamminedichloroplatinum (cisplatin). Renal toxicity as a side effect of cisplatin, a widely used antitumour agent, was markedly prevented by injection of selenite, without masking its antitumour activity[153]. Since the reduction of nephrotoxicity by selenium may improve the therapeutic value of cisplatin, this action is of considerable interest.

VI. MEDICAL APPLICATIONS

Selenium compounds for human use may be classified into two groups according to their purpose, one being as antidotes and the other as diagnostic drugs for diseases. At present, the single drug used as an antidote is selenium disulphide for treating seborrheic dermatitis and common dandruff. The use of selenium compounds is strictly controlled because of their high toxicity. If the deleterious effect of selenium could be controlled or alleviated, selenium compounds might be employed as possible antidotes for various human diseases. Several attempts at the chemical modification of biologically active compounds by replacing sulphur or other atoms with selenium have been made in the past to induce

antagonism or augment the action of the parent compounds[161-163]. Recently, good results have been achieved in such investigations; the excellent character of ebselen and selenazofurin as possible candidates in human medicine has already been mentioned.

Concerning the toxicity of organic selenium compounds, if selenium atoms or selenium-containing fragments are released by the metabolic degradation of the organic compounds, even though the latter seem to be of low toxicity, the effective toxicity of these selenium species may be expected to become enhanced. In particular, chronic toxicity due to accumulation in the organs of released selenium may be a major problem in long-term administration. Thus, in order to introduce organic selenium compounds as human medicines, extensive metabolic investigations including absorption, metabolism, accumulation and elimination, and also toxicity studies, are especially important. Further, a comprehensive evaluation of their effective dose:toxicity ratio is necessary.

Another application of selenium compounds is as radiopharmaceuticals for imaging organs and tumours. Although selenium-75 may not be an ideal radionuclide for diagnostic use, it offers several advantages, e.g. long half-life (118.5 d), ease of incorporation of selenium into organic molecules, increased stability *in vivo* of organic selenium compounds compared with the corresponding halogenated analogues and the possibility of preliminary feasibility studies by preparing selenium-73 labelled compounds ($t_{1/2} = 7.1$ h). Thus, selenium-75 labelled radiopharmaceuticals are of considerable value in diagnostic nuclear medicine. [^{75}Se]Selenomethionine has been used for pancreatic imaging for many years. Additionally, 6-(methyl[^{75}Se]selenomethyl)-19-norcholest-5(10)-en-3β-ol (scintadren) is also used clinically as an adrenal imaging agent[164]. For the same purpose, selenium-75 labelled compounds such as 19-selenocholesterol[165] and 24-(isopropylseleno)chol-5-en-3β-ol[166] as cholesterol analogues and 2[3,4-dimethoxyphenyl)ethyl]dimethylselenonium iodide[167] as a dopamine analogue have been synthesized. As a breast tumour-imaging agent, among the seleno derivatives of estrogen and estradiol examined, 16α-(methyl[^{75}Se]seleno)-17β-estradiol[168] is considered to be a good candidate. Selenium-75 labelled tertiary diamines, bis(β-morpholinoethyl)selenide and bis(β-piperidinoethyl)selenide, with high brain uptakes have been investigated as brain-imaging agents[169]. Further, 23-[^{75}Se]selena-25-homotaurocholate has been evaluated as a radiopharmaceutical for investigating the enterohepatic circulation[170].

VII. REFERENCES

1. M. A. Heinrich, Jr., and D. M. MacCanon, *Toxicol. Appl. Pharmacol.*, **2**, 33 (1960).
2. D. M. Aviado, J. Drimal, T. Watanabe and P. M. Lish, *Cardiology*, **60**, 113 (1975).
3. F. Fanconi, N. Manghi, A. Giotti, F. Martini and G. Dini, *Acta Pharmacol. Toxicol.*, **46**, 98 (1980).
4. K. O. Godwin, *Q. J. Exp. Physiol.*, **50**, 282 (1965).
5. K. O. Godwin and F. J. Fraser, *Q. J. Exp. Physiol.*, **51**, 94 (1966).
6. R. J. Shamberger, in *Selenium in Biology and Medicine* (Eds. J. E. Spallholz, J. L. Martin and H. E. Ganther), Avi, Westport, 1981, p. 391.
7. H. M. Perry, Jr., *J. Am. Diet. Assoc.*, **62**, 631 (1973).
8. H. M. Perry, Jr., E. F. Perry and M. W. Erlanger, in *Trace Substances in Environmental Health—VIII* (Ed. D. D. Hemphill), University of Missouri, Columbia, 1974.
9. H. Hilse, P. Oehme, W. Krause and K. Hecht, *Acta Physiol. Pharmacol. Bulg.*, **5**, 47 (1979).
10. J. T. Salonen, G. Alfthan, J. K. Huttunen, J. Pikkarainen and P. Puska, *Lancet*, **2**, 175 (1982).
11. T. Masukawa, J. Goto and H. Iwata, *Experientia*, **39**, 405 (1983).
12. R. W. Bryant, T. C. Simon and J. M. Bailey, *Biochem. Biophys. Res. Commun.*, **117**, 183 (1983).
13. Y. X. Wong, K. Bocker, H. Reuter, J. Kiem, G. V. Iyenger, F. Loogen, R. Gross and L. E. Feinendegen, *Klin. Wochenschr.*, **59**, 817 (1981).
14. Keshan Disease Research Group, *Chin. Med. J.*, **92**, 477 (1979).

15. Keshan Disease Research Group, *Chin. Med. J.*, **92**, 471 (1979).
16. R. A. Johnson, S. S. Baker, J. T. Fallon, E. P. Maynard, J. N. Ruskin, Z. Wen, K. Ge and H. J. Cohen, *N. Engl. J. Med.*, **304**, 1210 (1981).
17. N. W. Revis and N. Marusic, *J. Mol. Cell Cardiol.*, **10**, 945 (1978).
18. J. F. Van Bleet, L. Greenwood V. J. Ferrans and A. H. Rebar, *Am. J. Vet. Res.*, **39**, 997 (1978).
19. J. F. Van Bleet, V. J. Ferrans and W. E. Weirich, *Am. J. Pathol.*, **99**, 13 (1980).
20. T. Facchnetti, F. Delaini, M. Salmona, M. B. Donati, S. Feuerstein and A. Wendel, *Toxicol. Lett.*, **15**, 301 (1983).
21. I. S. Jamall and J. C. Smith, *Toxicol. Appl. Pharmacol.*, **80**, 33 (1985).
22. M. A. Heinrich, Jr., and D. M. MacCanon, *Toxicol. Appl. Pharmacol.*, **3**, 174 (1961).
23. C. E. Cross, G. Hasegawa, K. A. Reddy and S. T. Omaye, *Res. Commun. Chem. Pathol. Pharmacol.*, **16**, 695 (1977).
24. N. M. Elsayed, A. D. Hacker, K. Kuehn, M. G. Mustafa and G. N. Schrauzer, *Toxicol. Appl. Pharmacol.*, **71**, 398 (1983).
25. T. Ichinoe and M. Sagai, *Toxicol. Appl. Pharmacol.*, **66**, 1 (1982).
26. J. S. Bus, S. D. Aust and J. E. Gibson, *Res. Commun. Chem. Pathol. Pharmacol.*, **11**, 31 (1975).
27. S. T. Omaye, K. A. Reddy and C. E. Cross, *Toxicol. Appl. Pharmacol.*, **43**, 237 (1978).
28. G. F. Combs and F. J. Peterson, *J. Nutr.*, **113**, 538 (1983).
29. F. J. Peterson, G. F. Combs, J. L. Holtzman and R. P. Mason, *J. Nutr.*, **112**, 1741 (1982).
30. R. A. LeBoeuf and W. G. Hoekstra, *J. Nutr.*, **113**, 845 (1983).
31. K. Schwartz and C. M. Foltz, *J. Am. Chem. Soc.*, **79**, 3292 (1957).
32. D. F. Hafeman and W. G. Hoekstra, *J. Nutr.*, **107**, 666 (1977).
33. C. H. Gallagher, *Nature (London)*, **192**, 881 (1961).
34. D. G. Hafeman and W. G. Hoekstra, *J. Nutr.*, **107**, 656 (1977).
35. S. Z. Cagen and J. E. Gibson, *Toxicol. Appl. Pharmacol.*, **40**, 193 (1977).
36. R. F. Burk, R. A. Lawrence and J. M. Lane, *J. Clin. Invest.*, **65**, 1024 (1980).
37. R. F. Burk and J. M. Lane, *Toxicol. Appl. Pharmacol.*, **50**, 467 (1979).
38. R. F. Burk and J. M. Lane, *Fundam. Appl. Toxicol.*, **3**, 218 (1983).
39. B. A. Merrick, M. H. Davies, K. L. Johnson and R. C. Schnell, *Toxicol. Appl. Pharmacol.*, **72**, 102 (1982).
40. M. D. Maines and A. Kappas, *Proc. Natl. Acad. Sci. USA*, **73**, 4428 (1976).
41. R. F. Burk and B. S. S. Masters, *Arch. Biochem. Biophys.*, **170**, 124 (1975).
42. L. R. Shull, G. W. Buckmaster and P. R. Cheeke, *J. Environ. Pathol. Toxicol.*, **2**, 1127 (1979).
43. R. F. Burk and M. A. Correia, in *Selenium in Biology and Medicine* (Eds. J. E. Spallholz, J. L. Martin and H. E. Ganther), Avi, Westport, 1981, p. 86.
44. G. Siami, A. R. Schulert and R. A. Neal, *J. Nutr.*, **102**, 857 (1972).
45. G. F. Combs and M. L. Scott, *Poult. Sci.*, **54**, 1152 (1975).
46. K. P. MacConnell and G. L. Cho, *Am. J. Physiol.*, **213**, 150 (1967).
47. P. D. Whanger, N. D. Pedersen, J. Harfield and P. H. Weswig, *Proc. Soc. Exp. Biol. Med.*, **153**, 295 (1976).
48. K. P. McConnell and G. J. Cho, *Am. J. Physiol.*, **208**, 1191 (1965).
49. S. Wolffram, F. Arduser and E. Scharrer, *J. Nutr.*, **115**, 454 (1985).
50. D. M. Hadjimarkos, *Arch. Environ. Health*, **10**, 893 (1965).
51. J. W. Fidler, E. C. Naber and J. D. Latshaw, *Poult. Sci.*, **59**, 141 (1980).
52. N. N. Vilas, R. R. Bell and H. H. Draper, *J. Nutr.*, **106**, 589 (1976).
53. H. Negishi, K. Fujimoto and T. Kaneda, *J. Nutr. Sci. Vitaminol.*, **26**, 309 (1980).
54. T. Masukawa, T. Nishimura and H. Iwata, *Biochem. Pharmacol.*, **33**, 2635 (1984).
55. G. A. Pascoe, J. Sakai-Wong, E. Soliven and M. A. Correia, *Biochem. Pharmacol.*, **32**, 3027 (1983).
56. A. W. Halverson, D-T, Tsay, K. C. Triebwasser and E. I. Whitehead, *Toxicol. Appl. Pharmacol.*, **17**, 151 (1970).
57. J. T. Rotruck, A. L. Pope, H. E. Ganther and W. A. Hoekstra, *J. Nutr.*, **102**, 689 (1972).
58. J. T. Rotruck, A. L. Pope, H. E. Ganther, A. B. Swanson, D. G. Hafeman and W. G. Hoekstra, *Science*, **179**, 588 (1973).
59. M.-L. Hu, C. Chung and J. E. Spallholz, *J. Inorg. Biochem.*, **22**, 165 (1984).
60. J. G. Morris, W. S. Cripe, H. L. Chapman, Jr., D. F. Walker, J. B. Armstrong, J. D. Alexander, Jr., R. Miranda, A. Sanchez, J. R. Blair-West and D. A. Denton, *Science*, **223**, 491 (1984).
61. H. Iwata, T. Masukawa and S. Nakaya, *Biochem. Pharmacol.*, **28**, 2209 (1979).

62. H. Iwata, T. Masukawa, S. Kasamatsu, K. Inoue and H. Okamoto, *Experientia*, **33**, 678 (1977).
63. T. Masukawa and H. Iwata, *Life Sci.*, **21**, 695 (1977).
64. T. Westermark and M. Sandholm, *Acta Pharmacol. Toxicol.*, **40**, 70 (1977).
65. T. Westermark, *Acta Pharmacol. Toxicol.*, **41**, 121 (1977).
66. J. Veve, F. Vertongen and L. Molle, *Clin. Endocrinol. Metab.*, **14**, 629 (1985).
67. S. Hau and Z. Zhu, *Huanjing Kexue*, **3**, 18 (1982); *Chem. Abstr.*, **97**, 37802s (1982).
68. J. Li, S. Ren and D. Chen, *Huanjing Kexue Xuebao*, **2**, 91 (1982); *Chem. Abstr.*, **97**, 71210g (1982).
69. S. H. Wu, J. E. Oldfield, P. D. Whanger and P. H. Weswig, *Biol. Reprod.*, **8**, 625 (1973).
70. M. E. Roberts, *Toxicol. Appl. Pharmacol.*, **5**, 500 (1963).
71. J. L. Taylor and J. H. Brown, *Proc. Soc. Exp. Biol. Med.*, **145**, 32 (1974).
72. J. H. Brown and S. H. Pollock, *J. Nutr.*, **102**, 1413 (1972).
73. M. J. Parnham, J. Winkelmann and S. Leyck, *Int. J. Immunopharmacol.*, **5**, 455 (1983).
74. M. J. Parnham, S. Leyck, N. Dereu, J. Winkelmann and E. Graf, *Adv. Inflam. Res.*, **10**, 397 (1986).
75. A. Muller, E. Cadenas, P. Graf and H. Sies, *Biochem. Pharmacol.*, **33**, 3235 (1984).
76. A. Wendel, M. Fausel, H. Safayhi, G. Tiegs and R. Otter, *Biochem. Pharmacol.*, **33**, 3241(1984).
77. M. J. Parnham and S. Kindt, *Biochem. Pharmacol.*, **33**, 3247 (1984).
78. W. E. Rudzinski, T. M. Aminabhavi, N. S. Biradar and C. S. Patil, *Inorg. Chim. Acta*, **67**, 177 (1982).
79. N. S. Biradar, T. M. Aminabhavi, C. S. Patil and W. E. Rudzinski, *Inorg. Chim. Acta*, **78**, 47 (1983).
80. T. M. Aminabhavi, W. E. Rudzinski, N. S. Biradar and C. S. Patil, *Inorg. Chim. Acta*, **78**, 51 (1983).
81. J. E. Spallholz, J. L. Martin, M. L. Gerlach and R. H. Heinzerling, *Proc. Soc. Exp. Biol. Med.*, **143**, 685 (1973).
82. J. E. Spallholz, J. E. Martin, M. L. Gerlach and R. H. Heinzerling, *Proc. Soc. Exp. Biol. Med.*, **148**, 37 (1975).
83. J. E. Spallholz, J. E. Martin, M. L. Gerlach and R. H. Heinzerling, *Infect. Immun.*, **8**, 841 (1973).
84. R. E. Serfass and H. E. Ganther, *Nature (London)*, **255**, 640 (1975).
85. R. Boyne and J. R. Arthur, *J. Comp. Pathol.*, **89**, 151 (1979).
86. J. E. Spallholz, *Adv. Exp. Med. Biol.*, **135**, 43 (1981).
87. B. E. Sheffy and R. D. Schultz, *Fed. Proc. Fed. Am. Soc. Exp. Biol.*, **38**, 2139 (1979).
88. P. A. Talcott, J. H. Exon and L. D. Koller, *Cancer Lett.*, **23**, 313 (1983).
89. A. A. Nelson, O. G. Fitzhugh and H. O. Calvery, *Cancer Res.*, **3**, 230 (1943).
90. M. N. Volgarev and C. A. Tscherkes, in *Selenium in Biomedicine* (Ed. O. H. Muth), Avi, Westport, 1967, p. 179.
91. H. A. Schroeder, D. V. Frost and J. J. Balassa, *J. Chron. Dis.*, **23**, 227 (1970).
92. C. C. Clayton and C. A. Baumann, *Cancer Res.*, **9**, 575 (1949).
93. R. J. Shamberger and D. V. Frost, *Can. Med. Assoc. J.*, **100**, 682 (1969).
94. R. J. Shamberger and C. E. Willis, *CRC Crit. Rev. Clin. Lab. Sci.*, **2**, 211 (1971).
95. G. N. Schrauzer, D. A. White and C. J. Schneider, *Bioinorg. Chem.*, **7**, 23 (1977).
96. L. C. Clark, *Fed. Proc. Fed. Am. Soc. Exp. Biol.*, **44**, 2584 (1985).
97. C. D. Thomson and M. F. Robinson, *Am. J. Clin. Nutr.*, **33**, 303 (1980).
98. P. D. Whanger, *Fundam. Appl. Toxicol.*, **3**, 424 (1983).
99. G. N. Schrauzer, *Am. J. Clin. Nutr.*, **33**, 1892 (1980).
100. C. Ip, *Fed. Proc. Fed. Am. Soc. Exp. Biol.*, **44**, 2573 (1985).
101. J. A. Milner, *Fed. Proc. Fed. Am. Soc. Exp. Biol.*, **44**, 2568 (1985).
102. C. Ip, *Cancer Res.*, **41**, 4386 (1981).
103. M. M. Jacobs, C. F. Frost and F. A. Beams, *Cancer Res.*, **41**, 4458 (1981).
104. M. V. Marshall, M. S. Arnott, M. M. Jacobs and A. C. Griffin, *Cancer Lett.*, **7**, 331 (1979).
105. M. M. Jacobs, *Cancer Res.*, **43**, 1646 (1983).
106. G. N. Schrauzer and D. Ishmael, *Ann. Clin. Lab. Sci.*, **4**, 441 (1974).
107. D. Medina and F. Shepherd, *Cancer Lett.*, **8**, 241 (1980).
108. G. A. Greeder and J. A. Milner, *Science*, **209**, 825 (1980).
109. J. A. Milner and C. Y. Hsu, *Cancer Res.*, **41**, 1652 (1981).
110. H. J. Thompson, L. D. Meeker and S. Kokoska, *Cancer Res.*, **44**, 2803 (1984).
111. P. C. Srivastava and R. K. Robins, *J. Med. Chem.*, **26**, 445 (1983).
112. H. G. Mautner, S.-H., Chu, J. J. Jaffe and A. C. Sartorelli, *J. Med. Chem.*, **6**, 36 (1963).
113. S-H, Chu, *J. Med. Chem.*, **14**, 254 (1971).

114. S-H, Chu and D. D. Davidson, *J. Med. Chem.*, **15**, 1088 (1972).
115. S.-H, Chu, C.-Y. Shiue and M.-Y. Chu, *J. Med. Chem.*, **17**, 406 (1974).
116. S.-H. Chu, C.-Y. Shiue and M.-Y. Chu, *J. Med. Chem.*, **18**, 559 (1975).
117. M. Maeda, N. Abiko and T. Sasaki, *J. Med. Chem.*, **24**, 167 (1981).
118. W. C. Groutas, M. C. Theodorakis, W. A. F. Tomkins, G. Herro and T. Gaynor, *J. Med. Chem.*, **27**, 548 (1984).
119. S. C. Welch and J. M. Gruber, *J. Med. Chem.*, **22**, 1532 (1979).
120. C. H. Banks, J. R. Daniel and R. A. Zingaro, *J. Med. Chem.*, **22**, 572 (1979).
121. R. K. Robins, P. C. Srivastava, V. L. Narayanan, J. Plowman and K. D. Paull, *J. Med. Chem.*, **25**, 107 (1982).
122. D. G. Streeter and R. K. Robins, *Biochem. Biophys. Res. Commun.*, **115**, 544 (1983).
123. H. N. Jayaram, G. S. Ahluwalia, R. L. Dion, G. Gebeyehu, V. E. Marquez, J. A. Kelley, R. K. Robins, D. A. Cooney and D. G. Johns, *Biochem. Pharmacol.*, **32**, 2633 (1983).
124. T. J. Boritzki, D. A. Berry, J. A. Besserer, P. D. Cook, D. W. Fry, W. R. Leopold and R. C. Jackson, *Biochem. Pharmacol.*, **34**, 1109 (1985).
125. J. J. Kirsi, J. A. North, P. A. McKernan, B. K. Murray, P. G. Ganonico, J. W. Huggins, P. C. Srivastava and R. K. Robins, *Antimicrob. Agents Chemother.*, **24**, 353 (1983).
126. D. Medina and C. J. Oborn, *Cancer Lett.*, **13**, 333 (1981).
127. D. Medina, H. W. Lane and C. M. Tracey, *Cancer Res.*, **43**, 2460s (1983).
128. K. E. Grant, M. W. Conner and P. M. Newberne, *Toxicol. Appl. Pharmacol.*, **41**, 166 (1977).
129. R. A. LeBoeuf, B. A. Laishes and W. G. Hoekstra, *Fed. Proc. Fed. Am. Soc. Exp. Biol.*, **42**, 669 (1983).
130. R. J. Shamberger, *J. Natl. Cancer Inst.*, **44**, 931 (1970).
131. D. Medina, H. W. Lane and F. Shepherd, *Carcinogenesis*, **4**, 1159 (1983).
132. D. Medina and F. Shepherd, *Carcinogenesis*, **2**, 451 (1981).
133. C. Ip, *Cancer Res.*, **41**, 2683 (1981).
134. H. J. Thompson, L. D. Meeker, P. J. Becci and S. Kokoska, *Cancer Res.*, **42**, 4954 (1982).
135. H. J. Thompson and P. J. Becci, *J. Natl. Cancer Inst.*, **65**, 1299 (1980).
136. C. W. Welsch, M. Goodrich-Smith, C. K. Brown, H. D. Greene and E. J. Hamel, *Carcinogenesis*, **2**, 519 (1981).
137. M. M. Jacobs, B. Jansson and A. C. Griffin, *Cancer Lett.*, **2**, 133 (1977).
138. D. F. Birt, T. A. Lawson, A. D. Julius, C. E. Runice and S. Salmasi, *Cancer Res.*, **42**, 4455 (1982).
139. B. K. Soullier, P. S. Wilson and N. D. Nigro, *Cancer Lett.*, **12**, 343 (1981).
140. A. L. Moxon, *Science*, **88**, 81 (1938).
141. A. L. Moxon and K. P. DuBois, *J. Nutr.*, **18**, 447 (1939).
142. L. S. Jensen, *J. Nutr.*, **105**, 769 (1975).
143. G. O. Howell and C. H. Hill, *Environ. Health Perspect.*, **25**, 147 (1978).
144. C. H. Hill, *J. Nutr.*, **104**, 593 (1974).
145. J. Parizek and I. Ostadalova, *Experientia*, **23**, 142 (1967).
146. H. E. Ganther, C. Goudie, M. L. Sunde, M. J. Kopecky, P. Wagner, S. H. Oh and W. H. Hoekstra, *Science*, **175**, 1122 (1972).
147. H. Iwata, H. Okamoto and Y. Ohsawa, *Res. Commun. Chem. Pathol. Pharmacol.*, **5**, 673 (1973).
148. A. B. Kar, R. P. Das and B. Mukerji, *Proc. Natl. Inst. Sci., India, Part B*, **26**, 40 (1960).
149. P. A. Wagner, W. G. Hoekstra and H. E. Ganther, *Proc. Soc. Exp. Biol. Med.*, **148**, 1106 (1975).
150. S. C. Rastogi, J. Clausen and K. C. Srivastava, *Toxicology*, **6**, 377 (1976).
151. M. Chiba, N. Fujimoto and M. Kikuchi, *Toxicol. Lett.*, **24**, 235 (1985).
152. Z. M. Hollo and S. Slatarov, *Naturwissenschaften*, **47**, 87 (1960).
153. A. Naganuma, M. Satoh, M. Yokoyama and N. Imura, *Res. Commun. Chem. Pathol. Pharmacol.*, **42**, 127 (1983).
154. A. Naganuma and N. Imura, *Pharmacol. Biochem. Behav.*, **15**, 449 (1981).
155. T. A. Gasiewicz and J. C. Smith, *Biochim. Biophys. Acta*, **428**, 113 (1976).
156. C. H. Hill, *Fed. Proc. Fed. Am. Soc. Exp. Biol.*, **34**, 2096 (1975).
157. P. D. Whanger and P. H. Weswig, *Nutr. Rep. Int.*, **18**, 421 (1978).
158. A. Naganuma and N. Imura, *Res. Commun. Chem. Pathol. Pharmacol.*, **27**, 163 (1980).
159. H. Iwata, T. Masukawa, H. Kito and M. Hayashi, *Biochem. Pharmacol.*, **30**, 3159 (1981).
160. T. Masukawa, H. Kito, M. Hayashi and H. Iwata, *Biochem. Pharmacol.*, **31**, 75 (1982).
161. K. A. Scott and H. G. Mautner, *Biochem. Pharmacol.*, **13**, 907 (1964).
162. S.-H. Chu, G. R. Hillman and H. G. Mautner, *J. Med. Chem.*, **15**, 760 (1972).

163. R. N. Hauson, R. W. Giese, M. A. Davis and S. M. Costello, *J. Med. Chem.*, **21**, 496 (1978).
164. J. F. Chatal, B. Charbonnel and D. Guihard, *Clin. Nucl. Med.*, **3**, 71 (1978).
165. S. D. Sarkar, R. D. Ice, W. H. Beierwaltes, S. P. Gill, S. Balachandran and G. P. Basmadjian, *J. Nucl. Med.*, **17**, 212 (1976).
166. F. F. Knapp, Jr., T. A. Butler, L. A. Ferren, A. P. Callahan, C. E. Guyer and J. L. Coffey, *J. Med. Chem.*, **26**, 1538 (1983).
167. S. A. Sadek, G. P. Basmadjian, P. M. Huu and J. A. Rieger, *J. Med. Chem.*, **26**, 946 (1983).
168. S. A. Sadek, W. V. Kessler, S. M. Shaw, J. N. Anderson and G. C. Wolf, *J. Med. Chem.*, **25**, 1488 (1982).
169. H. F. Kung and M. Blau, *J. Nucl. Med.*, **21**, 147 (1980).
170. M. V. Merrick, M. A. Eastwood, J. R. Anderson and H. M. Ross, *J. Nucl. Med.*, **23**, 126 (1982).

CHAPTER **10**

Insertion and extrusion reactions

LARS HENRIKSEN

Department of General and Organic Chemistry, The H. C. Ørsted Institute, University of Copenhagen, DK-2100 Copenhagen, Denmark

I. INTRODUCTION

A. Scope and Limitations

The title 'selenium and tellurium insertion and extrusion reactions' strictly refers to the equation

$$A—B + E \rightleftharpoons A—E—B \tag{1}$$

$$(E = Se, Te; A, B = \text{any elements})$$
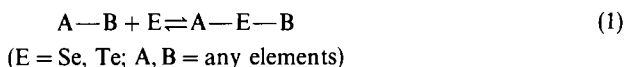
In accord with this definition, only reactions involving the free elements, E, are reviewed extensively. Reactions which establish or disrupt an A—E—B bridge connecting two independent A—Y/B—X species, or involve selenium and tellurium reagents other than the free elements, are included only when relevant to the main title.

The fields of organoselenium[1] and organotellurium[2,3] chemistry have been reviewed thoroughly up to 1971 and 1973, respectively, and the references cited should be consulted for early data. This review is concerned mainly with developments from these dates up to the present.

As a means of systematization, the reactions are classified according to the types of bond broken in the insertion or established in the extrusion reaction.

B. Theoretical Background

As discussed in the chapters on theoretical aspects and thermochemistry in the first volume of this book, quantum mechanical and thermodynamic data on organic selenium and tellurium compounds are rather meagre and certainly have not developed to an extent which allows generalized predictions with respect to kinetics or equilibria for organo-chalcogen compounds. In a qualitative sense, however, selenium and tellurium can be characterized as highly polarizable elements. The polarizability, α, can be expressed as[4]

$$\alpha = \frac{2}{3}\sum_n \frac{(m_x)_{n0}^2 + (m_y)_{n0}^2 + (m_z)_{n0}^2}{E_n - E_0}$$

where m = transient moment, 0 designates the ground state and n the excited states.

Going from second row to higher row elements in the Periodic Table, the energy gap between the potential excited states and the ground state diminishes, leading to a progressive increase in α. With respect to chemical reactivity, the polarizability serves as an indicator of the ability of a given species to tolerate disturbances of the electronic system, i.e. a high polarizability corresponds to low activation barriers for chemical reactions. Since selenium and tellurium are located roughly in the middle of the electronegativity

scale, their high polarizabilities allow facile reaction routes involving radical as well as cationic and anionic intermediates, all of which have been encountered. In addition, the ability of these elements to form tetracovalent (selenurane and tellururane) compounds makes pericyclic cycloaddition–cycloreversion reactions a fourth possible reaction path (see Section II.E).

II. HOMOGENEOUS BONDS

A. Carbon—Carbon Bonds

1. Insertions

The reaction normally proceeds towards the right in both thermal and photochemical processes and examples on insertions of the chalcogens into C—C bonds are only found in very special cases.

$$\overset{\diagdown}{\underset{\diagup}{C}} \text{—E—} \overset{\diagup}{\underset{\diagdown}{C}} \quad \Longleftrightarrow \quad \overset{\diagdown}{\underset{\diagup}{C}} \text{—} \overset{\diagup}{\underset{\diagdown}{C}} \text{—} \; + \; E$$
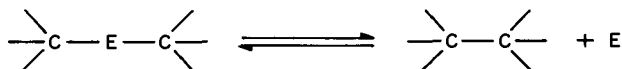
The benzocyclobutadiene **1** reacts with selenium in a thermal process to give the benzoselenophene **2**. Under similar conditions sulphur gives the isobenzothiophene **3** whereas tellurium is unreactive[5].

(1)   (2)

(3)
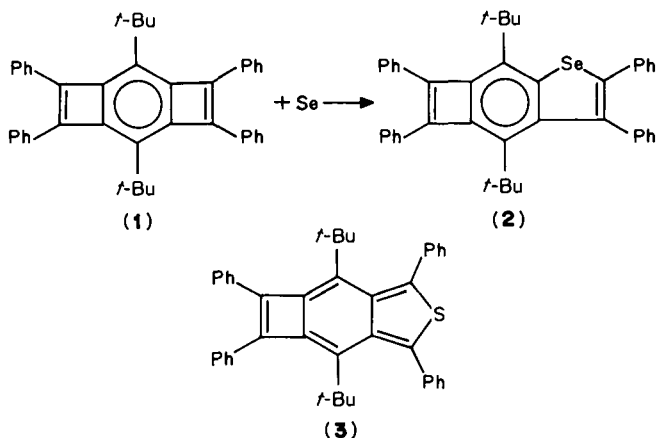
Bicyclo[5.1.0]octa-2, 5-diene (**4**) reacts with selenium (205 °C, 5h) to give 9-selenabicyclo[3.3.1]nona-2, 6-diene (**5a**) in a suggested biradical process. Prolonged heating leads to selenium extrusion with the formation of ethylbenzene and *o*-xylene[6]. In contrast, the tellura analogue **5b** prepared by an independent route extrudes tellurium at 175 °C with clean formation of **4**[7].

(4)   (5)

a : E = Se
b : E = Te

1, 1′, 3, 3′-Tetrasubstituted biimidazolidines (6a and b) on heating insert tellurium in the double bond with reversible formation of cyclic telluroureas (7a and b)[8]. Selenium insertion is reported for 6c. The reverse process in this case requires the presence of copper powder[9]. Although not proved, the process might involve intermediary chalcogen insertion in the C—C double bond.

	R	E
a	Me	Te
b	Et	Te
c	Ph	Se

(6)   (7)

Selenium and tellurium have been inserted in aryl—aryl bonds in an aided reaction, by heating the elements with diaryl sulphones[10]. A similar reaction between hexameric o-phenylenemercury and tellurium is assumed to involve a radical chain process and gives telluranthrene (8) in 72% yield[11].

$$ArSO_2Ar + E \xrightarrow{\sim 300\,°C} ArEAr + SO_2$$

(8)

2. Extrusion reactions

Benzylic selenides and tellurides (9) extrude the elements to give, fairly cleanly, the 1,2-diarylethanes (10).

$$ArCH_2\text{-E-}CH_2Ar \longrightarrow ArCH_2CH_2Ar + E$$

(9)   (10)

The reaction has been carried out thermally in the condensed phase at ca. 200 °C[12–14], by flash vacuum thermolysis at 600 °C[15–17], by the so-called benzyne hydrogenolysis method (an aided extrusion involving Se phenylation with concurrent Sterens rearrangement followed by Rany nickel mediated removal of the phenylseleno group) and by photolysis[14,18,19]. The ease of formation of benzylic chalcogenides (e.g. from alkali metal chalcogenides and the reactive benzylic halides) and the cleanness of the extrusion reaction make it an excellent route to m- (11) and p-2, 2-cyclophanes (12). Benzyl phenyl selenides also give diarylethanes but in this case selenium is retained as diphenyl diselenide. o-Bis(phenylselenomethyl)benzene gives benzocyclobutene (13) instead of an o-cyclophane[16,20]. Arenocyclobutenes are also formed on vacuum pyrolysis of the corresponding areno [c]-2, 5-dihydrotellurophenes[21].

PhSeCH_2CH = CH_2

(14)

PhSeCH_2C ≡ N

(15)

(11)   (12)   (13)

The reactions are undoubtedly of radical character. Scrambled products are observed from non-symmetric benzylic selenides and other compounds which may give rise to stabilized carbon radicals, e.g. diallyl tellurides[22] and also 14 and 15 display the C—C coupling reaction while diaryl and di-n-alkyl selenides do not[16].

The primary thermal and photochemical reactions of diselenides and ditellurides are the loss of one chalcogen atom to give the corresponding selenides and tellurides (see Section III.C). On sufficiently vigorous treatment the former compounds therefore give rise to the same products as the latter.

While diaryl selenides and tellurides do not extrude the chalcogen atom directly this atom is removed fairly cleanly with the formation of biaryls on treatment with degassed Raney nickel[23]. This reaction can also be carried out in a single operation from diaryltellurium dichlorides[23,24]. These and related methods for C—C bond formation from tellurides have recently been reviewed[25].

$$\left.\begin{array}{l} \text{ArEAr (E = Se, Te)} \\[2em] \text{Ar}_2\text{TeCl}_2 \end{array}\right\} \xrightarrow{\text{Raney Ni}} \text{ArAr}$$
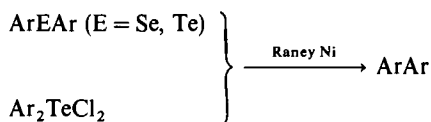
Recently the reactions of diaryl, arylalkynyl and arylalkyl tellurides with organomagnesium bromides in the presence of a Ni^{II} or Co^{II} phosphine catalyst have been described[26]. The reactions lead to C—C coupling with extrusion of tellurium. Products of coupling to the Grignard reagent are also observed. An intermediate (16) corresponding to metal insertion in a C—Te bond is suggested to account for the cross-coupled products.

$$\text{Ar}_2\text{Te} + \text{RMgBr} \xrightarrow[\text{Ni}^{II}\ \text{or}\ \text{Co}^{II}]{\text{THF}} \text{ArR} + \text{ArAr} + \text{RR}$$

$$\text{L}_2\text{M} \underset{\text{Ar}}{\overset{\text{TeAr}}{<}}$$

(16)

$$\text{L} = \text{R}_3\text{P}, \text{M} = \text{Ni,Co}$$
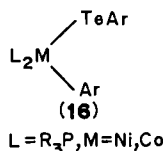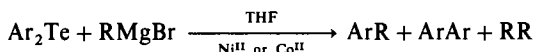
A series of α-(acylseleno)ketones (17) was found to undergo selenium extrusion with the formation of β-diketones on treatment with strong base (t-BuOK)[27]. The mechanism is suggested to involve enolate ion formation followed by internal displacement on the acylseleno carbon and subsequent loss of selenium with formation of the stabilized anion of the β-diketone (18)

$$\text{R}^1\text{COSeCH}_2\text{COR}^2 \xrightarrow{t\text{-BuO}^-} \text{R}^1\text{—C} \overset{\displaystyle{\parallel}^{\text{O}}}{\underset{\text{Se}}{<}} \text{CH} = \overset{\text{O}^-}{\underset{\displaystyle{\parallel}}{\text{CR}^2}} \longrightarrow$$

(17)

$$\text{R}^1\text{COCHCOR}^2 \xrightarrow{-\text{Se}} \text{R}^1\text{CO}\bar{\text{C}}\text{HCOR}^2$$
$$\underset{\displaystyle{\text{Se}^-}}{\mid}$$
$$\qquad\qquad\qquad\qquad\qquad (18)$$
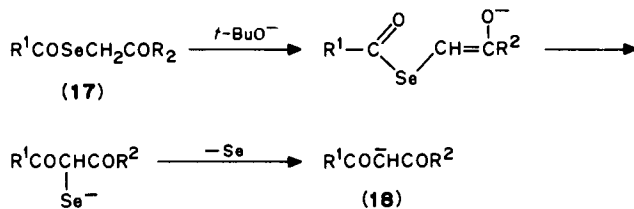
This result is interesting since it defines a lower limit for the basicity of carbanions reacting with selenium; stronger carbon bases readily insert selenium in the carbon—metal bond (see Section III.A.1).

Tetraalkylselenadiazolines (**19**) (available through a cycloaddition reaction between a selenoketone and a diazoalkane) undergo thermolysis with extrusion both of selenium and of nitrogen and formation of a $C=C$ bond[28-31]. In contrast to the sulphur analogues where the thermal reaction stops with formation of a thiirane and a phosphine is needed for the final extrusion of sulphur, the assumed selenirane intermediate (**20**) directly extrudes selenium with alkene formation. This reaction is noted to be superior to the sulphur route for the formation of highly crowded ethenes[27]. The photolysis of **19**, in contrast to the thermal reaction, gives selenium extrusion alone with formation of azines (**21**)[31].

$$19 \xrightarrow{h\nu} R_2^1 C = NN = CR_2^2$$

(**21**)
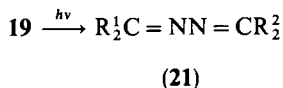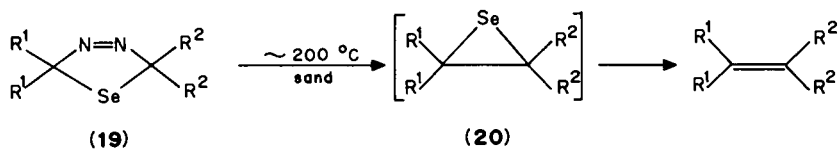
Selenium extrusion from **20** at or below room temperature is also reported in the conversion of oxiranes to alkenes with triphenylphosphine selenide[32], selenocyanate ion[33] and selenoamides[34].

B. Other Group IV Elements

Insertion reactions have been reported for Si—Si, Ge—Ge and Sn—Sn bonds. Kinetic comparisons indicate that the order of reactivities is $S > Se > Te$[35]. This order also appears in an exchange experiment according to the equation[36]

$$(Et_3M)_2E^1 + E^2 \longrightarrow (Et_3M)_2E^2 + E^1 \tag{1}$$

$$M = Si, Ge, Sn; (E^1, E^2) = (Te, Se); (Te, S); (Se, S)$$
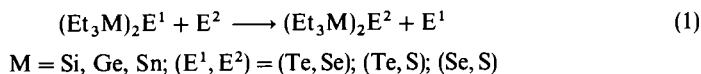
1. Si—Si bonds

In 1980 Wojnowska et al.[37] reported that one selenium atom was inserted in decamethylcyclopentasilane (**22**) to give the cycloselenapentasilane **23**, whereas the dodecamethylcyclohexasilane was unreactive.
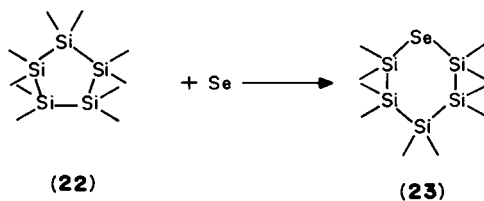
Later, octamethylcyclotetrasilane (**24**) was found to insert one or two selenium atoms to give **25** or **26** depending on the reaction temperature[38,39], and the conversion of hexa-*tert*-butylcyclotrisilane into **27** has recently been reported[40].

(24)   (25)   (26)

(27)
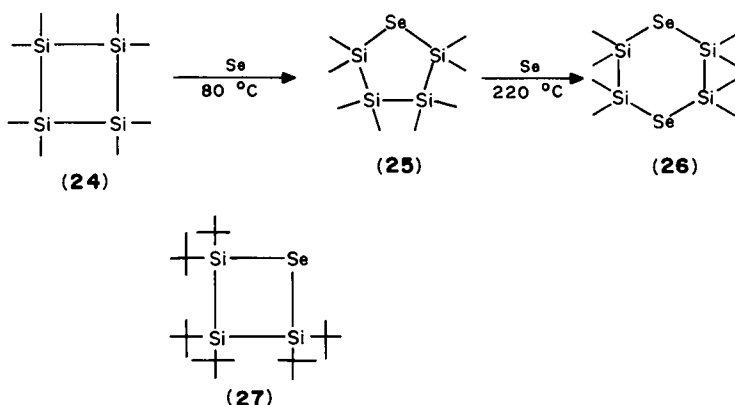
The tellura analogues of **23** and **25–27** have not been reported, although bis(trialkylsilyl)tellurides are known[36] and tellurium insertion in a Si—Si bond by an indirect route involving a silylphosphine has been reported (see Section II.C).

2. Ge—Ge and Sn—Sn bonds

Bochkarev and coworkers[35,36,41,42] have studied the reaction of hexa-substituted digermanes and observed the insertion of selenium while tellurium was unreactive[35].

$$R^1_3GeGeR^2_3 + Se \xrightarrow{\ 100\ °C\ } R^1_3GeSeGeR^2_3$$

$$R^1,\ R^2 = C_6F_5,\ alkyl$$
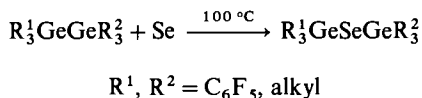
More recently the insertion of both selenium and tellurium into the Ge—Ge bond of 1,1,2,2-tetra-*tert*-butyldigermane to give the four-membered rings (**28**) (M = Ge, E = Se, Te) has been reported[43].

$$\left.\begin{array}{l}(t\text{-Bu})_2GeH—HGe(Bu\text{-}t)_2 + E\\ [(t\text{-Bu})_2Sn]_4 + E\end{array}\right\} \longrightarrow (t\text{-Bu})_2M\overset{E}{\underset{E}{\diagup\!\!\!\diagdown}}M(Bu\text{-}t)_2$$

(30)   (28)

E=Se,Te; M=Ge,Sn
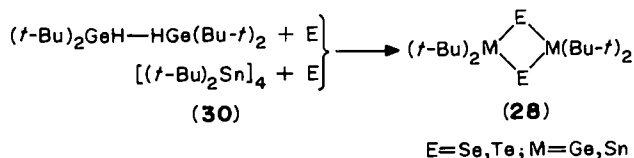
Hexaethyldistannane reacts with selenium insertion to give bis(triethylstannyl)selenide (**29**)[44], while octa-*tert*-butylcyclotetrastannane (**30**) inserts both selenium and tellurium with concomitant ring scission to give **28** (M = Sn, E = Se, Te)[45].

$$Et_3SnSeSnEt_3$$

(29)
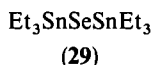
C. Group V Elements

1. N—N bonds

There appear to be no reports of the insertion of selenium or tellurium into an N—N bond or of the generation of such a bond by the extrusion of the elements. The 1,2,5-

selenadiazole ring system was found to lose selenium photochemically and thermally[46,47] or, as dialkyl selenide, on treatment with alkylmagnesium halide[48], but since ring opening rather than bond formation takes place these reactions are not considered further here.

2. P—P bonds

In the reaction of trimethylsilylphosphines (30) with tellurium[49,50], the primary insertion to give 31 is followed by an exchange reaction leading to diphosphinyl (32) and disilyl telluride (33). Compound 32 (R = Ph) extrudes tellurium to give 34 (R = Ph) whereas 34 (R = t-Bu) inserts tellurium in the P—P bond with formation of the corresponding 32. The reaction of bis(trimethylsilyl)-*tert*-butylphosphine with tellurium through a similar series of steps gives either the telluratriphosphetane (35) (low-temperature product) or the unstable telluradiphosphirane (36) (high-temperature product).

$$R_2PSiMe_3 \xrightarrow{Te} R_2PTeSiMe_3 \rightleftharpoons (R_2P)_2Te + (Me_3Si)_2Te$$

$$(30) \qquad\qquad (31) \qquad\qquad (32) \qquad (33)$$

$$32 \underset{R=\textit{t-Bu}}{\overset{R=Ph}{\rightleftharpoons}} R_2PPR_2 + Te$$

$$(34)$$

(35)   (36)

$$Ph_3PTePPh_3$$

$$(37)$$
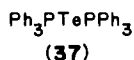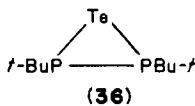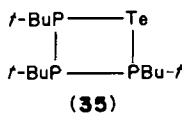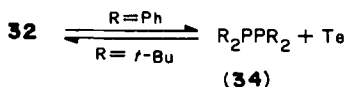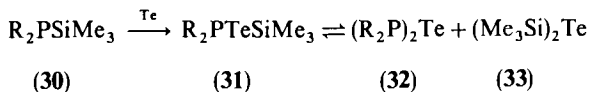
The structure of bis(triphenylphosphinyl)telluride (37) has been determined by X-ray crystallography[51] and similar structures suggested as intermediates in the tellurium exchange between phosphines and phosphinetellurides[52]. These are, however, not true insertion products since they are formed from and revert to two moles of phosphine.

The insertion of selenium in the P=P double bond of a hindered diphosphene (38) to give a selenadiphosphirane (39) has been described[53]. The selenium atom is extruded with regeneration of 38 on treatment with a phosphorus triamide.

$$RP{=}PR \underset{(Me_2N)_3P,}{\overset{Se,\,70\,°C}{\rightleftharpoons}} \quad RP \overset{Se}{\diagup\diagdown} PR$$

$$(38) \qquad\qquad\qquad (39)$$

$$-(Me_2N)_3PSe \qquad R = 2,4,6-(\textit{t-}Bu)_3C_6H_2$$
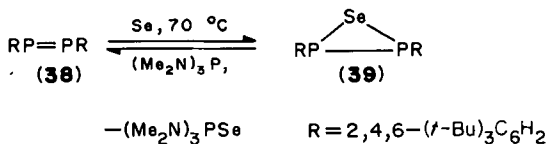
3. As—As and Sb—Sb bonds

Hexaphenylhexarsane (40) and pentamethylpentarsolane (41) insert selenium thermally in the As—As bonds with concomitant ring formation and the formation of 2,5-diphenyl-

1,3,4-triselena-2,5-diarsolane (**42**) and 2,4,6-trimethyl-1,3,5-triselena-2,4,6-triarsane (**43**), respectively[54].

$$(PhAs)_6 \xrightarrow[220\ ^\circ C]{Se} \quad (42)$$

(**40**)

$$(MeAs)_5 \xrightarrow[180\ ^\circ C]{Se} \quad (43)$$

(**41**)
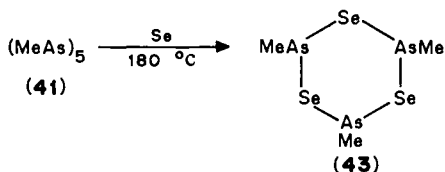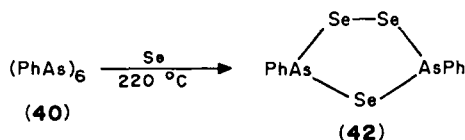
Selenium inserts in the As—As bonds of **44** to give a diselenatriarsolane ring (**45**)[55], the structure of which has been determined by X-ray crystallography[56]. Curiously, selenium was inserted faster than sulphur while attempted tellurium insertion was unsuccessful.

(**44**)   (**45**)
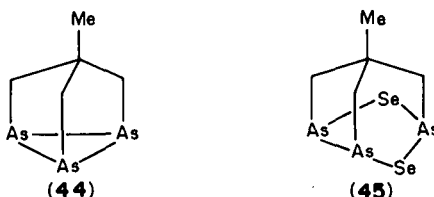
The insertion of selenium and tellurium into Sb—Sb bonds with the formation of distibinyl selenides and tellurides, respectively, has recently been reported[57].

$$R_2SbESbR_2$$

R	E
Me	Se, Te
Et	Se, Te
Ph	Se

D. Group VI Elements

1. General remarks

Compounds containing an E^2—E^1—E^2 moiety (E^1 = Se, E^2 = S, Se) as selenium rings and chains, as mixed sulphur—selenium rings or as diorgano polyselanes or poly-thiaselanes freely undergo exchange reactions under mild conditions which leave bonds to second-row elements untouched. These reactions often give rise to complex equilibrium mixtures and neat selenium insertion or extrusion may result. The high polarizability of selenium opens up four alternative reaction routes, all of which are experimentally supported. The exchange reactions may proceed uncatalysed via a (thermally or photochemically induced) free-radical pathway (equation 2), or in a concerted process (equation 3). Alternatively, generalized acids or bases may catalyse the exchange through cationic (equation 4) or anionic (equation 5) intermediates, respectively.

$$-E^1-E^2-E^1-- \rightleftharpoons -E^1-E^2\cdot + \cdot E^1- \longrightarrow \text{reaction chain} \qquad (2)$$

$$2-E^1-E^2-E^1- \rightleftharpoons \begin{matrix} -E^1 \\ \\ -E^1 \end{matrix} E^2 \begin{matrix} E^1- \\ \\ E^2-E^1- \end{matrix} \rightleftharpoons \begin{matrix} -E^1 & E^2-E^1- \\ | & + | \\ -E^1 & E^2-E^1- \end{matrix} \qquad (3)$$

$$-E^1-E^2-E^1-- + A^+ \longrightarrow \begin{matrix} E^1A + {}^+E^2-E^1- \\ \text{or} \\ -E^1-E^2A + {}^+E^1- \end{matrix} \longrightarrow \text{reaction chain} \qquad (4)$$

$$-E^1-E^2-E^1- + B^- \longrightarrow \begin{matrix} -E^1B + {}^-E^2-E^1- \\ \text{or} \\ -E^1-E^2-B + {}^-E^1- \end{matrix} \longrightarrow \text{reaction chain} \qquad (5)$$
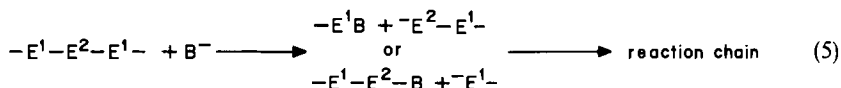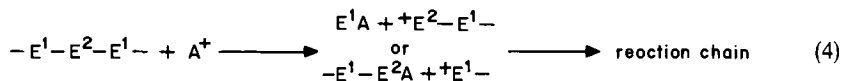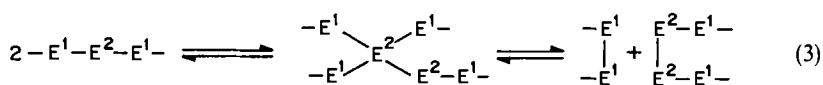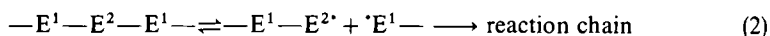
2. Selenium and interchalcogen compounds

On dissolution in CS_2, pure Se_8 has been found to equilibrate with Se_7 and Se_6 rings within 5 min at room temperature[58]. The Se_2S_5 ring (46) prepared from diethyltitanium pentasulphide and selenium dichloride undergoes disproportionation with $t_{1/2} \approx 1$ h in CS_2 at room temperature to give, specifically, the six- and eight-membered rings, 47 and 48. Concerted addition of a chalcogen—chalcogen bond to a selenium atom with formation of an intermediary selenurane (49) is suggested to account for the ease and specificity of the exchange process[59].
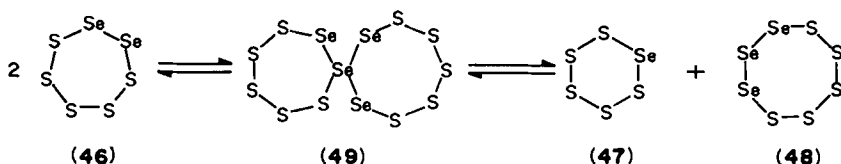
A similar type of mechanism is suggested by mechanistic studies of the decomposition of tetraorganotellururanes (50) to give diorganotellurides and C—C coupled products[60] and may also be involved in the extrusion of tellurium from tetrakis(alkylthio)tellururanes (51) with formation of disulphides[61].

$$(RS)_4Te \xrightarrow{\sim 100\,°C} 2RSSR + Te$$
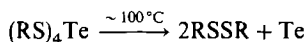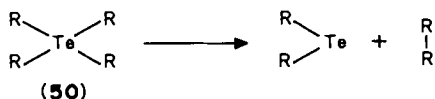
(51)

A rapid base-catalysed exchange process in selenium chains has been observed by ^{77}Se NMR[62]. A solution of polyselenide ion in DMF with an average chain length of 4 shows a single broad signal at ca. 50°C but distinct signals from tetra- and penta-selenide ion at -60 °C. Obviously these anionic exchange processes are even faster than those observed in neutral rings.

3. Dialkyl(aryl) polyselanes and thiaselanes

The reactions of 1,3-diorgano 1,3-dithia-2-selanes (52) [bis(alkylthio) selenides] with nucleophiles have been studied. With hydroxides the reaction proceeds according to equation 6[63], indicating attack on selenium with subsequent disproportionation of the Se^{II} species formed. In contrast, sulphur nucleophiles attack on S with formation of a disulphide and selenium (equation 7). This latter reaction is suggested to be involved in the handling of selenium by biological systems[63-65].

$$2\,RSSeR + 6\,OH^- \longrightarrow 4\,RS^- + Se + SeO_3{}^{2-} \tag{6}$$

(52)

$$52 + R^1S^- \longrightarrow RSSR^1 + RSSe^- \longrightarrow RS^- + Se \tag{7}$$
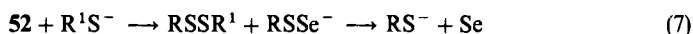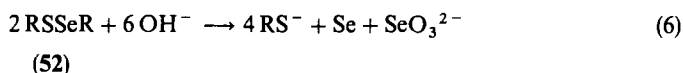
A study[66] of the selenium extrusion from the two isomeric purinyl-1,3-dithia-2-selanes 53 and 54 in an aqueous medium showed a curious difference between the two isomers: 53 was stable at all pH values, whereas the rate of selenium extrusion from 54 increased from low pH to reach a maximum at pH 6.7 followed by a decrease to a minimum at pH 8.9 and a steady rise at higher pH values

(53)   (54)
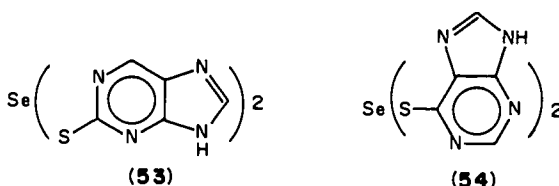
The photochemical formation of mixed dimethylthiaselanes from dimethyl disulphide and selenium has been mentioned but no experimental details were given[67].

It is a long established fact that diorgano polyselanes (55) are formed in thermal reactions between selenides or diselenides and elemental selenium[1] and that the pyrolysis of benzylic diselenides at temperatures below those leading to total selenium extrusion and C–C coupling (see Section III.C) gives a mixture of monoselenide and 55[12,13].

$$RSe_2R + Se \longrightarrow RSe_nR \xleftarrow[-Se]{RX} Se_m{}^{2-}$$

(55)   (56)

$(n \geqslant 3)$
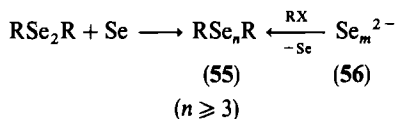
The alkylation of polyselenide ions (56; $n \geqslant 3$) in DMF or DMSO solution[68] is accompanied by precipitation of selenium and the average selenium content in 55 is ca. 2.4 atoms per molecule regardless of the chain length in 56. ^{77}Se NMR has revealed the presence of all the polyselanes with chain lengths 2–6 and the coupling pattern in the [77]Se–[77]Se satellite spectrum has proved the chain structure. An identical mixture of 55 has been observed on treatment of pure diselenide with selenium in the presence of an acid catalyst, indicating that an equilibrium mixture is formed. Thus the Se–Se exchange reaction catalysed by selenolate and/or polyselenide ion (equation 4, Section II.D.1) has a rate comparable to or higher than that of the alkylation of these ions.

Attempts to separate the individual compounds (55) by chromatography normally result in selenium extrusion and concentration of the diselenide. Undoubtedly column materials such as silica gel and alumina act as acid catalysts for the Se–Se exchange processes. Instability of 55 to TLC has been reported previously[13].

A few benzylic triselanes, notably with halogen substituents (57), are able to pass through a silica gel column unchanged. Some of these have been isolated from the alkylation of polyselenide ion[68,69] and one structure (57, Ar = 2,4-Cl$_2$C$_6$H$_3$) determined by X-ray crystallography[69]. However, even these compounds revert to the equilibrium mixture on treatment with strong acid. The bis(o-bromo- and -iodo-benzyl)tetraselanes 58 also pass unchanged through silica gel as shown by ^{77}Se NMR, but have not been separated from the corresponding triselanes.

$$ArCH_2SeSeSeCH_2Ar \qquad o\text{-}XC_6H_4CH_2Se_4CH_2C_6H_4X\text{-}o$$

$$(57) \hspace{5cm} (58)$$

$$X = Br, I$$
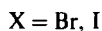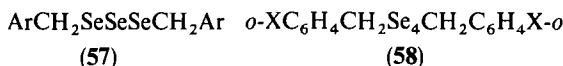
4. Selenium(II) and tellurium(II) dichalcogenocarbamates

Dialkyldiselenocarbamate ions (59), in contrast to their thio analogues, on mild oxidation form a mixture of a bis(dialkylselenocarbamoyl)selenide (60) and a bis(dialkyldiselenocarbamato)selenium(II) (61)[70,71]. The latter structure has been confirmed by X-ray crystallography[72,73]. N-Alkyldiselenocarbamates (59; R^1 = H) give the unstable 61 (R^1 = H)[74], while trimethyldiselenocarbazate is oxidized to the diselenide (62; R^1 = Me, R^2 = NMe$_2$)[71].

$$(R_2NCSe)_2Se$$
$$(60)$$

$$4\ R_2NCSe_2^- \xrightarrow{\text{[O]}}$$
$$(59)$$

$$Se, H^+ \Big\updownarrow (EtO)_3P$$

$$R_2NC\overset{Se}{\underset{Se}{\diagdown}}\hspace{-0.2cm}Se\overset{Se}{\underset{Se}{\diagdown}}\hspace{-0.2cm}CNR_2$$
$$(61)$$

$$(R^1R^2NCSe_2)_2$$
$$(62)$$
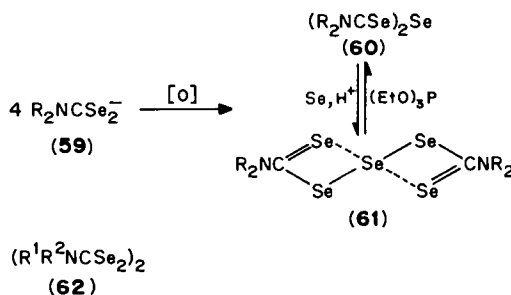
Compounds 60 and 61 are readily interconverted; 60 is equilibrated with selenium by acid catalysis to give 61 almost quantitatively; the deselenation 61 ⟶ 60 requires that selenium is removed, e.g. by a phosphite. The equilibrium 2 62 ⇌ 60 + 61 was observed for R^1 = Ph, R^2 = Me. In this case 61 spontaneously extrudes selenium to give 62 on attempted isolation[71].

$$Y-C\overset{E^2}{\underset{E^2}{\diagdown}}\hspace{-0.2cm}E^1\overset{E^2}{\underset{E^2}{\diagdown}}\hspace{-0.2cm}C-Y$$
$$(63)$$

$$Y = RO, R_2N$$
$$E^1 = Se, Te$$
$$E^2 = S, Se$$
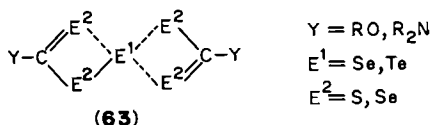
A number of compounds of the general structure 63 are known (see Ref. 75 for a recent review). These are often prepared from the YCE$_2^-$ ions and an Se^{IV} or Te^{IV} species. In an alternative preparation[76] the anions react with selenium or tellurium pentathionate, a reaction which may be considered as an analogue of the anionic exchange processes in selenium chains (Section II.D.2).

$$^-O_3SSE^1SSO_3^- + 2\,YCE_2^- \longrightarrow 63 + 2\,S_2O_3^{2-}$$
$$E^1 = Se, Te$$
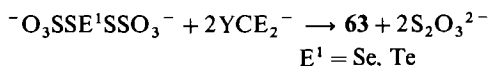
In addition to **61**, one compound of structure **63** [Y $= (CH_2)_5N, E^2 = S, E^1 = Se$] has been prepared by acid-catalysed selenium insertion in the corresponding disulphide and there is reason to believe that this insertion is general as far as the resulting **63** is a stable structure[77].

E. Bonds Between Group VI and VIII Metals

In recent years it has been demonstrated that selenium and tellurium can be inserted in metal—metal bonds of the Group VI–VIII metals. The insertion of one, two and four selenium atoms in the Cr—Cr bond of dicyclopentadienylhexacarbonyldichromium has recently been reported[78]. Brunner *et al.*[79] found that four selenium atoms are inserted in the Mo—Mo triple bond of **64** to give **65**, whereas a different type of compound (**66**) is obtained by the insertion in the W—W triple bond of the tungsten analogue of **64**.

$$C_5Me_5(CO)_2Mo\equiv Mo(CO)_2C_5Me_5 \xrightarrow{\text{Se}} $$

(64)

(65)

(66)
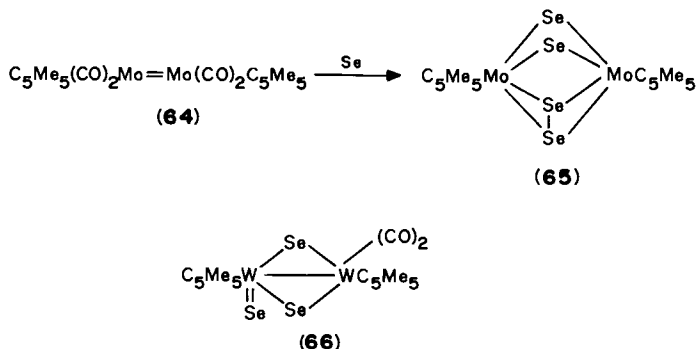
Hofmann and Werner[80] investigated the insertion of chalcogens in a Co—Co single bond, viz. the reaction **67** ⟶ **68**, and found the order of reactivities S > Se > Te.

(67)   **(68)**

E = S, Se, Te

The facile insertion of selenium in Co—Co and Rh—Rh double bonds has been reported by Herrmann *et al.*[81], who observed the conversion **69** ⟶ **70**.

(69)   **(70)**

M = Co, Rh

The insertion of both selenium and tellurium in osmium and ruthenium cluster compounds has also been reported[82].

III. HETEROGENEOUS BONDS INVOLVING CARBON

A. Bonds to Hydrogen or Group IA or IIA Elements

1. General remarks

The most common and reliable method for the generation of selenols and tellurols (71) involves the insertion of the free elements in the (partially ionic) bonds between carbon and the Group IA and IIA metals. The reactive carbanionic intermediates may be generated by direct hydrogen–metal exchange or via halogenation and halogen–metal exchange (equation 8). Moreover, the air-sensitive selenols and tellurols are usually not isolated but derivatized *in situ*, directly from the metal salts or with preceding protonation. Therefore, it is natural to treat the insertion of selenium and tellurium in the C—H and the C—Group IA and C—Group IIA metal bonds jointly. The insertion of tellurium in C—metal bonds has recently been reviewed[83].

$$CH \xrightarrow[\text{or}]{B^-H^+} C^-M^+ \xrightarrow{E} CE^-M^+ \xrightarrow{H^+} CEH \qquad (8)$$

$$\text{(i)}X_2 \qquad\qquad (71)$$
$$\text{(ii)}M$$

An indication of the strength of a carbon base needed for insertion of selenium is found in the observation that metal enolates ($pK_A \approx 20$) give insertion products (72) isolated as methyl selenides (73) in high yields (equation 9)[84] while the anions of β-dicarbonyl compounds ($pK_A \approx 10$) are formed spontaneously from the corresponding selenolates (Section II.A.2). On the other hand, alkali cyanides ($pK_A \approx 9$) readily insert both selenium and tellurium with formation of the corresponding chalcogenocyanates[1,3]. This shows that not only the strength but also the softness (cf. Pearson[85]) of the anion influence the insertion reaction.

$$(72) \qquad\qquad (73) \qquad (9)$$

The insertion depicted in equation 9 probably also constitutes the initial reaction in the reported[86] formation of 74 from pentanone, selenium and aziridines.

(74)

R = H, Me

2. Alkynes

The insertion of selenium and tellurium in metal—alkyne bonds (equation 10) is well documented[1,3].

$$RC{\equiv}C^-M^+ + E \longrightarrow RC{\equiv}CE^-M^+$$

$$E = Se, Te; \; M = Li, Na, K, MgX \qquad\qquad (10)$$

A number of recent examples on the use of these reactions are collected in Table 1.

Trofimov and coworkers[100,101] investigated the reaction of selenium and tellurium with acetylene in the presence of potassium hydroxide in dipolar aprotic solvents (DMSO and HMPA) at about 100 °C. These conditions do not lead to insertion. Instead, a formal addition of H_2E giving divinyl chalcogenides (77) predominates. The mechanism involved is still obscure. Pre-formed selenide ion does not give the addition product[100]. A mechanism involving nucleophilic addition of a $ROSe^-$ species was proposed[101] but seems improbable in view of the rapid disproportionation of Se^{II} to give selenite and polyselenide ion[102] in the media employed. The latter ions might, however, add to the acetylene and a rapid Se–Se exchange (Section II.D.2) will then produce the assumed ethynylselenolate intermediate.

(77)   E = Se, Te
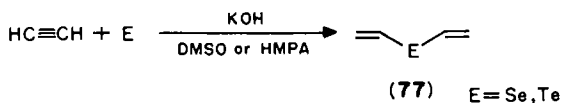
3. Arylmetal compounds

The insertion of selenium[1] and tellurium[3] in the C—metal bonds of arylmetals is by far the most widespread and reliable route to seleno- and telluro-phenols and their derivatives. Recently, diphenyl diselenide and ditelluride have received renewed interest as the stable precursors of several important reagents for organic synthesis, e.g. selenols, tellurols, selenyl halides and seleninic acids. A number of authors have reinvestigated their formation from arylmetals. The results are compared in Table 2. The data show that phenyllithium in THF offers the best choice of conditions and that the advantage is particular striking for the tellurium compound.

Another recent contribution[108] introduces the purification of areneselenolates via Se-arylthioselenocarbamates (78). The aryllithium path has also been used for the introduction of selenium[109,110] and tellurium[111] into five-membered heterocycles. In thiophenes the α-lithium reagent can be prepared by H–Li exchange while the β-reagent requires halogen–Li exchange[109,112]. Two chalcogen atoms have been introduced by a two-step insertion procedure as in 79[113,114], 80[112] and 81[112,115,116], while tellurium atoms were introduced in 82 in a single step[117]. The ferrocene derivative 83 was obtained by selenium insertion in 1,1'-ferrocenyldilithium[118].

ArSeO(S)NMe$_2$

(78)

(79)

(80)   (81)

$E^1, E^2 =$ S and/or Se and/or Te

(82)

(83)
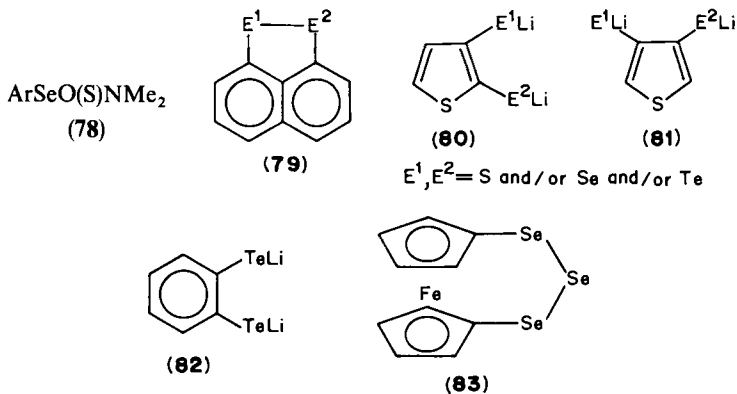
TABLE 1. Products from 1-alkynylchalcogenates $(RO\equiv CE^-M^+)$ formed according to equation 10

Reagent	Product				Ref.
CY$_2$		R	E	Y	
		Ph	Se	Se	87
		H	Se	Se	88
		H	Se	S/Se	89
		Ph	Se	Se	90
H$^+$	**(75)**				91
	(76)^a				92, 93
(i) ICH$_2$Cl (ii) Te^{2-}					94
(i) BuLi (ii) BuLi/t-BuOK (iii) Se					95
R^{2}X	RC$\equiv$CER^2	R	E	R^2	
		t-Bu	Se	CH$_2$CH=CH$_2$	96, 97
		Me$_3$Si	Se	CH$_2$CH=CH$_2$	96
		Me, t-Bu	Se	SiMe$_3$	97
		Me$_3$Si	Se	CH$_2$C$\equiv$CH	97
		H	Se	Me	98
		H	Te	Me	98

^{a} Compound **76** was originally assumed to have the ditellurolan structure analogous to **75**[99]. Structure **76** has subsequently been determined by X-ray diffraction[93].

TABLE 2. Preparation of diphenyl diselenide and diphenyl ditelluride

$$2\,PhM + 2E \longrightarrow 2\,PhE^-M^+ \xrightarrow{[O]} PhEEPh$$
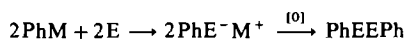
E	M	Solvent	Yield (%)	Ref.
Se	MgBr	Et$_2$O	55–71^a	103
Se	MgBr	Et$_2$O	64–70^b	104
Se	Li	THF	80	105
Te	MgBr	Et$_2$O	48	106
Te	MgBr	THF	55–85	107
Te	Li	Et$_2$O	51	106
Te	Li	THF	100	105

^{a}Oxidation with air.
^{b}Oxidation with bromine.

4. Alkyl- and alkenyl-metals

The reaction of benzylmagnesium chloride with selenium is reported to give up to 71% of products derived from benzylselenomagnesium chloride[119] and vinylmagnesium bromide reacts with tellurium to give vinyltelluromagnesium bromide, from which 72% of Te-vinyl thiotellurocarbamate (84) was isolated[120].

(84)

The reaction of methyl- and butyl-lithium in diethyl ether is reported to give the selenolates pure and in almost quantitative yields (room temperature, 15 min)[121]. The reaction of alkyllithiums with tellurium proceeds readily in THF. Yields of 89 and 84% of dibutyl and di-*tert*-butyl ditelluride, respectively, are reported by this route[122]. Sodium and lithium carboranes insert selenium in the C—metal bond to give after oxidation the dicarboranyl diselenides[123].

5. Insertions not involving carbanions

The reaction of benzylic halides with sodium polyselenide in DMSO may lead to selenium insertion in the benzylic C—H bonds with formation of a diselenobenzoate (85)[102]. The mechanism probably involves a series of 1,2-eliminations in benzylpoly-selenide anions (equation 11) since it is only observed with acidic α-protons and it requires the presence of excess of base.

$$\text{Ph--CH(SeR)}_2$$

(86)

The first elimination step seems documented since the reaction can be arrested and diselenoacetals (86) trapped. Whether the last step forming 85 is another elimination as depicted or alternatively a hydride transfer to selenium is unknown.

The insertion of selenium in the C—H bond of dimethylformamide in the presence of sodium hydroxide has been described[124] (equation 12). The authors discount a car-banionic intermediate since no products from the condensation of such species were found. On the other hand, an addition-elimination sequence such as equation 11 is highly improbable. Polyselenide ion is formed under the reaction conditions[102] but the formyl hydrogen atom has hydride rather than acidic character. The observation of sodium

selenide which is not formed by selenium disproportionation makes it plausible that polyselenide addition in this case is followed by hydride transfer to selenium.

$$Me_2NCHO + Se \xrightarrow{HO^-} Me_2NC(O)Se^- + Se^{2-} \tag{12}$$

B. Covalent Carbon—Metal Bonds (Group III–VIII Metals)

1. Aluminium

An efficient preparation of dimethylaluminium methyl selenide (87) has appeared[125].

$$Me_3Al + Se \xrightarrow[\text{reflux, 3 h}]{PhMe} Me_2AlSeMe$$

(87)
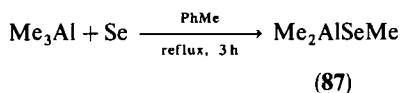
2. Group IV metals

The reported[126] conversion 88 → 89 may involve preliminary Se insertion in the C—Sn bonds.

(88)   (i) Se
             (ii) MeLi
             (iii) PhCH₂Cl   (89)
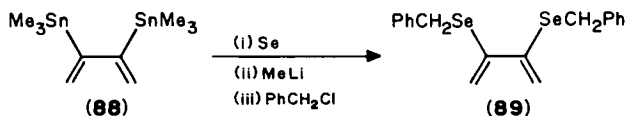
3. Group VI metals

Insertion of selenium in the C—M bonds of carbene complexes (90) with M = Cr, W takes place with phenyl isoselenocyanate as the Se-transfer reagent and gives the corresponding selenoketone complexes (91)[127].

$$(CO)_5M = CAr_2 \xrightarrow{PhNCSe} (CO)_5MSe = CAr_2$$

(90)   (91)

M = Cr, W
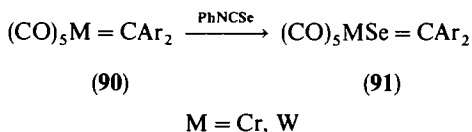
The conversion of 92 into O-methyl selenobenzoate with elemental selenium[128] could proceed via a type 91 intermediate.

(92)   (93)
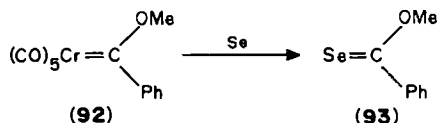
Metal carbyne complexes (94) readily insert two selenium atoms in the C—M bond with formation of diselenocarboxylato complexes (95)[129].

(94)   (95)
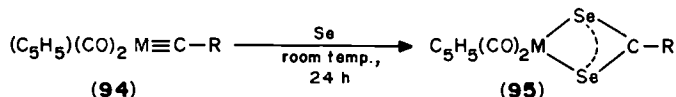
M = Mo; R = CH₂Bu-t
M = W ; R = C₆H₄Me-p

4. Group VIII metals

The cobalt complex **96** inserts selenium directly in the C—Co bond with formation of **97**, while the trinuclear bis(carbyne) cobalt clusters **98** react with selenium insertion in C—Co bonds and simultaneous carbon–carbon coupling to give **99**[130].

(96)   **(97)**

$$L_3 = MeC(CH_2PPh_3)_3$$

(98)   **(99)** $L = C_5H_5$
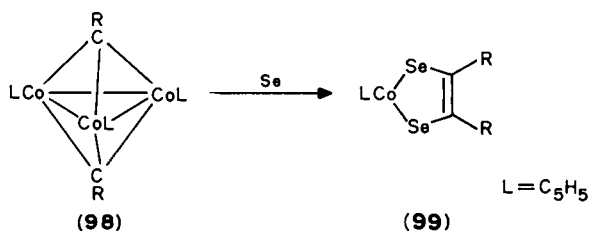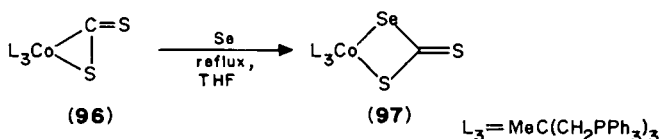
Reaction of the rhodium complex **100** with sulphur, selenium and tellurium results in ultimate replacement of the metal with a chalcogen atom to give **101**. The order of reactivities is $S > Se > Te$[131]. A reaction path involving initial insertion in the C—Rh bond could be envisaged.

(100)   **(101)**
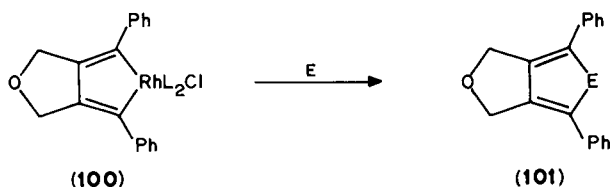
C. Bonds to Group VB–VIIB Elements

1. Nitrogen

The occurrence of the C—E—N moiety is mainly restricted to heterocycles of the selenazole type. Such compounds readily extrude selenium in thermal and photochemical processes. The chemistry of the 1,2,3- and 1,2,4-selenadiazole and the 1,2,3,4-selenatriazole rings has recently been reviewed[132]. The selenium extrusion is part of a fragmentation pattern initiated by the loss of a Y≡N unit (equation 13) and will not be treated in further detail here.

$$(13)$$

(Y,Y=RC,N or N,N)
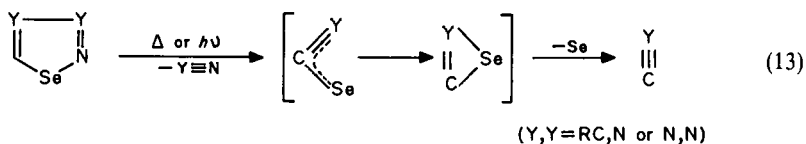
2. Group VIB elements

The thermally or photochemically induced extrusion of selenium and tellurium from diorgano diselenides (**102**) and ditellurides (**103**) to give, respectively, diorgano-selenides (**104**) and -tellurides (**105**) and the converse insertions (equation 14) have received much attention.

$$\text{REER} \underset{}{\overset{\Delta \text{ or } h\nu}{\rightleftharpoons}} \text{RER} + \text{E}$$

$$(\mathbf{102})\,\text{E}=\text{Se} \qquad (\mathbf{104})\,\text{E}=\text{Se} \qquad\qquad (14)$$

$$(\mathbf{103})\,\text{E}=\text{Te} \qquad (\mathbf{105})\,\text{E}=\text{Te}$$
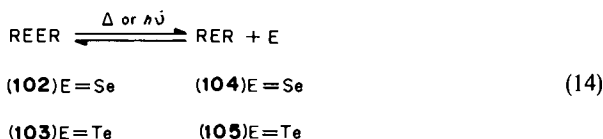
Krafft and Lyons[133] studied the thermal reaction of **104** (R = Ph) with selenium and obtained about 33% conversion into **102**. At temperatures above 220 °C the converse reaction took place. A later study[134] of the same reaction at about 290 °C indicated that an equilibrium mixture of selenium and mono-, di- and tri-selane is formed. Lardon[12] investigated the thermal reaction of **102** (R = PhCH$_2$). At 150–170 °C an equilibrium between **102, 104** and polyselanes is observed whereas above 200 °C the reaction proceeds with further loss of selenium and formation of bibenzyl. A similar behaviour of **102** (R = Ph$_2$CH) has been reported[13]. Compound **103** (R = PhCH$_2$) extrudes tellurium to give **105** at a lower temperature (ca. 120 °C) than its selenium analogue[18]. Flash vacuum thermolysis of **102** (R = Me) at 550 °C gives rise to a mixture of the corresponding **104**, methane and methaneselenol[135]. On UV irradiation in the absence of oxygen **102** and **103** (R = PhCH$_2$) cleanly extrude one chalcogen atom with formation of **104**[136,137] and **105**[18,138], respectively. It has been noted that **103** reacts faster than **102** and that the rate for **103** (R = PhCH$_2$) is about 10 times that of **103** (R = Et) in the photochemical process.

The thermal and photochemical chalcogen extrusion from **102** and **103** is generally discussed in terms of two competing radical type scissions (equations 15 and 16, respectively).

$$\text{REER} \begin{cases} \longrightarrow 2\text{RE}^{\cdot} & (15) \\ \qquad (\mathbf{106}) & \\ \longrightarrow \text{REE}^{\cdot} + \text{R}^{\cdot} & (16) \end{cases}$$
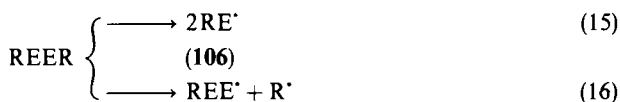
Equation 15 has the lower activation energy but produces only the low-energy chalcogen-based radicals (**106**). The fate of these apart from recombination can only be the attack on a chalcogen atom of the starting material giving a trivial reaction when the two R groups are identical but gives scrambling of different R groups (equation 17). Equation 16 with the higher activation energy also produces the more reactive carbon-based radicals which give rise to extrusion products **104, 105** and hydrocarbons (equation 18).

$$\text{R}^1\text{E}^{\cdot} + \text{R}^1\text{EER}^2 \longrightarrow \begin{cases} \text{R}^1\text{EER}^1 + \text{R}^2\text{E}^{\cdot} \\ \text{R}^1\text{EER}^2 + \text{R}^1\text{E}^{\cdot} \end{cases} \qquad (17)$$

$$\text{R}^{\cdot} + \text{REER} \longrightarrow \begin{cases} \text{RER} + \text{RE}^{\cdot} \\ \text{RR} + \text{REE}^{\cdot} \end{cases} \qquad (18)$$
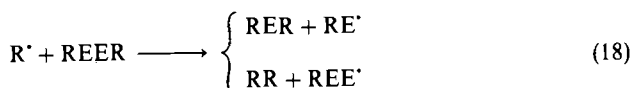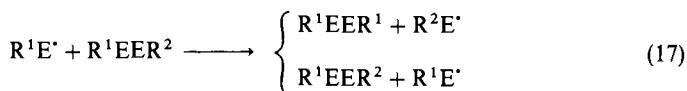
These concepts are supported by two facts: firstly, a clean extrusion reaction from **102** is observed only when R$^{\cdot}$ is a stabilized carbon radical; and secondly, a pronounced increase in the rate of the conversion **102** to **104** is observed on introduction of a phosphorus(III) species. The use of a tris(dialkylamino)phosphite in the thermal extrusion of selenium from

102 (R = Me) has been reported[139]. The quantum yield in the photochemical conversion of **102** (R = PhCH$_2$) rises from 0.16 in the absence[137] to 4.7 in the presence of triphenylphosphine[140]. The rates of the photochemical selenium extrusion from **102** (R = PhCH$_2$, Et, Me, Ph) is raised by several orders of magnitude on addition of methyldiphenylphosphine. The relative half-lives of the four compounds are given as 1:6:24:240, indicating that C—Se bond breaking is still involved in or before the rate-determining step[141,142]. Similar but less pronounced trends are reported for **103** (R = PhCH$_2$, Et)[138]. In accord with these observations, the role of the phosphine is assumed to be the trapping of the organoselenyl radical **106** as **107** in competition with its recombination. Further, the formation of a phosphine chalcogenide facilitates the C—E bond breaking and a radical chain is set up through equations 18 and 19.

$$106 + PR_3 \longrightarrow R^1EPR_3 \longrightarrow R^\cdot + EPR_3 \qquad (19)$$
$$(107)$$
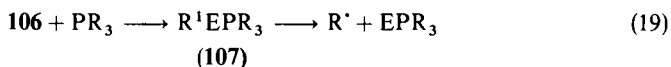
The acid-catalysed insertion of selenium in a C—Se bond in bis(selenocarbamoyl)selenides **(60)** has been discussed in another connection (Section II.D). A mechanistically related reaction with ultimate selenium extrusion takes place between dialkyl(aryl) diselenides and **60** (equation 20)[102,143].

$$(R_2^1NCSe)_2Se + 2\,\mathbf{102} \rightleftharpoons 2R_2^1NCSeSeR + Se \qquad (20)$$
$$(60)$$
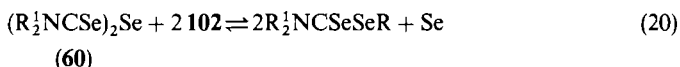
The reaction is initiated by electrophilic activation of **60**. It is reversible and various dialkyl and alkylacyl polyselanes are observed in the reaction mixture[102]. The removal of selenium by coupling to the conversion **60** to **61** displaces the equilibrium to the right and makes the reaction a useful synthetic route to diselenocarbamates **108** inaccessible by nucleophilic substitution reactions (equation 21)[143]. The equilibrium **20** has also been observed with diselenides **109**[102] and **110**[102] and appears to be general for acyl-type selenides and diselenides.

$$2(R_2^1NCSe)_2Se + 3\,R^2SeSeR^2 \longrightarrow 4R_2^1NCSe\text{-}SeR^2 + (R_2^1NCSe_2)_2Se \qquad (21)$$
$$\quad(60)\qquad\qquad\quad(102)\qquad\qquad\quad(108)\qquad\qquad\quad(61)$$

$$(EtOCSe)_2 \qquad (PhCOSe)_2$$
$$(109)\qquad\qquad(110)$$
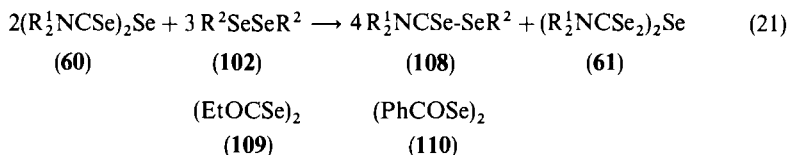
The reactions shown in equation 22 have been reported. These reactions may involve selenium insertion in a C—S bond in the thiazet **111** and its subsequent extrusion during different reactions[144].

$$(22)$$
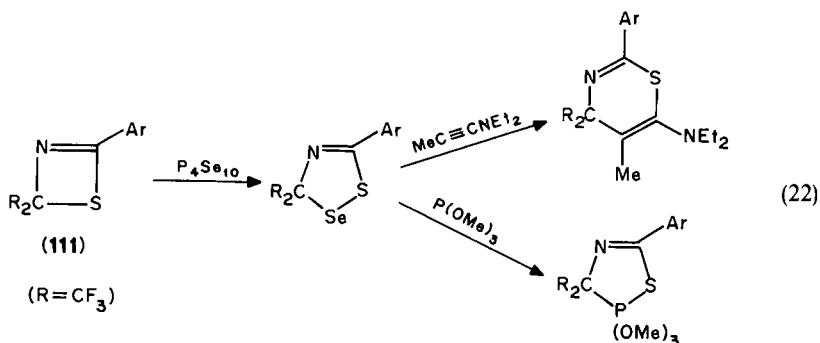
In the presence of bromine selenium is inserted in one double bond of carbon diselenide with simultaneous bromination of the other selenium atom with formation of 1,2,3-tri-

selenetan-4-(Se,Se-dibromoselone) (112), the structure of which was determined by X-ray crystallography[145]. The reaction is specifically catalysed by bromide ion and involves (1) the formation of selenium bromide, (2) the reversible generation of bromodiselenide (113) and tribromide ions and (3) attack by 113 on carbon diselenide followed by cyclization and bromine addition[102,145].

$$2\,Se + Br_2 \longrightarrow Se_2Br_2 \underset{\xrightarrow{\hspace{1.2cm}}}{\overset{2\,Br^-}{\rightleftharpoons}} BrSe_2^- + Br_3^- \xrightarrow{CSe_2}$$

$$(113)$$

$$(112)$$

3. Group VIIB elements

The insertion of tellurium in C—I bonds is reported as a synthetic route to diorganotellurium diiodides (114)[3,83].

$$2RI + Te \longrightarrow R_2TeI_2$$
$$(114)$$

IV. HETEROGENEOUS BONDS INVOLVING ELEMENTS OTHER THAN CARBON

A. Bonds to Hydrogen and to Alkali Metals

1. Elements outside Group VI

By analogy with the finding for carbon (Section III.A), the base-induced insertion of selenium and tellurium in A—H bonds appears to be a general reaction provided that A⁻ is sufficiently nucleophilic. However, insertions under neutral conditions are also recorded in particular for third-row and higher row elements.

The insertion of selenium into a boron—hydrogen bond with formation of diboranyldiselenide (115) has been reported[146].

$$(115)$$

Similar reactions (equation 23) of stannanes, germanes and silanes with both selenium and tellurium have been observed.

$$2\,R_3MH + 2\,E \longrightarrow 2\,R_3MEH \longrightarrow (R_3M)_2E + H_2 \qquad (23)$$
$$\hspace{3cm}(116) \hspace{4cm}(117)$$

Some selenols (116) have been observed[44,147], but more often the reactions proceed to give selenides 117[36,44,147]. The cyclic stannyl selenide and tellurides (118a and b) and 119 were obtained from the elements and dimethylstannane[148,149].

(118)   (119)

(a) E = Se
(b) E = Te

Selenium dissolves in boiling piperidine and morpholine in the presence of certain lead salts, notably Pb_3O_4. Diaminopolyselanes (120) have been isolated from the solutions[150,151]. The reaction could involve insertion in the N—H bond followed by oxidation.

$$R_2N\text{-}Se_n\text{-}NR_2$$
$$(120)$$
$$R_2 = (CH_3)_5 \ (n = 4)$$
$$R_2 = (CH_2)_2O(CH_2)_2 \ (n = 2, 3, 4)$$
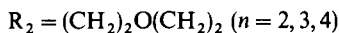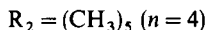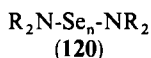
2. Group VI elements

Selenium readily inserts in the E—metal bonds of thiolate and selenolate species. The formation of sodium selenosulphate from selenium and sodium sulphite and the dissolution of selenium in alkali metal selenides with formation of alkali metal polyselenides are well known[1] examples on this type of reaction.

In spite of the vast number of papers claiming the diselenide ion (121) as an intermediate in the preparation of dialkyl diselenides (122) (equation 24), the occurrence of this ion is dubious at least in some solvents. Sharp and Koehler[152] studied the reaction of selenium and sodium selenide in liquid ammonia and observed by UV spectroscopy the tri-, tetra- and hexa-selenide ions. Their results further indicate that the equilibrium constant for disproportionation of 121 into mono- and tri-selenide ion is of the order of 10^7. A reinvestigation[62] of the formation of 122 from selenium, hydrazine, base and alkyl halides in DMF[153] (equation 25) showed that the reduction of selenium stopped at the triselenide ion stage and further reduction to 122 only took place after the introduction of the alkyl halide.

$$Se^{2-} + Se \longrightarrow Se_2^{2-} \xrightarrow{2\,RX} RSeSeR \qquad (24)$$

$$(121) \qquad\qquad (122)$$

$$4RO^- + 4Se + N_2H_4 + 4RX \longrightarrow 2\,122 + N_2 + 4ROH + 4X^- \qquad (25)$$
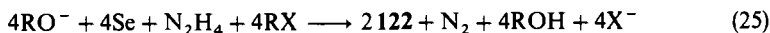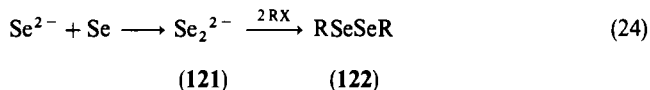
Preliminary low-temperature ^{77}Se NMR results in DMF[62] indicated the presence in this solvent of the tetra-, penta- and hexa-selenide ion whereas no sign of 121 was observed.

This type of insertion is particularly rapid in dipolar aprotic solvents. A solution of sodium phenylmethaneselenolate in DMF was found to dissolve two atoms of selenium[62].

$$PhCH_2SeNa \xrightarrow[DMF]{Se} PhCH_2Se_3Na$$

The insertion reactions are reversible and selenium is rapidly extruded on protonation of the salts.

Recently, the reaction of 1,1-ferrocene-dithiolate and -diselenolate with selenium to give **123** has been reported[118,154].

(123)   E=S,Se
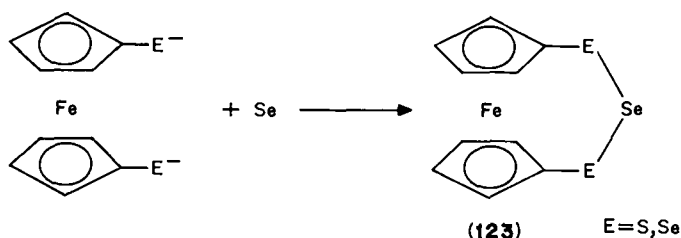
Tellurium shows less tendency than selenium to undergo these reactions. However, the strongly nucleophilic sodium telluride reacts with tellurium to give sodium di- and tetra-telluride[3,83].

$$Na_2Te \xrightarrow{Te} Na_2Te_2 \xrightarrow{Te} Na_2Te_4$$
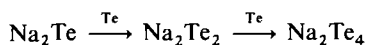
B. Miscellaneous

The insertions of selenium in boron—mercury[155,156] and boron—iodine bonds[146] have been reported. The latter report also contains an example on selenium extrusion from a diboranyl diselenide (equation 26).

$$4R_2BI + 4Se \longrightarrow 2(R_2BSe)_2 \xrightarrow[-2R_3B]{-Se} \text{(ring)} \quad (26)$$
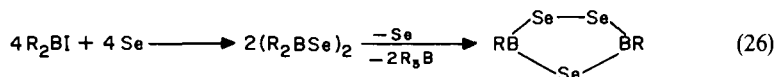
The insertion of tellurium in a Si—P bond was mentioned earlier (Section II.C).

A ready insertion of selenium in the nitrogen—chlorine bonds of two *N,N*-dichloroamides, i.e. the conversions **124** to **125** and **126** to **127**, have been described[157].

$$C_6F_5SO_2NCl_2 \xrightarrow{Se} C_6F_5SO_2N = SeCl_2$$

(124)   **(125)**

$$C_6F_5CONCl_2 \xrightarrow{Se} C_6F_5CON = SeCl_2$$

(126)   **(127)**
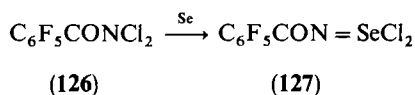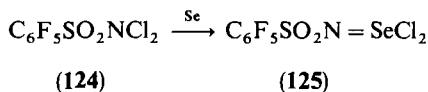
Dimanganyl diselenide (**128**) on treatment with a phosphine extrudes one selenium atom with simultaneous metal—metal coupling to give **129**[158].

$$[C_5H_5Mn(CO)_2Se]_2 \xrightarrow[-Se]{Ph_3P} C_5H_5(CO)_2Mn \text{—} Mn(CO)_2C_5H_5$$

(128)   **(129)**
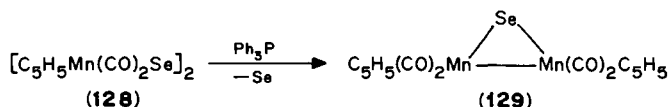
V. REFERENCES

1. D. L. Klayman and W. H. H. Günther (Eds.), *Organic Selenium Compounds*, Wiley, New York, 1973.
2. W. C. Cooper (Ed.), *Tellurium*, Van Nostrand Reinhold, New York, 1971.

3. K. J. Irgolic, *The Organic Chemistry of Tellurium*, Gordon and Breach, New York, 1974.
4. K. B. Wiberg, *Physical Organic Chemistry*, Wiley, New York, 1963, p. 138.
5. F. Toda and K. Tanaka, *Chem. Lett.*, 1451 (1979).
6. E. Culbertson, J. H. Gall and D. D. MacNicol, *Tetrahedron Lett.*, **36**, 3207 (1977).
7. E. Culbertson and D. D. MacNicol, *J. Chem. Soc., Chem. Commun.*, 498 (1974).
8. M. F. Lappert, T. R. Martin and G. M. McLaughlin, *J. Chem. Soc., Chem. Commun.*, 635 (1980).
9. A. Schönberg, E. Singer and W. Stephan, *Chem. Ber.*, **116**, 2068 (1983).
10. Ref. 1, p. 31.
11. N. L. M. Dereu and R. A. Zingaro, *J. Organomet. Chem.*, **212**, 141 (1981).
12. M. A. Lardon, *Ann. N. Y. Acad. Sci.*, **192**, 132 (1972).
13. J. Y.C. Chu and J. W. Lewicki, *J. Org. Chem.*, **42**, 2491 (1977).
14. A. Couture, A. Lablanche-Combier, R. Lapouyade and G. Felix, *J. Chem. Res. (S)*, 258 (1979).
15. T. Otsubo, F. Ogara, H. Yamaguchi, H. Higuchi and S. Misumi, *Synth. Commun.*, **10**, 595 (1980).
16. H. Higuchi, T. Otsubo, F. Ogara, H. Yamaguchi, Y. Sakata and S. Misumi, *Bull. Chem. Soc. Jpn.*, **55**, 182 (1982).
17. H. Higuchi and S. Misumi, *Tetrahedron Lett.*, **23**, 5571 (1982).
18. H. K. Spencer and M. P. Cava, *J. Org. Chem.*, **42**, 2937 (1977).
19. H. Higuchi, M. Kugimiya, T. Otsubo, Y. Sakata and S. Misumi, *Tetrahedron Lett.*, **24**, 2593 (1983).
20. H. Higuchi, Y. Sakata, S. Misumi, T. Otsubo, F. Ogura and H. Yamaguchi, *Chem. Lett.*, 627 (1981).
21. E. Cuthbertson and D. D. MacNicol, *Tetrahedron Lett.*, 1893 (1975).
22. D. L. J. Clive, P. C. Anderson, N. Moss and A. Singh, *J. Org. Chem.*, **47**, 1641 (1982).
23. J. Bergman, *Tetrahedron*, **28**, 3323 (1972).
24. J. Bergman, R. Carlson and B. Sjöberg, *Org. Synth.*, **57**, 18 (1977).
25. J. Bergman, in *Proceedings of the Fourth International Conference on the Organic Chemistry of Selenium and Tellurium* (Eds. F. J. Berry and W. R. McWhinnie), University of Aston in Birmingham, Birmingham, 1983, p. 215.
26. S. Uemura, S. I. Fukuzawa and S. R. Patil, *J. Organomet. Chem.*, **243**, 9 (1983).
27. H. Ishihara and Y. Hirabayashi, *Chem. Lett.*, 1007 (1978).
28. T. G. Back, D. H. R. Barton, M. R. Britten-Kelly and F. S. Guziec, Jr., *J. Chem. Soc., Perkin Trans. 1*, 2079 (1976).
29. E. R. Cullen, F. S. Guziec, Jr., and C. T. Murphy, *J. Org. Chem.*, **47**, 3563 (1982).
30. A. Krebs, W. Rüger, B. Ziegenhagen, M. Hebold, I. Hardte, R. Müller, M. Schütz, M. Wietzke and M. Wilke, *Chem. Ber.*, **117**, 277 (1984).
31. F. S. Guziec, Jr., C. J. Murphy and E. R. Cullen, *J. Chem. Soc., Perkin Trans. 1*, 107 (1985).
32. D. L. Clive and C. V. Denyer, *J. Chem. Soc., Chem. Commun.*, 253 (1973).
33. J. M. Behan, R. A. W. Johnstone and M. J. Wright, *J. Chem. Soc., Perkin Trans. 1*, 1216 (1975).
34. A. Ogawa, J. Miyake, S. Murai and N. Sonoda, *Tetrahedron Lett.*, **26**, 669 (1985).
35. M. N. Bochkarev, N. S. Vyazankin, L. N. Bochkarev and G. A. Razuvaev, *J. Organomet. Chem.*, **110**, 149 (1976).
36. N. S. Vyazankin, M. N. Bochkarev and L. P. Sanina, *Zh. Obshch. Khim.*, **38**, 414 (1968).
37. M. Wojnowska, W. Wojnowski and R. West, *J. Organomet. Chem.*, **199**, C1 (1980).
38. E. Hengge and H. G. Schuster, *J. Organomet. Chem.*, **231**, C17 (1982).
39. E. Hengge and H. G. Schuster, *J. Organomet. Chem.*, **240**, C65 (1982).
40. H. Weidenbruch and A. Schafer, *J. Organomet. Chem.*, **269**, 231 (1984).
41. M. N. Bochkarev, L. P. Mairova, N. S. Vyazankin and G. A. Razuvaev, *J. Organomet. Chem.*, **82**, 65 (1974).
42. M. N. Bochkarev, G. A. Razuvayev and N. S. Vyazankin, *Izv. Akad. Nauk SSSR. Ser. Khim.*, 1820 (1975).
43. M. Wojnowska, M. Noltemeyer, H. -J. Füllgrabe and A. Meller, *J. Organomet. Chem.*, **228**, 229 (1982).
44. N. S. Vyazankin, M. N. Bochkarev and L. P. Sanina, *Zh. Obshch. Khim.*, **36**, 1961 (1966).
45. H. Puff, R. Gattermayer, R. Hundt and R. Zimmer, *Angew. Chem.*, **89**, 556 (1977).
46. C. L. Pedersen and N. Hacker, *Tetrahedron Lett.* 3981 (1977).
47. C. L. Pedersen, *J. Chem. Soc., Chem. Commun.*, 704 (1974).
48. V. Bertini, A. DeMunno, A. Menconi and A. Fissi, *J. Org. Chem.*, **39**, 2294 (1974).
49. W. -W. duMont, R. Hensel and T. Severengis, *Phosphorus Sulfur*, **18**, 73 (1983).

50. W. -W. duMont, T. Severengis and B. Meyer, *Angew. Chem.*, **95**, 1025 (1983); *Angew. Chem., Int. Ed. Engl.*, **22**, 983 (1983).
51. T. Austad, T. Rød, K. Åsa, J. Songstad and A. H. Norburg, *Acta Chem. Scand.*, **27**, 1939 (1973).
52. W. -W. duMont and H. -J. Kroth, *J. Organomet. Chem.*, **113**, C35 (1976).
53. M. Yoshifiyi, K. Shibayama and N. Inamoto, *Chem. Lett.*, 603 (1984).
54. J. Ellermann and L. Brehm, *Chem. Ber.*, **117**, 2675 (1984).
55. D. Herrmann, *Z. Anorg. Allg. Chem.*, **416**, 50 (1975).
56. G. Thiele, H. W. Rotter, M. Lietz and J. Ellermann, *Z. Naturforsch., Teil B*, **39**, 1344 (1984).
57. H. J. Breunig and H. Jawad, *J. Organomet. Chem.*, **277**, 257 (1984).
58. R. Steudel and E. -M. Strauss, *Z. Naturforsch., Teil B*, **36**, 1085 (1981).
59. R. Steudel and E. -M. Strauss, *Angew. Chem.*, **96**, 356 (1984); *Angew. Chem., Int. Ed. Engl.*, **23**, 362 (1984).
60. S. A. Glover, *J. Chem. Soc., Perkin Trans. 1*, 1338 (1980), and references cited therein.
61. B. Nakhdjavan and G. Klar, *Justus Liebigs Ann. Chem.*, 1683 (1977).
62. L. Henriksen, O. Nielsen and H. Eggert, in preparation.
63. K. L. Jenkins, *Can. J. Biochem.*, **46**, 1417 (1968).
64. H. E. Ganther, *Biochemistry*, **10**, 4089 (1971).
65. J. L. Kice and H. Slebocka-Tilk, *J. Am. Chem. Soc.*, **104**, 7123 (1984).
66. M. Czauderna and K. Samochoka, *J. Chem. Soc., Perkin Trans. 2*, 765 (1983).
67. L. W. Hillen and R. L. Werner, *J. Chromatogr.*, **79**, 319 (1973).
68. H. Eggert, O. Nielsen and L. Henriksen, *J. Am. Chem. Soc.*, **108**, 1725 (1986).
69. S. Larsen and L. Henriksen, in preparation.
70. D. Barnard and D. T. Woodbridge, *J. Chem. Soc.*, 2922 (1961).
71. L. Henriksen, *Synthesis*, 771 (1982).
72. S. Esperås, S. Husebye and Å. Rolandson, *Acta Chem. Scand., Ser. A*, **29**, 608 (1975).
73. R. O. Gould, *J. Chem. Soc., Dalton Trans.*, 908 (1976).
74. L. Henriksen, *Int. J. Sulfur Chem.*, **8**, 389 (1973).
75. S. Husebye, in Ref. 25, p. 298.
76. O. Foss, *Inorg. Synth.*, **4**, 91 (1953).
77. L. Henriksen, unpublished results.
78. L. Y. Goh, C. Wei and E. Sinn, *J. Chem. Soc., Chem. Commun.*, 462 (1985).
79. H. Brunner, J. Wachter and H. Wintergerst, *J. Organomet. Chem.*, **235**, 77 (1982).
80. W. Hofmann and H. Werner, *Angew. Chem.*, **93**, 1088 (1981); *Angew. Chem., Int. Ed. Engl.*, **20**, 1014 (1981).
81. W. A. Herrmann, C. Bauer and J. Weichmann, *J. Organomet. Chem.*, **243**, C21 (1983); *Chem. Ber.*, **117**, 1271 (1984).
82. B. F. G. Johnson, J. Lewis, P. G. Lodge, P. R. Raithby, *J. Chem. Soc., Chem. Commun.*, 719 (1979).
83. N. Petragnani and J. V. Comasseto in Ref. 25, p. 98.
84. D. Liotta, G. Zima, C. Barnum and M. Saindane, *Tetrahedron Lett.*, **21**, 3643 (1980).
85. R. G. Pearson (Ed.), *Hard and Soft Acids and Bases*, Dowden, Hutchinson and Ross, Strondsburg, PA, 1973.
86. F. Asinger and M. K. Schmitz, *Monatsh. Chem.*, **113**, 1191 (1982).
87. R. Mayer and A. K. Müller, *Z. Chem.*, **4**, 384 (1964).
88. E. M. Engler and V. V. Patel, *J. Am. Chem. Soc.*, **96**, 7376 (1974).
89. E. M. Engler and V. V. Patel, *J. Org. Chem.*, **40**, 387 (1975).
90. H. Poleschner and E. Fanghängel, *J. Prakt. Chem.*, **324**, 691 (1982).
91. R. Myer, B. Hunger, R. Prousa and A. K. Müller, *J. Prakt. Chem.*, **35**, 294 (1967).
92. M. V. Lakshmikanthan, M. P. Cava, M. Albeck, L. Engman and P. Carrol, *Tetrahedron Lett.*, **22**, 4199 (1981).
93. S. L. Bender, N. F. Haley and H. R. Luss, *Tetrahedron Lett.*, **22**, 1495 (1981).
94. S. L. Bender, M. R. Detty and N. F. Haley, *Tetrahedron Lett.*, **23**, 1531 (1982).
95. H. Hommes, H. D. Verkruijsse and L. Brandsma, *J. Chem. Soc., Chem. Commun.*, 366 (1981).
96. E. Schaumann and F. -F. Grabley, *Tetrahedron Lett.*, **21**, 4251 (1980).
97. R. S. Sukhai and L. Brandsma, *Recl. Trav. Chim. Pays-Bas*, **98**, 55 (1979).
98. S. I. Radchenko, *Zh. Org. Khim.*, **13**, 2229 (1977).
99. M. L. Petrov, V. J. Laishev and A. A. Petrov, *Zh. Org. Khim.*, **15**, 2596 (1979).

100. B. A. Trofimov, S. V. Amosova, N. K. Gusarova and G. K. Musorin, *Tetrahedron*, **38**, 713 (1982), and references cited therein.
101. B. A. Trofimov, S. V. Amosova, N. K. Gusarova, V. A. Potapor and A. A. Tatarinova, *Sulfur Lett.*, **1**, 151 (1983).
102. L. Henriksen, in Ref. 25, p. 242.
103. D. C. Foster, *Org. Synth.*, Coll. Vol. III, 771 (1955).
104. H. J. Reich, M. L. Cohen and P. S. Clark, *Org. Synth.*, **59**, 141 (1980).
105. D. Seebach and A. K. Beck, *Chem. Ber.*, **108**, 314 (1975).
106. N. Petragnani and M. de Moura Compos, *Chem. Ber.*, **96**, 249 (1963).
107. W. S. Haller and K. J. Irgolic, *J. Organomet. Chem.*, **38**, 97 (1972).
108. K. -Y. Jen and M. P. Cava, *J. Org. Chem.*, **48**, 1449 (1983).
109. S. Gronowitz, A. Konor and A. -B. Hörnfeldt, *Chem. Scr.*, **10**, 159 (1976).
110. K. -Y. Jen, N. Benforemo, M. P. Cava, W. -S. Huang and A. G. MacDiarmid, *J. Chem. Soc., Chem. Commun.*, 633 (1983).
111. L. Engman and M. P. Cava, *Organometallics*, **1**, 470 (1982).
112. V. P. Litvinov and I. A. Dzhunaev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 777 (1982).
113. D. Dauplaise, J. Meinwald, J. C. Scott, H. Temkin and J. Clardy, *Ann. H. Y. Acad. Sci.*, **313**, 382 (1978).
114. J. Meinwald, D. Dauplaise and J. Clardy, *J. Am. Chem. Soc.*, **99**, 7743 (1977).
115. L. -Y. Chiang, P. Shu, D. Holt and D. Cowan, *J. Org. Chem.*, **48**, 4713 (1983).
116. K. Lerstrup, D. O. Cowan and T. J. Kistenmacher, *J. Am. Chem. Soc.*, **106**, 8303 (1984).
117. K. Lerstrup, D. Talham, A. Bloch, T. Poehler and D. Cowan, *J. Chem. Soc., Chem. Commun.*, 336 (1982).
118. R. E. Hollands, A. G. Osborne and I. Townsend, *Inorg. Chim. Acta*, **371**, L541 (1979).
119. V. P. Krasnov, V. I. Naddaka, V. P. Gar'kin and V. I. Minkin, *Zh. Org. Khim.*, **14**, 2620 (1978).
120. F. Wudl and D. Nalewajek, *J. Organomet. Chem.*, **217**, 329 (1981).
121. M. Tiecco, L. Testaferri, M. Tingoli, D. Chianelli and M. Montanucci, *Synth. Commun.*, **13**, 617 (1983).
122. L. Engman and M. P. Cava, *Synth. Commun.*, **12**, 163 (1982).
123. L. I. Zakharin, N. Yu. Krainova, G. G. Zhigarev and I. V. Pisareva, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1650 (1982).
124. K. Kondo, N. Sonoda and H. Sakurai, *J. Chem. Soc., Chem. Commun.*, 160 (1974).
125. A. P. Kozikowski and A. Ames, *J. Org. Chem.*, **43**, 2735 (1978).
126. H. J. Reich, in Ref. 25, p. 258.
127. H. Fischer and S. Zeuner, *Z. Naturforsch., Teil B*, **38**, 1365 (1983).
128. E. O. Fischer and S. Riedmüller, *Chem. Ber.*, **107**, 915 (1974).
129. D. S. Gill, M. Green, K. Marsden, I. Moore, A. Guy Orpen, F. Gordon, A. Stone and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1343 (1984).
130. (a) C. Bianchini and A. Meli, *J. Chem. Soc., Chem. Commun.*, 156 (1983); (b) K. Vollhardt, C. Peter and E. C. Walborsky, *J. Am. Chem. Soc.*, **105**, 5507 (1983).
131. A. Scheller, W. Winther and E. Müller, *Justus Liebigs Ann. Chem.*, 1448 (1976).
132. A. R. Katrtzky and C. W. Rees (Eds.), *Comprehensive Heterocyclic Chemistry* (Eds. A. R. Katritzky and C. W. Rees), Vol. 6, Pergamon Press, Oxford, 1984, pp. 349, 354 and 587.
133. F. Krafft and R. E. Lyons, *Chem. Ber.*, **27**, 1761 (1894).
134. A. Silverwood and M. Orchin, *J. Org. Chem.*, **27**, 3401 (1962).
135. T. Hirabayashi, S. Mohmand and H. Bock, *Chem. Ber.*, **115**, 483 (1982).
136. W. Stanley, M. R. van De Mark and P. L. Kumler, *J. Chem. Soc., Chem. Commun.*, 700 (1974).
137. J. Y. C. Chu, D. G. Marsh and W. H. H. Günther, *J. Am. Chem. Soc.*, **97**, 4905 (1975).
138. D. H. Brown, R. J. Cross and D. Millington, *J. Organomet. Chem.*, **125**, 219 (1977).
139. I. A. Nuretdinov, E. V. Bayandina and G. M. Vinokurova, *Zh. Obshch. Khim.*, **44**, 2588 (1974).
140. J. Y. C. Chu and D. G. Marsh, *J. Org. Chem.*, **41**, 3204 (1976).
141. R. J. Cross and D. Millington, *J. Chem. Soc., Chem. Commun.*, 455 (1975).
142. D. H. Brown, R. J. Cross and D. Millington, *J. Chem. Soc., Dalton Trans.*, 159 (1977).
143. I. Johannsen, K. Lerstrup, L. Henriksen and K. Bechgaard, *J. Chem. Soc., Chem. Commun.*, 89 (1984).
144. K. Burger and R. Ottlinger, *Synthesis*, 44 (1978).
145. S. Larsen and L. Henriksen, *Acta Chem. Scand., Ser. A*, **38**, 289 (1984).
146. F. Riegel and W. Siebert, *Z. Naturforsch., Teil B*, **29**, 719 (1974).

147. N. S. Vyazankin and M. N. Bochkarev, *Zh. Obshch. Khim.*, **37**, 1037 (1967).
148. B. Mathiasch, *Z. Anorg. Allg. Chem.*, **432**, 269 (1977).
149. A. Blecher and B. Mathiasch, *Z. Naturforsch., Teil B*, **33**, 246 (1978).
150. O. Foss and V. Janickis, *J. Chem. Soc., Chem. Commun.*, 833 (1977).
151. O. Foss and V. Janickis, *J. Chem. Soc., Dalton Trans.*, 620 (1980).
152. K. W. Sharp and W. H. Koehler, *Inorg. Chem.*, **16**, 2258 (1977).
153. L. Syper and J. Mlochowski, *Synthesis*, 439 (1984).
154. A. G. Osborne, R. E. Hollands, J. A. K. Howard and R. F. Bryan, *J. Organomet. Chem.*, **205**, 395 (1981).
155. V. I. Bregadze, V. Ts. Kampel, A. Ya. Usiatinsky and O. B. Ponomareva, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1434 (1982).
156. V. I. Bregadze, V. Ts. Kampel, A. Ya Usiatinsky, O. B. Ponomareva and N. N. Godovikov, *J. Organomet. Chem.*, **233C**, 33 (1982).
157. A. V. Zibarev, G. N. Dolenko, S. A. Krupoder, L. N. Malazow, O. K. Poelshcuk, G. G. Furin and G. G. Yakobson, *Zh. Org. Khim.*, **16**, 390 (1980).
158. M. Herberhold, D. Reiner, B. Zimmer-Gasser and U. Schubert, *Z. Naturforsch., Teil B*, **35**, 1281 (1980).

CHAPTER **11**

Compounds with Se—N and Te—N bonds

G. KIRSCH

Laboratoire de Carbochimie et Synthèse Organique, Université de Metz, Faculté des Sciences, Ile du Saulcy, 57045-Metz Cédex, France

L. CHRISTIAENS

Institut de Chimie Organique, Université de Liège, Sart-Tilman, 4000-Liège, Belgium

Part Two: Heterocyclic Compounds with Se—N and Te—N Bonds

This chapter deals with organic compounds with selenium—nitrogen and tellurium—nitrogen bonds, and is divided into two parts. Part One relates to compounds with non-cyclic Se—N and Te—N bonds and Part Two treats heterocyclic derivatives containing Se—N or Te—N bonds.

The literature for the two parts, gathered together at the end of the chapter in Section XIII, has been reviewed since 1972 up to the end of Volume 102 for *Chemical Abstracts*. Several books and reviews discussing this subject have appeared[1–14], including an overview of the chemistry of selenium and tellurium heterocycles[15]. Some unreported results are also mentioned, together with comparisons with the sulphur-containing analogues.

PART ONE. NON-CYCLIC COMPOUNDS WITH Se—N AND Te—N BONDS

I. INTRODUCTION

Among compounds with Se—N and Te—N bonds, the former have been the most studied. Sometimes in the literature different names have been chosen for designating the same derivatives, especially in the Se—N series. As a rule, there is no ambiguity with regard to selenenamides, seleninamides and selenonamides, but the compounds $RSeN = CR^1R^2$ have been named selenoximes, selenylimines, selenoimines and selenenamides. The same problem arises with $R_2Se = NR^1$ which have been named selenimides, seleniliimines and selenium imides. In this chapter we have used the following nomenclature for the main structures:

$RSeNR^1R^2$ Selenenamides
$RSeONR^1R^2$ Seleninamides
$RSeO_2NR^1R^2$ Selenonamides
(Amides from organotellurium acids are not known)
$RSeN = CR^1R^2$ Selenenimines
$R\underset{\parallel}{\underset{O}{Se}}N = CR^1R^2$ Seleninimines

(Tellureninimes and tellurinimes are not known)
$R^1R^2Se = NR^3$ Selenimides and derivatives
$R^1R^2Te = NR^3$ Tellurimides
$RN = Se = NR$ Seleniumdiimides
$RN = Te = NR$ Telluriumdiimides
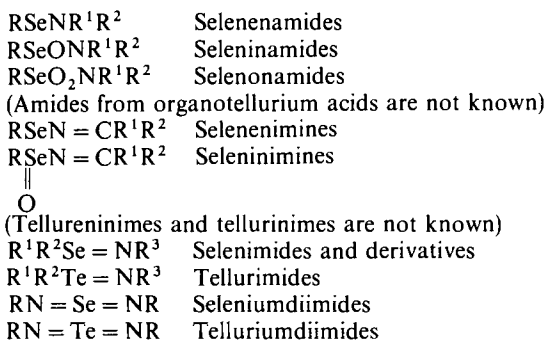
II. NITROGEN DERIVATIVES OF SELENENIC, SELENINIC AND SELENONIC ACIDS

The amidic nitrogen compounds derived from these acids are named selenenamides, seleninamides and selenonamides, respectively.

A. Selenenamides $RSeNR^1R^2$

1. Preparation

Selenenamides (1) the amides of selenenic acids, are obtained from the corresponding selenenic acid, RSeOH, or from the acid chloride or bromide. Most of the preparations start from an aryl or alkyl selenenyl chloride or bromide (2)[1,4,16,17] (equation 1).

$$RSeX + R^1R^2R^3N \longrightarrow RSeNR^1R^2 \qquad (1)$$
$$\quad (2) \qquad\qquad\qquad (1)$$

$$X = Cl, Br; \ R = aryl, alkyl; \ R^1, R^2, R^3 = H, CH_3, \text{etc.}$$
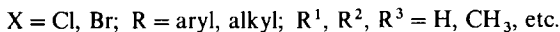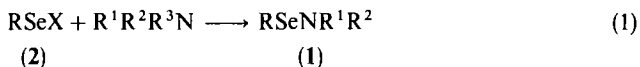
Instead of selenenyl chloride, selenocyanate can be used[4]. Phenylselenenic acid has also been used to prepare selenenamides. In this case, the acid is generated *in situ* from a selenoxide elimination reaction[16] (equation 2).

$$\underset{\underset{Et}{|}}{PhCOCH\underset{\overset{\parallel}{O}}{Se}Ph} \xrightarrow{Et_2NH} PhSeNEt_2 + PhCOCH=CHMe \qquad (2)$$

Table 1 summarizes the selenenamides prepared by these methods.

N-Phenylselenophthalimide (3) and *N*-phenylselenosuccinimide (4) can be considered as particular selenenamides. They are prepared by the reaction of phenylseleninyl chloride with potassium phthalimide (equation 3) and of phenyl allyl selenide (or diphenyl selenide) with *N*-chlorosuccinimide (equation 4), respectively[17].

$$PhSeCl + K^+{}^-N\underset{}{} \longrightarrow PhSe-N\underset{}{} \qquad (3)$$

$$(3)$$
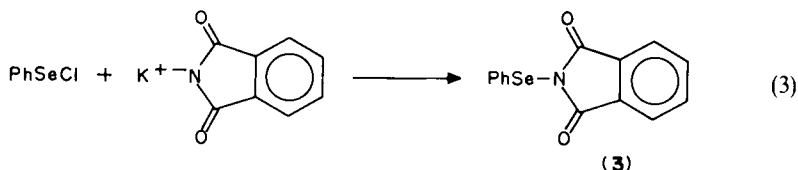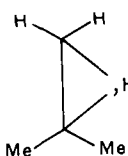
TABLE 1. Selenenamides prepared by reaction 1:
$RSeX + R^1R^2R^3N \longrightarrow RSeR^1R^2$

R	X	R^1, R^2, R^3	Ref.
DNP[a]	Br	Ph, H, H	1
DNP[a]	BR	H, H, H	1
DNP[a]	OMe	H, H, H	1
Pr	Cl	Me, Me, H	4
Et	Cl	Me, H, H[b]	4
CF_3	Cl	Ph, H, H[c]	4
1-Naph	Cl	2-Naph, H, H	4
Ph	Cl	Me, Me, H	
Ph	Br	Et, Et, H	16a, b
Ph	OH	i-Pr, i-Pr, H	
DNP[a]	Cl		21
Ph	Cl	Et, Et, $SiMe_3$	16c
Ph	Cl	Me, COMe, SiMe	16c

[a]DNP = 2,4-dinitrophenyl.
[b]Mono- or di-substitution at Se occurs depending on the ratio of the reactants.
[c]The corresponding selenenamide is obtained as an intermediate in the reaction but the rearrangement product is isolated (see Section II.A.2).

(4)
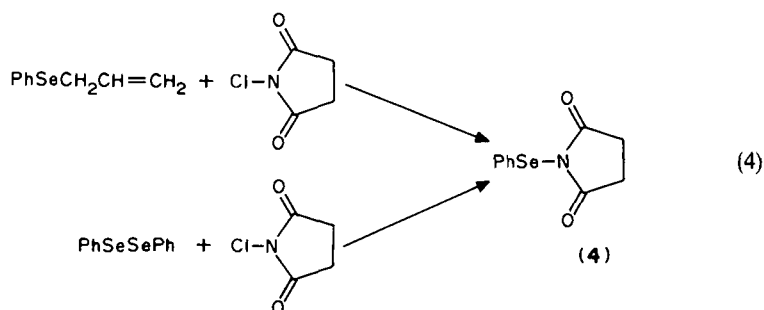
2. Chemical properties

Selenenamides present interesting chemical properties themselves and in their synthetic applications. Hydrolysis of selenenamides gave back the selenenic acids[16]. In certain cases selenenamides rearrange in a Hofmann–Martins-type reaction. For example, reaction of 2,4-dinitrophenylselenenyl bromide (5) with 1-naphthylamine does not lead to the expected selenenamide 6 but to 4-(1-aminonaphthyl)-2',4'-dinitrophenyl selenide (7) (equation 5).

(5)
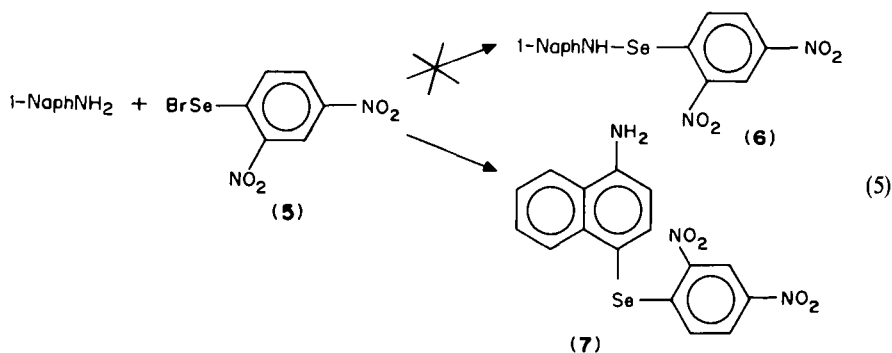
This reaction takes place also with 2-naphthylamine; then the rearrangement leads to the 1-(2-aminonaphthyl) selenide.

In general, when rearrangement takes place it affects the *para* position if this position is free.

Various other examples are described in the literature[1,18].

3. Selenenylation reactions

N, N-Disubstituted phenylselenenenamides are useful selenenylation reagents. They react with β-dicarbonyl compounds to give dicarbonyl selenides (**8**)[16] (equation 6). With alkenes in the presence of acetic anhydride they give benzeneselenenyl acetate (**9**)[16] (equation 7). With some enones they give α-(phenylseleno-β-dialkylamino) ketones (**10**)[16] (equation 8), and with aldehydes they give α-phenylselenoaldehydes (**11**)[19a,b] (equation 9).

(6)

(7)

(8)

$$Ph(CH_2)_3CHO \xrightarrow{PhSeNEt_2} Ph(CH_2)_2CHCHO \tag{9}$$

$$\underset{\text{SePh}}{|}$$

(11)
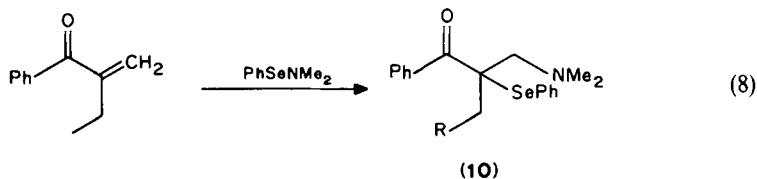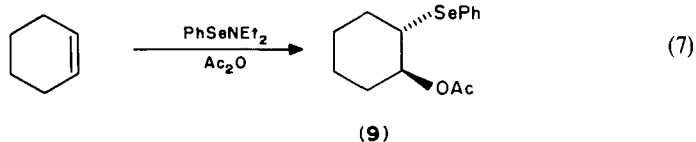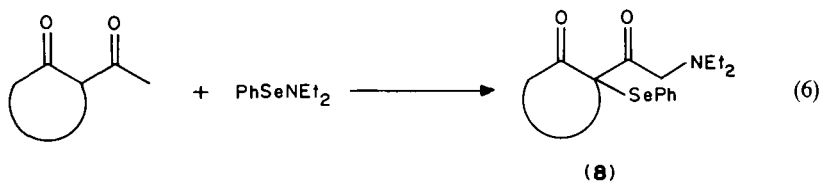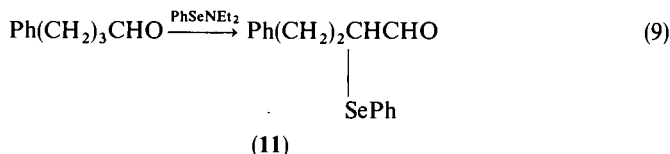
An extensive study of the addition of N,N-dimethylbenzeneselenenamide to dimethyl-acetylene dicarboxylate has also been made[20] (equation 10). The product of the reaction was a mixture of the maleate and fumarate esters **12** and **13**. However, a kinetic study in chloroform showed that the addition was a second-order reaction and that in the early stage only one product, the maleate ester **12**, is formed. The fumarate ester **13** appears later and slowly approaches the equilibrium concentration. A simple thermal rotation around the double bond seems to be the mechanism involved in the equilibration of the two isomers.

$$PhSeNMe_2 \;+\; Me_2OCC{\equiv}CCO_2Me \longrightarrow$$

(12)   **(13)**

$$\tag{10}$$
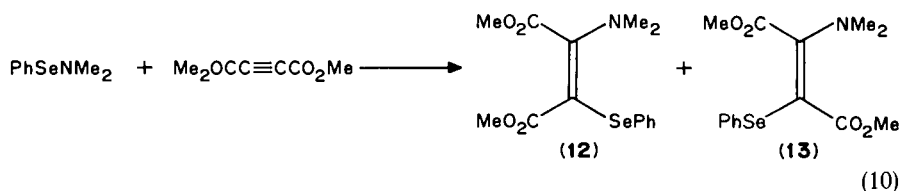
4. Addition to carbonyl compounds

Like sulphenamides, selenenamides condense with carbonyl compounds to give the selenenimine derivatives[22]. For example, 2,4-dinitrophenylselenenylamide (**14**) condenses with acetone to give the corresponding selenenimine (**15**) (equation 11).

(14)   **(15)**

$$\tag{11}$$
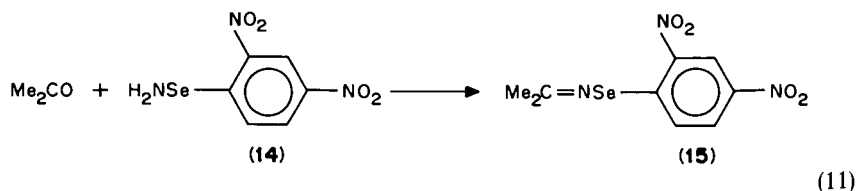
5. Chemical properties of N-phenylselenophthalimide (N-PSP) and N-phenylselenosuccinimide

These reagents, in presence of tributylphosphine, have been used for the conversion of alcohols into the corresponding phenyl selenides[23] (equation 12). However, when the reaction was applied to an allylic 3-sterol, the 3-phthalimido derivative was formed instead of the expected selenide[24].

$$ROH + N\text{-}PSP \rightarrow RSePh \tag{12}$$

In the presence of water and under catalysis, N-PSP adds to alkenes to form a hydroxyselenide (**16**) (equation 13) or phenylselenolactone (**17**)[25a,b,c] (equation 14).

$$PhCH = CH_2 + N\text{-}PSP \xrightarrow[H^+]{H_2O} PhCHCH_2SePh \tag{13}$$

$$\underset{\text{OH}}{|}$$

(16)

$$CH_2=CHCH_2CH_2COOH + N\text{-}PSP \longrightarrow PhSeCH_2 \quad \text{(17)} \tag{14}$$

$$\text{(17)}$$
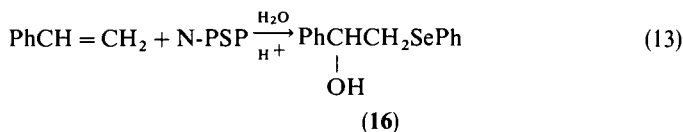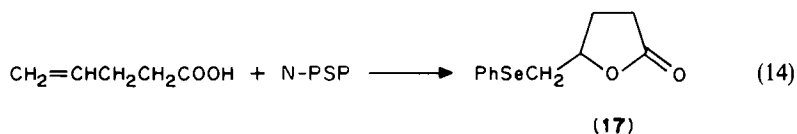
ω-Ethylenic amines have been cyclized by use of N-PSP[25d]. Transformation of carboxylic acids into their phenyl selenoesters can also be achieved by use of N-PSP[26]. N-PSP was recently used for the preparation of S-acylphenylselenenyl sulphides (18) from thiocarboxylic acids[27] (equation 15).

$$RC(=O)SH + N\text{-}PSP \longrightarrow RC(=O)SSePh \tag{15}$$
$$\textbf{(18)}$$
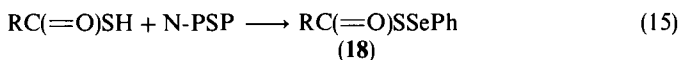
B. Seleninamides

Only a few preparations of seleninamides have been described[1,4], and no improvements in the methods have been made in the last 20 years. The classical routes to these derivatives are via equations 16–18.

$$p\text{-}NO_2C_6H_4SeO_2H \xrightarrow{SOCl_2} p\text{-}NO_2C_6H_4SeOCl \xrightarrow{conc.\ NH_3} p\text{-}NO_2C_6H_4SeONH_2 \tag{16}$$

$$MeCONHC_6H_4SeCN \xrightarrow[2.\ conc.\ NH_3]{1.\ HNO_3,\ 0\ °C} MeCONHC_6H_4SeONH_2 \tag{17}$$

$$(p\text{-}NO_2C_6H_4Se)_2 \xrightarrow[2.\ conc.\ NH_3]{1.\ HNO_3,\ -5\ °C} p\text{-}NO_2C_6H_4SeONH_2 \tag{18}$$
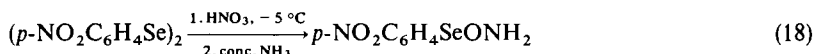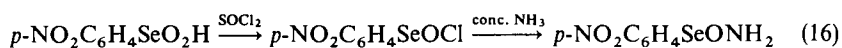
The reaction of phenylselenenyl chloride or phenylselenium trichloride with N-chloroamides and N-trimethylsilylbenzamides, respectively (equation 19) produces a compound (19) which can be considered as a dichloroselenium derivative of N-benzoylbenzeneseleninamide[28]. Hydrolysis of the dichloro derivatives 19 yields benzene-seleninic acid[28] (equation 20). Treatment of 19 with chlorine or HCl gives phenylselenium trichloride together with N-chlorobenzamide or benzamide, respectively[28].

$$PhSeCl + PhCONHCl$$

$$PhSeCl_3 + PhCONHSiMe_3$$

$$\begin{array}{c} Cl \\ | \\ PhSeNHCOPh \\ | \\ Cl \end{array} \tag{19}$$

$$\textbf{(19)}$$

$$\begin{array}{c} Cl \\ | \\ PhSeNHCOPh + H_2O \rightarrow PhSeO_2H \\ | \\ Cl \end{array} \tag{20}$$
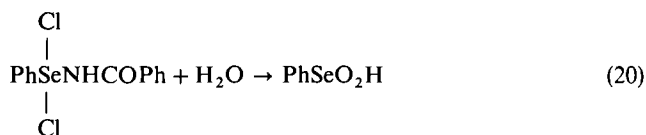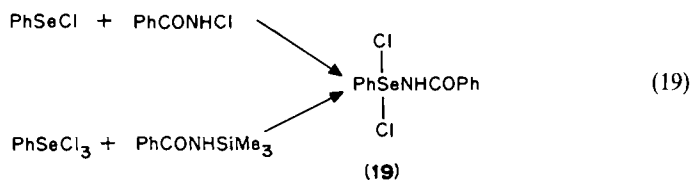
C. Selenonamides

Very few studies of selenonamides have been made. Preparations of the amides by reaction of the corresponding methyl selenoesters with ammonia or amines have been

described[29,30] (equation 21).

$$PhSeO_3Me + R^1R^2NH \longrightarrow PhSO_2NR^1R^2 \qquad (21)$$

$$R^1 = R^2 = H; \; R^1, \; R^2 = H, \; Me; \; R^1 = R^2 = Me$$
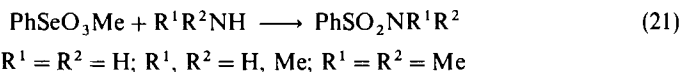
Studies of the chemical properties of selenonamides have not yet been published.

III. SELENENIMINES AND SELENINIMINES

Among the simple structures containing the Se—N moiety, selenenimines and selenini-mines have been very little studied. The first examples of these compounds were described in 1976[31].

A. Preparation

The first selenenimines (20) and seleninimines (21) were prepared by reaction of the corresponding chlorides with the appropriate imine[31] (equation 22).

$$RC_6H_4Se(O)_nCl + NH = C(p\text{-Tol})_2 \longrightarrow RC_6H_4Se(O)_nN = C(p\text{-Tol})_2 \qquad (22)$$

$$R = H, NO_2 \qquad\qquad n = 0 \; (20)$$
$$n = 1 \; (21)$$
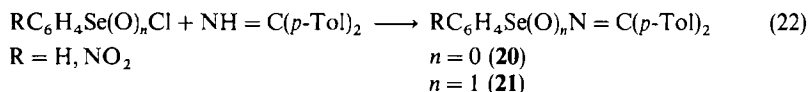
Compounds 20 were obtained easily but the reaction failed for the preparation of 21 with R = H. Preparation of 21 from 20 by oxidation with m-chloroperbenzoic acid also failed. The imines 20 and 21 were prepared for the study of the planar inversion at the nitrogen atom.

At the same time another study was published on the same subject[21], in which the preparation was effected by reaction of ketones with phenylselenenamides[22] (equation 23). Table 2 summarizes the compounds prepared by this method.

$$R^1R^2CO + NH_2SeR^3 \longrightarrow R^1R^2C = NSeR^3 \qquad (23)$$
$$(22)$$
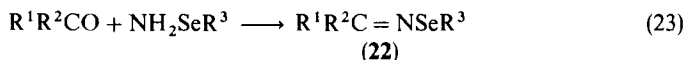
The same condensation applied to orthoesters yields some particular selenenimines (23) (equation 24). The different imines prepared by this method are reported in Table 3.

$$R^1C(OR^2)_2 + NH_2SeR^3 \longrightarrow \underset{R^2-X}{\overset{R^1}{>}}C=NSeR^3 \qquad (24)$$
$$XR^2 \qquad\qquad\qquad (23)$$
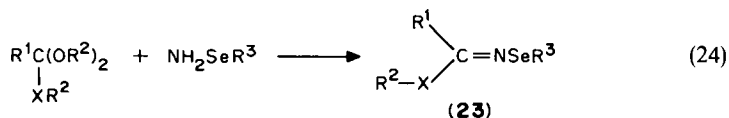
Oxidation of phenols by phenylseleninic anhydride (Barton's oxidation) in the presence of hexamethyldisilazane gives another preparation of phenylselenenimine (24)[32] (equation 25).

TABLE 2. Selenenimines (22) prepared by condensation of ketones with selenen-amides (equation 23)

R^1	R^2	R^3
t-Bu	pTol	o-NO$_2$C$_6$H$_4$
t-Bu	p-Tol	2,4-di-NO$_2$C$_6$H$_3$
Me	Me	o-NO$_2$C$_6$H$_4$

TABLE 3. Selenenimines (23) prepared by con-
densation of selenenamides with orthoesters[a]
(equation 24)

R^1	R^2	R^3	X
H	Et	$o\text{-}NO_2C_6H_4$	O
Ph	Me	$o\text{-}NO_2C_6H_4$	O
Ph	Et	$o\text{-}NO_2C_6H_4$	O
OEt	Et	$o\text{-}NO_2C_6H_4$	O
$o\text{HOC}_6H_4$	$PhCH_2$	$o\text{-}NO_2C_6H_4$	S
Me	Ph	$o\text{-}NO_2C_6H_4$	S
Ph	$PhCH_2$	$o\text{-}NO_2C_6H_4$	S
2-Tol	$PhCH_2$	$o\text{-}NO_2C_6H_4$	S

[a]In the starting orthoesters R is Me or Et.

(24)   (25)
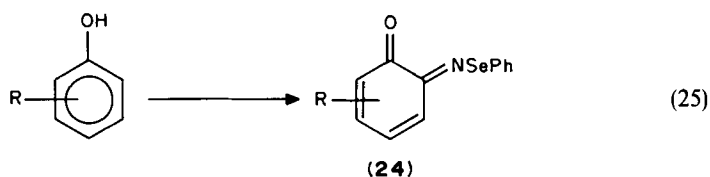
B. Chemical Properties

The chemical properties of the imines have been less studied, but some physicochemical studies have been carried out[21,31]. However, some chemical properties of 24 have been described[32].

Treatment of 24 with thiophenol at room temperature yields the corresponding aminophenol (25), whereas treatment with zinc in acetic anhydride gives the acet-amidoacetate (26).

(25)   (26)
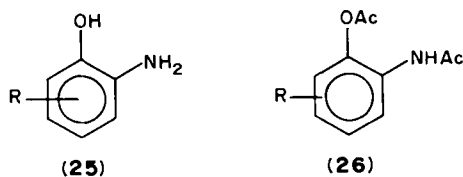
IV. SELENIMIDES AND DERIVATIVES

A. Selenimides

1. Preparation

N-Substituted selenimides have been prepared by different methods depending on the oxidation state of the selenium in the starting material.

   a. *Preparation from selenides* (Se^{II}) (*method A*). The selenimides 27 and 28 are obtained by reaction of selenides with chloramine-T or -B[33-37] (equations 26 and 27).

$$R^1SeR^2 + NaNClSO_2Tol\text{-}p \longrightarrow R^1R^2Se = NSO_2Tol\text{-}p \qquad (26)$$
$$\text{Chloramine-T} \qquad\qquad\qquad (27)$$

$$R^1SeR^2 + NaNClSO_2Ph \longrightarrow R^1R^2Se = NSO_2Ph \qquad (27)$$
$$\text{Chloramine-B} \qquad\qquad\qquad (28)$$
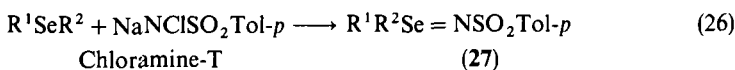
b. Preparations from Se^{IV} *species.* Selenimides can be prepared in different ways starting from Se^{IV} species.

(i) Method B. The addition of *t*-BuOCl to a selenide gives an Se^{IV} addition product, which on treatment with an *N*-sodioarylsulphonamide or benzamide yields the corresponding selenimide[35,38] (equation 28). This synthesis can be realized in a one-pot reaction.

$$R^1SeR^2 \xrightarrow{\ t\text{-BuOCl}\ } R^1R^2Se(OBu\text{-}t)Cl \xrightarrow[\text{(NaNHCOAr)}]{\ NaNHSO_2Ar\ } R^1R^2Se = NSO_2Ar$$
$$(R^1R^2Se = NCOAr) \qquad (28)$$
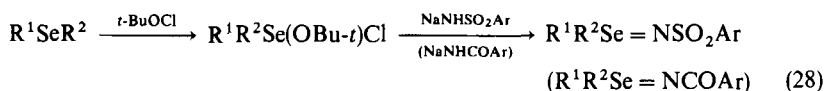
However, when the reaction is attempted with diphenyl selenide, the expected selenimide is not obtained but another Se^{IV} compound, **29**, is isolated[35].

$$Ph_2Se(OH)NHSO_2Tol\text{-}p$$
$$(29)$$
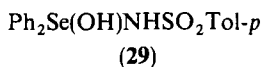
(ii) Method C. Treatment of a dichloroselenide with sodium L(−)-menthylate followed by reaction with *N*-sodiophenylsulphonamide gives the selenimide **30**[29] (equation 29). This method allows the preparation of the selenimide **30** with one of the enantiomers in slight excess.

$$R^1R^2SeCl_2 \xrightarrow{\ Na\,L(-)\text{-menthylate}\ } R^1R^2Se(Cl)\text{-}L(-)\text{-menthylate}$$
$$\xrightarrow{\ PhSO_2NHNa\ } R^1R^2Se = NSO_2Ph \qquad (29)$$
$$(30)$$
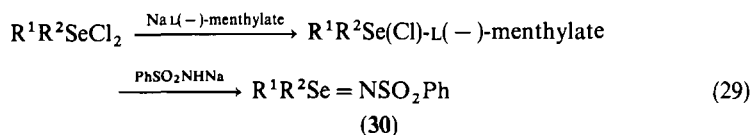
An attempt to prepare the diphenylselenimide **31** directly by the action of ammonia on diphenylselenium dichloride failed and gave instead the quaternary ammonium salt **32**[40].
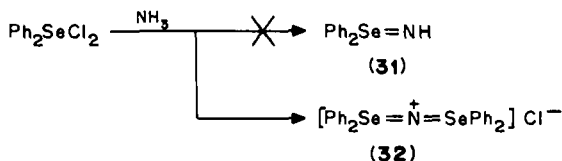
(iii) Method D. Condensations of selenoxides with amides give the corresponding selenimides[35,37] in good yields (equation 30).

$$NH_2SO_2R \qquad {R^1 \atop R^2}{>}Se = NSO_2R$$
$$R^1R^2Se{=}O + \quad \text{or} \quad \longrightarrow \quad \text{or} \qquad (30)$$
$$NH_2COR \qquad {R^1 \atop R^2}{>}Se = NCOR$$
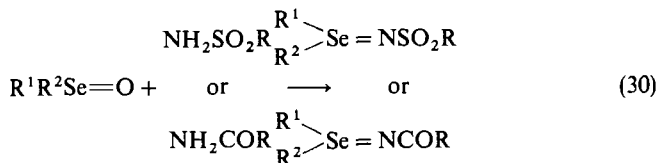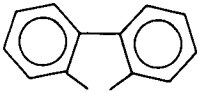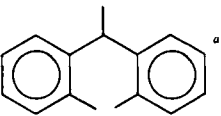
TABLE 4. Selenimides $R^1R^2Se = NR^3$ prepared by different methods

R^1	R^2	R^3	Method	Refs.
Ph	Ph	SO_2Ph	A	34, 35
Ph	Ph	$SO_2Tol\text{-}p$	A	34, 35
Ph	Ph	$SO_2C_6H_4Cl\text{-}p$	A	34, 35
Ph	Ph	$SO_2C_6H_4NO_2\text{-}p$	A	34, 35
Ph	Ph	$SO_2C_6H_4NO_2\text{-}o$	A	34, 35
$p\text{-}Tol$	$p\text{-}Tol$	SO_2Ph	A	34, 35
$p\text{-}Tol$	$p\text{-}Tol$	$SO_2Tol\text{-}p$	A	34, 35
		$SO_2Tol\text{-}p$	A	33
		$SO_2Tol\text{-}p$	A	36
$-(CH_2)_4-$		$SO_2Tol\text{-}p$	A	35, 37
$-(CH_2)_5-$		$SO_2Tol\text{-}p$	A	37
$PhCH_2$	$PhCH_2$	$SO_2Tol\text{-}p$	A	37
Ph	Ph	SO_2Ph	B	38
Ph	Ph	COPh	B	38
$PhCH_2$	$PhCH_2$	$SO_2Tol\text{-}p$	B	35
Me	Ph	$SO_2Tol\text{-}p$	B	35
$-(CH_2)_4-$		$SO_2Tol\text{-}p$	B	35
Me	Ph	$SO_2Tol\text{-}p$	C	39
Me	$p\text{-}BrC_6H_5$	$SO_2Tol\text{-}p$	C	39
$PhCH_2$	$PhCH_2$	$SO_2Tol\text{-}p$	D	35
$-(CH_2)_4-$		$SO_2Tol\text{-}p$	D	35
Ph	Ph	Ph	D	37
Ph	Ph	$p\text{-}ClC_6H_4$	D	37
Ph	Ph	CCl_3	D	37
Ph	$p\text{-}An$	Ph	D	37
Ph	$p\text{-}Tol$	Ph	D	37
$PhCH_2$	$PhCH_2$	CCl_3	D	37
$p\text{-}BrC_6H_4$	Me	SO_2Ph	D	41
$p\text{-}BrC_6H_4$	Me	$COCF_3$	D	41

[a]In the case of selenoxanthene, method A gave a mixture of cis- and trans-isomers which could be separated by fractional recrystallization.

The reactions are run in chloroform with the sulphonamides and in acetic anhydride with the carboxamides. These condensations work better when an electron-donating group is present in the selenoxide and an electron-withdrawing group in the amide.

Table 4 summarizes the selenimides prepared by the various methods.

2. Chemical properties

a. Reduction. Reduction of *N*-tosyl selenimides to yield the selenide can be achieved quantitatively by refluxing the imide with triphenylphosphine in chloroform, ethanol or a

mixture of benzene and acetic acid[36] (equation 31).

$$Ph(Me)Se = NTos \xrightarrow[\text{solvent}]{Ph_3P} PhSeMe \qquad (31)$$
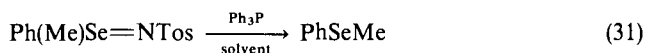
9-Phenylselenoxanthene N-tosylimide has been reduced by $NaBH_4$ to the 9-phenylselenoxanthene[37].

b. *Base and acid treatments.* Basic hydrolysis of N-tosyl and N-acyl selenimides in methanol gives access to the corresponding selenoxides[34,37] (equation 32).

$$\begin{matrix} R^1R^2Se = NTos \\ or \\ R^1R^2Se = NAcyl \end{matrix} \xrightarrow[\text{MeOH}]{KOH(NaOH)} R^1R^2Se = O \; + \; \begin{matrix} H_2NTos \\ or \\ H_2NAcyl \end{matrix} \qquad (32)$$
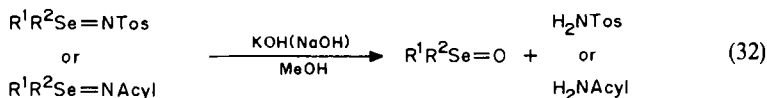
Treatment of N-tosyl selenimide with water in the presence of silica gel also gives the selenoxide[36].

In one particular case, N-tosyl pentamethyleneselenimide (33) was treated with concentrated sulphuric acid at $-50\,^{\circ}C$, but instead of the expected N-unsubstituted selenimides a crystalline product was isolated, for which spectral and elemental analyses indicated the selenurane structure 34[37] (equation 33). The reaction took place by a Se—N bond cleavage rather than by the expected N—SO_2 cleavage.

$$\qquad (33)$$

(33)   (34)
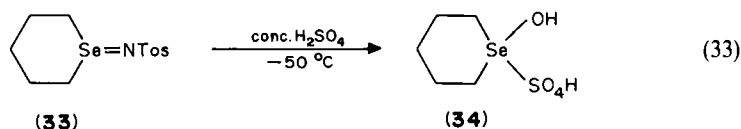
c. *Reaction with halogenating agents.* Treatment of selenimides with hydrogen chloride or chlorine produces the corresponding disubstituted selenium dichloride in quantitative yield[34]. Disubstituted dihalogenoselenium derivatives can also be obtained by treatment of N-tosyl or N-acyl selenimides with acetyl chloride, triphenylphosphine dibromide or chlorotrimethylsilane[75] (equation 34).

$$R^1R^2Se = N \begin{cases} COR \\ SO_2R \end{cases} \xrightarrow[\text{Me}_3\text{SiCl}]{\substack{\text{MeCOCl} \\ Ph_3PBr_2}} R^1R^2SeX^2 \qquad (34)$$

$$X = Cl, Br$$
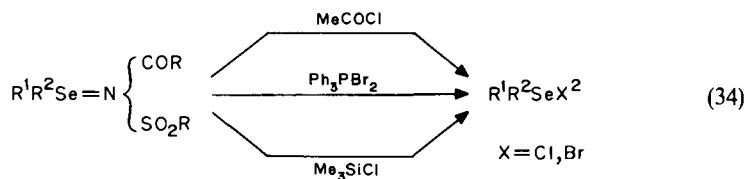
d. *Action of oxidizing agents.* Some oxidations of selenimides have been tried with potassium permanganate[37], hydrogen peroxide[34,37] or nitrogen oxide[34]. While different workers found that oxidation by potassium permanganate in water yields the corresponding selenones, they do not agree about the oxidation with 30% hydrogen peroxide. Some workers[34] found that this oxidation gave the selenones, whereas others[37] obtained the selenoxide or the selenimide hydrate (35) (equation 35).

$$Ph_2Se = NTos \xrightarrow[\text{r.t.}]{H_2O_2} Ph_2Se \begin{matrix} \diagup NHTos \\ \diagdown OH \end{matrix} \qquad (35)$$

(35)
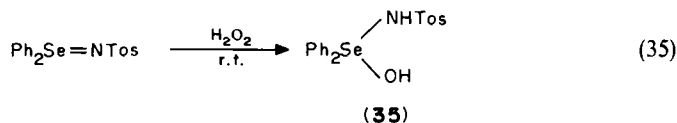
However, when diphenyl *N*-phenylsulphonylselenimide is oxidized under the same conditions, the diphenyl selenoxide is obtained.

e. Thermal behaviour. The thermal behaviour of the different *N*-substituted selenimides has been studied. When *N*-tosyl selenimides are heated in a solvent in sealed tubes, reduction occurs and the corresponding selenides and sulphonamides are obtained[37] (equation 36).

$$R^1R^2Se{=}NTos \longrightarrow R^1R^2Se + TosNH_2 \qquad (36)$$
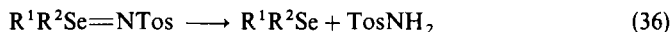
Heating *N*-acyl selenimides at 140–160 °C in DMF produces the selenide together with the isocyanate[37]. This last product is isolated as its phenylcarbamate, as shown in equation 37. Only in the case of *N*-trichloroacetyl diphenylselenimides is the corresponding imide obtained instead the carbamate.

$$R^1R^2Se = NCOR^3 \xrightarrow[\text{(2) PhNH}_2]{\text{(1) 160 °C/DMF}} R^1R^2Se + PhNHCONR^3 \qquad (37)$$
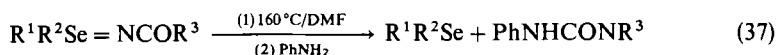
9-Phenylselenoxanthenetosylimine has been isolated as the *cis*- and *trans*-isomers **36** and **37**.[36]

(36)   (37)
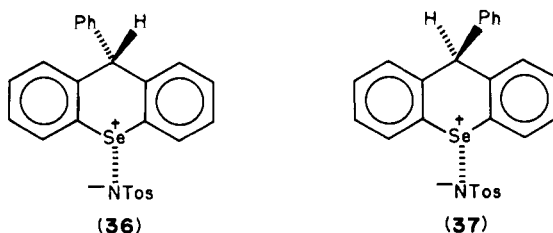
Refluxing the *trans*-isomer **37** in toluene yields the rearrangement product **38**. Under the same conditions the *cis*-isomer **36** does not rearrange or isomerize to **37**. When the reaction is catalysed by DABCO (1,4-diazabicyclo[2.2.2]octane), rearrangement takes place with either isomer even in benzene at room temperature.

(38)
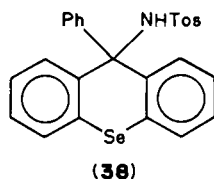
When other bases are used, such as sodium methoxide or carbanions from Grignard reagents, rearrangement does not occur but 9-substituted 9-phenylselenoxanthene (**39**) are obtained.

(39)

R = MeO, Me, *p*-Tol
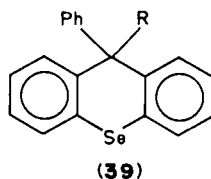
f. Physicochemical properties. The pK_a values of different N-tosyl selenimides (**40**) have been measured in acetonitrile[42]. Their values range from 6.63 to 10.03. A $\rho\sigma$ analysis indicated that the pK_a values were determined by the inductive and mesomeric effects of R.

$$RC_6H_4SeCH_2Ph$$
$$\parallel$$
$$NTos$$

(**40**)
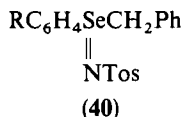
$$R = p\text{-Me}, m\text{-Me}, p\text{-MeO}, m\text{-MeO}, p\text{-NMe}_2, p\text{-Br}, m\text{-Br}, p\text{-Cl}$$

B. Se-Chloroselenimides

1. Preparation

The first examples of these compounds were prepared by reaction of N,N-dichlorophenylsulphonamide with arylselenotrimethylsilane[43,44] (equation 38). This synthesis has been extended to N,N-dichloro-N-acyl derivatives[44].

$$ArSe\ SiMe_3 + Ar'SO_2NCl_2 \longrightarrow ArSe = NSO_2Ar' \quad (38)$$
$$\mid$$
$$Cl$$
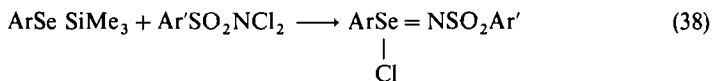
Several other methods have also been used for the preparation of these compounds. Equations 39 show the different syntheses used and Table 5 gives the compounds prepared:

$$
\left.
\begin{array}{l}
(a)\ ArSeSiMe_3 + Ar'SO_2NCl_2 \\[4pt]
(b)\ ArSeCl + Ar'SO_2NNaCl \\[4pt]
(c)\ ArSeCl + Ar'CONCl_2 \\[2pt]
\qquad\quad 2 : 1 \\[4pt]
(d)\ ArSeCl_3 + Ar'SO_2NCl_2 \\[4pt]
(e)\ ArSeCl_3 + Ar'CONCl_2 \\[4pt]
(f)\ ArSeCl_3 + Ar'C\!\!\begin{array}{l}\diagup NSiMe_3 \\ \diagdown OSiMe_3\end{array} \\[4pt]
(g)\ ArSeSeAr + Ar'CONCl_2
\end{array}
\right\}
\longrightarrow
\begin{array}{l}
ArSe\!=\!NAr' \\
\mid \\
Cl
\end{array}
\quad (39)
$$
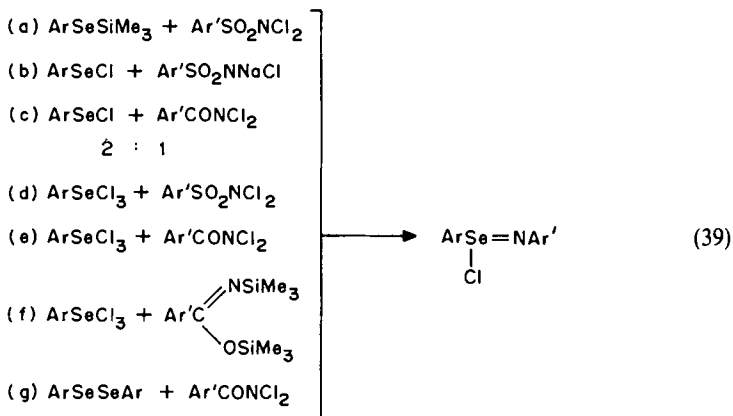
2. Chemical properties

Some of the chemical properties of *Se*-chloroarylselenimides have been studied. Hydrolysis by water with or without the presence of silver oxide yields the corresponding seleninic acids[43,44,45] (equation 40).

$$ArSe = NR \xrightarrow[(Ag_2O)]{H_2O} ArSeO_2H + RCONH_2 \quad (40)$$
$$\mid$$
$$Cl$$

TABLE 5. Se-Chloroarylselenimides synthesized.

$$ArSe = NAr'$$
$$|$$
$$Cl$$

Ar	Ar'	Method in equation 39	Ref.
Ph	PhSO$_2$	a, b, c, e	43, 44, 45
Ph	p-TolSO$_2$	a	44
Ph	p-ClC$_6$H$_4$SO$_2$	a	44
Ph	p-NO$_2$C$_6$H$_4$SO$_2$	a	44
p-Tol	PhSO$_2$	a	44
p-BrC$_6$H$_4$	PhSO$_2$	a	44
p-NO$_2$	PhSO$_2$	a	44
Ph	PhCO	c, e, f, g	45
Ph	p-TolCO	g	45
Ph	p-BrC$_6$H$_4$CO	g	45
Ph	p-NO$_2$C$_6$H$_4$CO	g	45
Ph	3,5-(NO$_2$)$_2$C$_6$H$_3$CO	g	45
p-Tol	p-BrC$_6$H$_4$CO	g	45
p-ClC$_6$H$_4$	p-ClC$_6$H$_4$CO	g	45

Reaction of hydrogen chloride or chlorine leads to the formation of the corresponding arylselenium trichloride (equation 41).

$$ArSe = NR \xrightarrow[\text{or } Cl_2]{\text{HCl}} ArSeCl_3 + RCONH_2 \qquad (41)$$
$$|$$
$$Cl$$

It has also been shown that substitution of chlorine by various nucleophiles is possible[31,32] (equation 42). The nucleophiles used include ammonia, imines, alcohols, alcoholates and phenolates. However, the compounds obtained by this route are unstable.

The property of Se-chloroselenimides to add to double bonds is interesting. The addition of various Se-chloro N-arylsulphonylselenimides to styrene to yield new selenimides has been described[44] (equation 43).

$$ArSe = NR \xrightarrow{Nu} ArSe = NR \qquad (42)$$
$$|\qquad\qquad\qquad\quad |$$
$$Cl\qquad\qquad\qquad\; Nu$$

$$ArSe = NSO_2Ar' + PhCH = CH_2 \longrightarrow PhCH = CHSe = NSO_2Ar' \qquad (43)$$
$$|\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad |$$
$$Cl\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\; Ar$$

When the reaction is carried out with Se-chloro N-acylselenimides, 1,4-cycloaddition products are isolated[45] (equation 44).

$$ArSe = NCOAr' + PhCH = CH_2 \longrightarrow \qquad\qquad (44)$$
$$|$$
$$Cl$$

3. Se-dichloro-N-ary1seleninyl Se-chloroselenimides ArSeCl₂N = SeClAr

These compounds are obtained by reaction of *Se*-dichloro diarylselenides with bis(trimethylsilyl)amines[46] or arylseleninyl trichlorides with *N*-chloro-bis(trimethylsilyl)amines[47] (equation 45).

$$Ph_2SeCl_2 + (Me_3Si)_2NH$$

$$Ph_2Se_2NCl_3 \qquad (45)$$

$$PhSeCl_3 + (Me_3Si)_2NCl$$
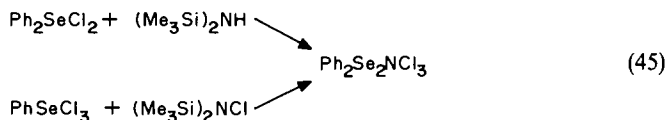
It is not yet known whether the structure of the product is covalent (41) or ionic (42).

$$\underset{\textbf{(41)}}{\overset{\displaystyle\mathop{PhSeN}\limits_{\substack{| \\ Cl}}=\mathop{SeAr}\limits_{\substack{| \\ Cl}}}{\overset{\displaystyle Cl}{|}}} \qquad \underset{\textbf{(42)}}{\left[\mathop{ArSe}\limits_{\substack{| \\ Cl}}\!\!=\!\!=\!\!=\!N=\!\!=\!\!=\mathop{SePh}\limits_{\substack{| \\ Cl}}\right]^{+}Cl^{-}}$$
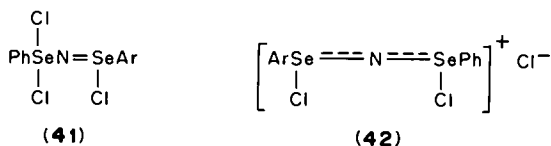
Hydrolysis of the phenyl derivative leads to phenylseleninic acid. Treatment with hydrochloric acid or with chlorine gives phenylselenium trichloride[47]. The product decomposes on heating giving a mixture of phenylselenium trichloride and phenyl-selenenyl chloride (equation 46).

$$Ph_2Se_2NCl_3 \xrightarrow{\Delta} PhSeCl + PhSeCl_3 + N_2 \qquad (46)$$

C. Selenoximides

1. Preparation

The only synthesis of this type of compound which has been published is the condensation of diarylselenones with *N*-sulphurylarenesulphonamides[48,49] (equation 47). All attempts to prepare these compounds by condensations of diarylselenones with *N*-sulphinylarylamines, *N*-sulphinyltrimethylsylilamines or *N*-sulphinylarylcarboxamides failed[47].

$$Ar_2SeO_2 + Ar'SO_2NSO \longrightarrow SO_2 + Ar_2Se = NSO_2Ar' \qquad (47)$$
$$\overset{\displaystyle\|}{O}$$

$$Ar = Ph, \, p\text{-Tol}, \, Ar' = Ph, \, p\text{-Tol}, \, p\text{-NO}_2C_6H_4$$
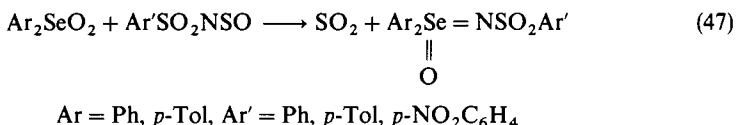
The products prepared were solids and were characterized by IR spectroscopy.

2. Chemical reactivity

Only the action of bases and acids on selenoximides has been studied[49]. Basic hydrolysis of the oximides yields the corresponding selenones, whereas treatment with hydrochloric acid (4 moles per mole) gave the *Se*-dichloro diarylselenide, arylsulphonamide and chlorine.

V. NITROGEN DERIVATIVES OF SELENIUM DIOXIDE

Among these compounds N-substituted selenium diimides have been the most studied derivatives. Only one example of an N-substituted selenium oximide (**43**) is known[50].

$$PhNH_2 + SeOCl_2 \longrightarrow PhN = Se = O$$
$$(43)$$
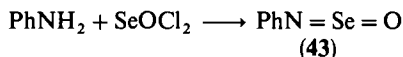
A. N-Selenium Diimides RN = Se = NR

1. Preparation

Selenium diimides are prepared by condensation of amines, amides and their derivatives with selenium, selenium tetrahalides or oxyselenohalides[51-53]. Table 6 summarizes the different methods available for the preparation. The diimides formed are sensitive to moisture and decompose to selenious acid[52].

2. Chemical properties

Selenium diimides have been reported to be good aminating agents. Thus, olefins can be aminated in the allylic position by N-substituted selenium diimides (equation 48) and many examples of such reactions have been described[51].

R = *t*-Bu, Tos

$$(48)$$
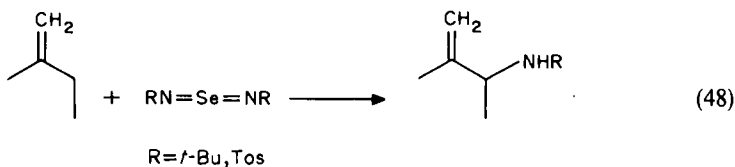
Treatment of a diene with N-tosyl selenium diimide yields the 1, 2-diamination product (equation 49).

$$(49)$$
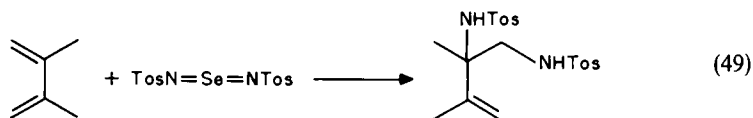
TABLE 6. Preparation of N-substituted selenium diimides RN = Se = NR

Starting material	Selenium vector	Product	Ref.
Chloramine-T	Se	$(TosN)_2Se$	51
t-BuNH$_2$	SeCl$_4$	$(t$-BuN)$_2$Se	51
TosNH$_2$	SeCl$_4$	$(TosN)_2Se$	51
RN(SiMe$_3$)$_2$ (R = PhSO$_2$, PhCO, MeCO)	SeF$_4$	$(RN)_2Se$	52
RSO$_2$N(SiMe$_3$)$_2$ R = Me, Ph)	SeF$_4$	$(RSO_2N)_2Se$ + RSO$_2$N = SeF$_2$	53
(Me$_3$Si)$_2$O	(PhSO$_2$N)SeF$_2$	$(PhSO_2N)_2Se$	53

The reaction with the selenium diimides certainly goes through a [4 + 2] cycloaddition compound (44), and the same reaction with sulphur diimide actually stops at the cycloaddition stage[54].

(44)
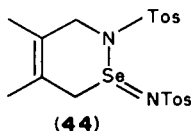
Diphenylsulphonyl selenium diimide (45) reacts with compounds having a double-bonded oxygen moiety to give the corresponding N-sulphonyl derivatives (46)[55] (equation 50).

$$PhSO_2N = Se = NSO_2Ph + E = O \longrightarrow 2PhSO_2N = E + SeO_2 \qquad (50)$$

$$\text{(45)} \qquad\qquad\qquad\qquad\qquad \text{(46)}$$
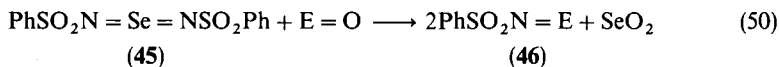
$E = RCH$ with $R = C_6H_5, p\text{-}BrC_6H_4, p\text{-}NO_2C_6H_4$; Me_2NCH; Me_2S; Ph_3P; Ph_2Se; Ph_2SeO, PhN; $p\text{-}Et_2NC_6H_4N$

Diacyl selenium diimides are less reactive in this condensation. Dibenzoyl selenium diimide reacts only with dimethyl sulphoxide. Diacetyl derivatives react rapidly with aldehydes. The compounds 47 obtained by treatment of triphenylphosphine oxide with diacyl selenium diimides yield the nitrile 48 when treated with triphenylphosphine[42] (equation 51).

$$RCON = PPh_3 \xrightarrow[Ph_3P]{} RCN \qquad (51)$$

$$\text{(47)} \qquad\qquad \text{(48)}$$
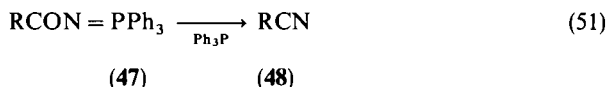
Ditosyl and diacyl selenium diimides have also been used for the synthesis of selenadiazole and oxaselenazine (see Part Two, Section III.A).

B. Se-Dichloroseleniumimide RN = SeCl$_2$

1. Preparation

The first preparation of these compounds was described in 1967[56] by the reaction N, N-dichloroamines or N, N-dichloroamides with selenium or with selenium tetrachloride (equation 52).

$$RNCl_2 + Se\ (SeCl_4) \rightarrow RNSeCl_2\ (+ Cl_2) \qquad (52)$$
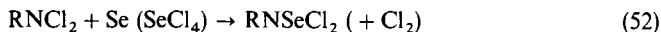
The method has been extended to N, N-dichloroarylsulphonamides ($R = ArSO_2$), N, N-dichlorophosphonamides $[R = (Et_2O)PO]$ and N, N-dichlorocarbonates ($R = CO_2Et$).

2. Chemical properties

Some chemical properties of the derivatives have been studied[57]; they were found to be very reactive. They hydrolyse to the amines or amides and selenious acid. On acidolysis with formic acid, Se-dichloroarylsulphonyl selenium imide gave the arylsulphonamide and selenium oxychloride (equation 53).

$$ArSO_2NSeCl_2 + HCOOH \longrightarrow ArSO_2NH_2 + SeOCl_2 \qquad (53)$$

The chlorine atom can be substituted by various nucleophiles such as amines, alcoholates, phenolates, glycol and ethylene oxide. For example, *Se*-dichlorophenylsulphonyl selenium imide (49) reacts with *N*-trimethylsilylmorpholine to give the *Se*-dimorpholinophenylsulphonyl selenium imide (50) (equation 54).

$$PhSO_2NSeCl_2 + 2 Me_3SiN\bigcirc O \longrightarrow PhSO_2NSe\left(-N\bigcirc O\right)_2 \quad (54)$$

$$\textbf{(49)} \qquad\qquad\qquad\qquad\qquad\qquad\qquad \textbf{(50)}$$
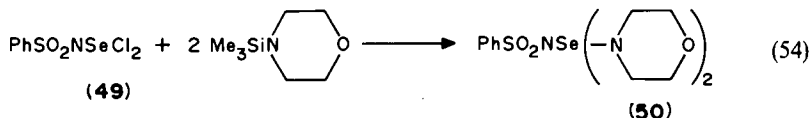
An addition product (51) with styrene has also been prepared (equation 55).

$$PhSO_2NSeCl_2 + 2PhCH=CH_2 \longrightarrow PhSO_2NSe(CH_2CHClPh)_2 \quad (55)$$

$$\textbf{(53)}$$
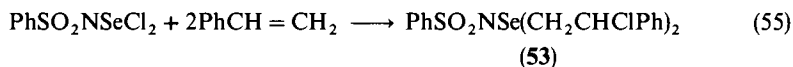
C. Se-Diamido-Se-dichloroselenium (RCONH)₂SeCl₂

Aromatic and aliphatic chloroamides react with selenium in a 2:1 ratio to give *Se*-diamido-*Se*-dichloroselenium derivatives[58,59] (equation 56).

$$2RCONHCl + Se \longrightarrow (RCONH)_2SeCl_2 \quad (56)$$

$$R = Me, Ph, p\text{-Tol}, p\text{-BrC}_6H_4, p\text{-ClC}_6H_4, 2,4\text{-Cl}_2C_6H_3$$
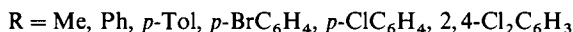
Another preparation is possible by reaction of *N*-trimethylsilylamides with selenium tetrachloride (equation 57). The products are thermally unstable and are cleaved by hydrochloric acid or chlorine to the corresponding amides or *N*-chloroamides, together with selenium tetrachloride[59].

$$2\,ArCONHSiMe_3 + SeCl_4 \longrightarrow (PhCONH)_2\,SeCl_2 \quad (57)$$
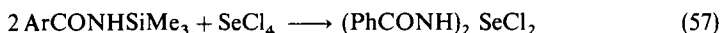
D. Miscellaneous

1. Amidoselenious esters

Diamidoselenious acid derivatives are prepared by reaction of selenious esters with a primary amine[60] (equation 58).

$$(MeO)_2SeO + 2MeNH_2 \rightleftharpoons (MeNH)_2SeO \quad (58)$$

Amidoselenious acid esters are obtained by reaction of selenium oxide with *N*-trimethylsilylamines[61] (equation 59).

$$R_2NSiMe_3 + SeO_2 \longrightarrow R_2NSeOSiMe_3 \quad (59)$$
$$\overset{\parallel}{O}$$

$$R_2N = \text{morpholine, piperidine, diethylamine}$$
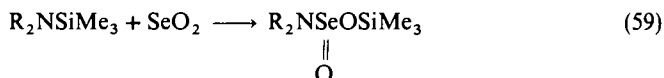
Treatment of latter compounds with water yields the corresponding pyroselenites (52) (equation 60).

$$R_2NSeOSiMe_3 \xrightarrow{\;H_2O\;} [R\overset{+}{N}H_2]_2\,Se_2O_5{}^{2-} \quad (60)$$
$$\overset{\parallel}{O} \qquad\qquad\qquad \textbf{(52)}$$
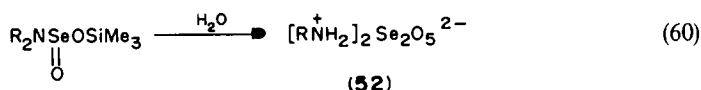
2. Aminoselanes

An example of preparation of an aminotetraselane is given in equation 61[62].

$$\text{HN} \diagup\diagdown + \text{Se} + \text{Pb}_3\text{O}_4 \longrightarrow \left(\diagup\diagdown \text{N} \right)_2 \text{Se}_4 \tag{61}$$

The same treatment with morpholine gives a mixture of tetra- and tri-aminoselanes (selanes are structures with three or more consecutive Se atoms).

VI. COMPOUNDS WITH Te—N BONDS

The only type of derivatives prepared in this series are tellurimides and tellurium imides.

A. Tellurimides R'₂TeNR²

1. Preparation

The first tellurimide was obtained by reaction of chloramine-T with 2, 2′-biphenylene telluride (53)[63] (equation 62).

$$\xrightarrow[\text{solvent}]{\text{chloramine-T}} \tag{62}$$

(53)
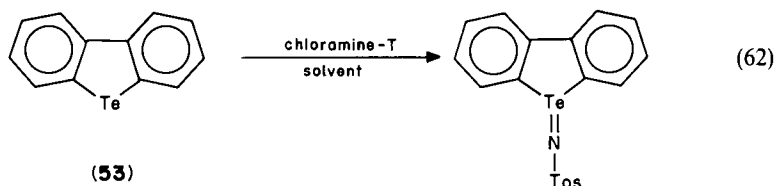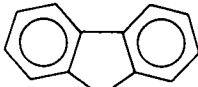
Like the selenimides, tellurimides have also been prepared by reaction of telluroxide with N-substituted sulphonamides[41,64] or amides[41,65,66] (equation 63) and by reaction of Te-chloro-Te-butoxytelluride with N-sodiosulphonamides[65] (equation 64). A recent method allows also the synthesis directly from tellurides[67] (equation 65).

$$R_2{}^1\text{TeO} \xrightarrow{R^2NH_2} R_2{}^1\text{TeNR}^2 \tag{63}$$

$$(R^2NH_2 = \text{amide or sulphonamide})$$

$$R_2{}^1\text{Te} + Me_3\text{COCl} \longrightarrow R_2{}^1\text{Te} \diagup\diagdown^{Cl}_{OCMe_3} \longrightarrow R_2{}^1\text{Te} = NSO_2R^2 \tag{64}$$

$$R_2{}^1\text{Te} \xrightarrow{TosN_3} R_2{}^1\text{TeNTos} \tag{65}$$
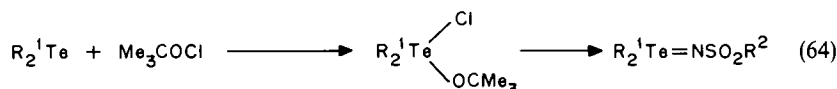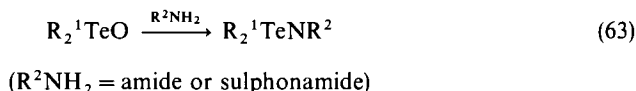
Condensation with amides (equation 63) takes place when the telluroxide substituents are sufficiently electron donating and the amide susbtituents sufficiently electron withdrawing.

Table 7 summarizes the tellurimides prepared by the different methods.

TABLE 7. Tellurimides $R_2{}^1TeNR^2$ prepared

R^1	R^2	Method (equation)	Ref.
(Biphenylene ring)[a]	Tos	62	63
p-An	Tos	63–65	64, 41, 66
p-An	$PhSO_2$	63–65	64, 4, 646
p-An	$PhCH_2SO_2$	63–65	64, 41, 66
Ph	Tos	64, 65	41, 65
Ph	$PhSO_2$	64, 65	41, 65
Ph	$PhCH_2SO_2$	64, 65	41, 65
p-Tol	$PhCH_2SO_2$	63	65
p-ClC_6H_4	$PhCH_2S_2O_2$	63	65
p-BrC_6H_4	$PhCH_2SO_2$	63	65
p-An	CCl_3CO	63	41
p-An	m- or p-$NO_2C_6H_4CO$	63	41
p-$NMe_2C_6H_4$	CCl_3CO	63	41
p-$NMe_2C_6H_4$	m- or p-$NO_2C_6H_4CO$	63	41
Ph	CF_3CO	63	41
p-Tol	CF_3CO	63	41
m-Tol	CF_3CO	63	41
p-An	CF_3CO	63	41
p-$Me_2NC_6H_4$	CF_3CO	63	41
p-ClC_6H_4	CF_3CO	63	41
p-BrC_6H_4	CF_3CO	63	41

[a]Biphenylene ring = $R_2{}^1$

Spectroscopic and X-ray diffraction studies of these compounds showed that they are highly bipolar with a considerable positive charge on tellurium. This fact allows one to write the structures in the form 54 or 55 when necessary.

$$R_2{}^1Te = NSO_2R \longleftrightarrow R_2{}^1Te^+ - N^-SO_2R$$
$$(54)$$

$$R_2{}^1Te = NCOR \longleftrightarrow R_2{}^1Te^+ - N^-COR \longleftrightarrow R_2{}^1Te^+ - N = \overset{O^-}{\underset{|}{C}}R$$
$$(55)$$
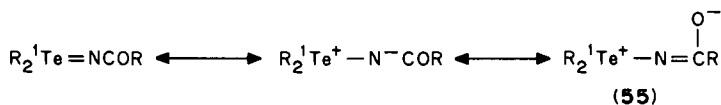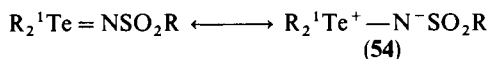
As a considerable double bond character is possible in structure 55, the authors[66] claimed that the separation of the *syn* (56) and *anti* (57) isomers was possible by recrystallization. The *syn* isomer is stabilized by charge interaction.

(56)   (57)
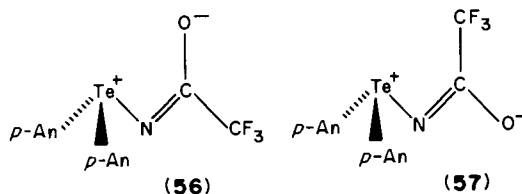
2. Chemical properties

a. Reduction. Tellurimides are reduced to the corresponding tellurides with triphenylphosphine[68] (equation 66).

$$R_2^1Te = NR^2 \xrightarrow{Ph_3P} (R^1)_2Te \qquad (66)$$

$$R^1 = Ph, \ p\text{-An}; \ R^2 = p\text{-Tos}, \ CF_3CO$$
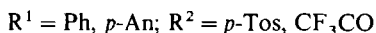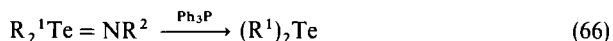
On reduction of *N*-tosylimides, $Ph_3P^+N^-Tos$ is obtained as a by-product, whereas the reduction of *N*-trifluoroacetylimide leads to triphenylphosphine oxide via the hygroscopically unstable $Ph_3PNCOCF_3$.

b. Reaction with electrophilic reagents. Tellurimides are cleaved at the Te—N bond by electrophilic reagents[69] (equation 67).

$$(p\text{-}RC_6H_4)_2Te = NR^1 + X^-Y^+ \longrightarrow (p\text{-}RC_6H_4)_2TeX_2 + R^1NY_2 \qquad (67)$$
$$R = H, \ OMe; \ R^1 = PhSO_2, \ CF_3CO;$$
$$XY = HCl, \ Cl_2, \ AcCl, \ Ac_2O, \ AcOH$$
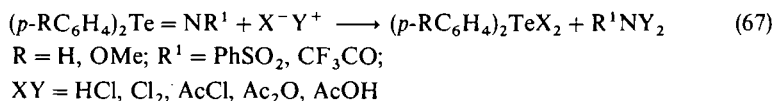
c. Reaction with active methylene compounds. Tellurimides react with dimedone at room temperature to yield the telluronium ylide[70] (equation 68).

$$R = H, OMe \ ; \ R^1 = Tos, PhSO_2, CF_3SO_2$$
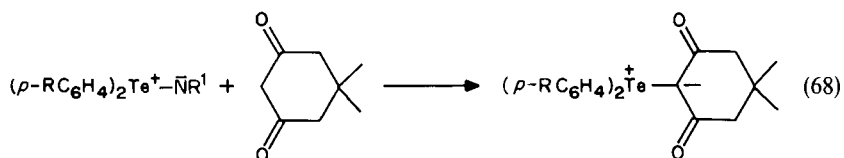
d. Reaction with aldehydes. Reaction of aldehydes and *N*-tosyltellurimides gave the *N*-tosylaldimines and telluroxides[57,71] (equation 69).

$$R_2^1Te^+ —NTos + RCHO \longrightarrow p\text{-}RC_6H_4CH = NTos + (p\text{-}RC_6H_4)_2TeO \qquad (69)$$
$$R^1 = Ph, \ p\text{-An}; \ R = Me_2NC_6H_4, \ p\text{-}NO_2C_6H_4$$
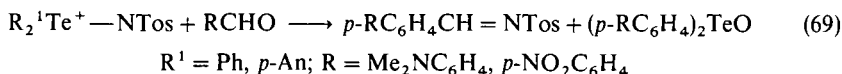
However, there are some limitations to the reaction. Thus trifluoroacetyltellurimides do not react[71], and although the reaction occurs well with aromatic aldehydes and with aldehydes having no α-hydrogen, in other cases it leads to unidentified mixtures[67].

B. *Te*-Chloro-*N*-tosyltellurimide RTe(Cl) = NTos

These compounds have been prepared by three different routes[72] (equation 70).

$$Ar = Ph, \ p\text{-An}, \ p\text{-}EtOC_6H_4, \ p\text{-}ClC_6H_4; \ Ar' = p\text{-}Tol; \ X = Cl, Br$$
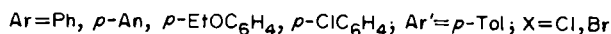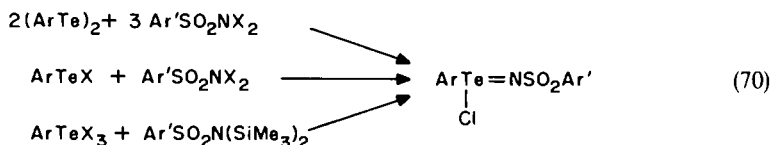
Different chemical properties were investigated[72]. The chlorine atom in the molecule can undergo substitution by activated amines, e.g. N-trimethylsilylmorpholine. Treatment with hydrochloric acid or water gives the aryltellurium trichloride and the aryltellurinyl halide, respectively, together with the corresponding sulphonamide.

The Te-chlorotellurimide 56 reacts with dimedone to give the condensation product 57, which in turn can react with another dimedone molecule in the presence of a base to give 58 (equation 71).

$$(71)$$
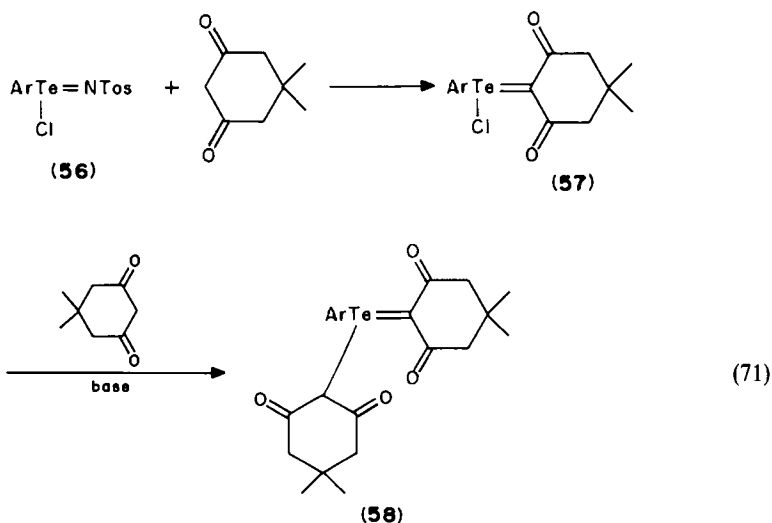
C. Nitrogen Derivatives of Tellurium Dioxide

Four types of derivatives have been prepared, starting from tellurium tetrahalides:
(a) Dihalotellurium imides (59)[73] (equation 72).

$$TeX_4 + (Me_3Si)_2NR \longrightarrow RN=TeX_2 \qquad (72)$$
$$(59)$$

$$X = F, Cl; \quad R = MeCO, PhSO_2, Tos$$
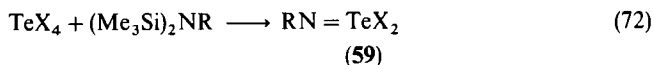
(b) Tellurium diimides (60)[73] (equation 73).

$$TeX_4 + 2(Me_3Si)_2NR \longrightarrow RN=Te=NR \qquad (73)$$
$$(60)$$

$$X = F, Cl; \quad R = MeCO, PhSO_2, Tos$$
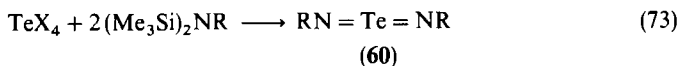
(c) Dihalo-Te-diaminotellurium (61)[74] (equation 74).

$$TeX_4 + Me_3SiNR_2 \longrightarrow (R_2N)_2TeX_2 \qquad (74)$$
$$(61)$$

$$X = Cl, F; \quad R = Et; \quad R_2N = morpholine, piperidine$$
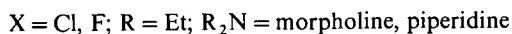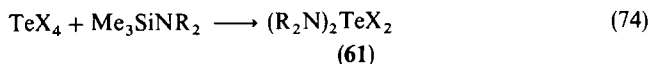
(d) Diamino-Te-tellurium imides (**62**)[74] (equation 75).

$$(R_2N)_2TeX_2 + (Me_3Si)_2NR^1 \longrightarrow (R_2N)_2Te = NR \qquad (75)$$

$$(62)$$
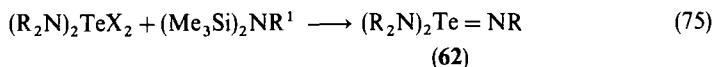
$$X = F;\ R_2N = \text{morpholine};\ R^1 = PhSO_2,\ \text{Tos}$$

Derivatives **59** and **60** behave in the same manner on hydrolysis or on treatment with acids. In both cases, tellurium oxide is obtained on hydrolysis together with the amide, and tellurium tetrachloride with the amide on treatment with hydrochloric acid. When treated with N-trimethylsilylmorpholine, **59** yields **62**, and so does **61** when treated with N,N-trimethylsilylarylsulphonamides.

PART TWO. HETEROCYCLIC COMPOUNDS WITH Se—N AND Te—N BONDS

VII. INTRODUCTION

This second part deals only with heterocyclic systems bearing at least one Se—N or Te—N bond. Other heterocycles containing Se (or Te) and nitrogen but not bound to each other were recently reviewed by Renson[15] in Volume 1 of this book and are not covered in this chapter. Thus this part completes Renson's chapter. We refer frequently to Renson's chapter; in order to present a complete and readable review here, some repetition and overlap was necessary, but this has been kept to the minimum.

VIII. THREE- AND FOUR-MEMBERED RINGS

The chemistry of this type of molecule is poorly documented. Selenaziridines cannot be obtained by treatment of oxaziridines with potassium selenoxanthate[76]. Decomposition of 1,2-benzodithiole-3-selenoximide (**63**) leads to the intermediate **64**, which rearranges with extrusion of sulphur[77] (equation 76).
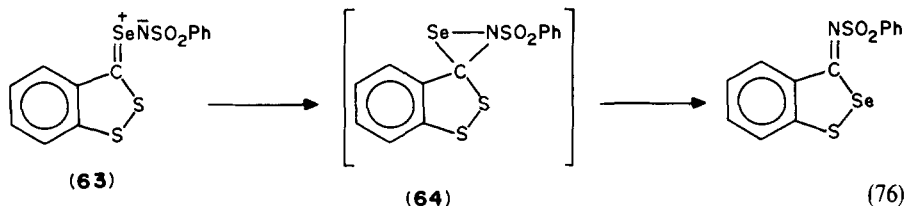
An interesting spiro heterocycle (**66**) has been synthesized[78] through the reaction of SeOCl₂ with **65** (equation 77).
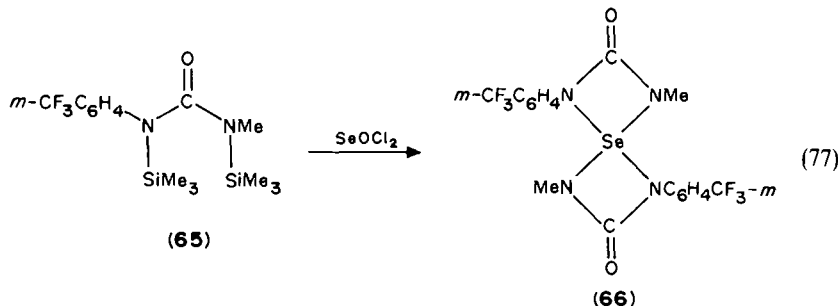
IX. FIVE-MEMBERED RINGS

A. One Se—N bond

In addition to the work of Lalezari *et al.*[79], Renson[15] has reviewed heterocycles containing N and either Se or Te.

1. 1,2-Selenazoles, (d)-condensed systems and derivatives

a. Synthesis. (i) 1,2-Selenazoles and (d)-condensed systems. The parent heterocycle (1,2-selenazole or isoselenazole) and its 3-methyl derivative were first mentioned in 1962[80]. They were obtained by reaction of selenocyanic acid with acrolein or but-3-yn-2-one. Using similar methodology, a general synthesis of isoselenazoles and the corresponding (d)-condensed systems was described in 1975[15]. More recently[81], preparations of 3-, 5- or 3,5-substituted isoselenazoles (68) were reported. The ring formation step consists in an intramolecular nucleophilic substitution in hydroxylamine-O-sulphonic acids of α,β-acetylenic carbonyl compounds (67) (equation 78).

$$(78)$$
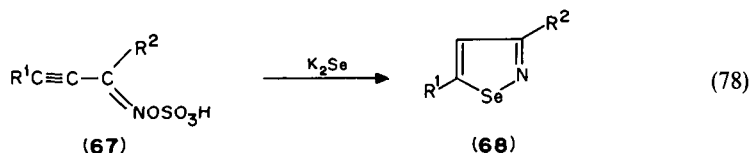
Benzeneselenenyl halides containing *ortho*-carbonyl groups can be involved in similar cyclizations, affording 1,2-benzisoselenazoles. This reaction is fairly general and several condensed systems have been described[15]. In some cases electrophilic cyclization of aldoximes (69) also affords (d)-condensed 1,2-selenazoles (70)[82] (equation 79).

$$(79)$$

X = S or Se ; PPA = polyphosphoric acid
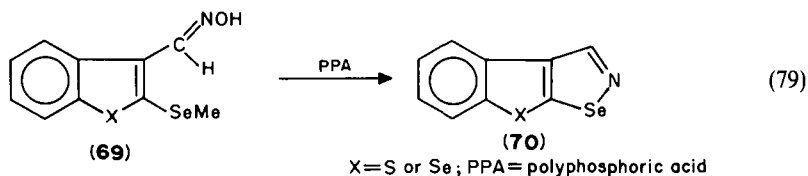
The polyphosphoric acid treatment of the corresponding ketoximes leads to condensed 1,3-selenazole systems through an initial Beckman rearrangement[99].

The oximation of 2-selenocyanobenzophenone or acetophenone was found to afford the corresponding benzisoselenazole *N*-oxides[83]. Other syntheses of condensed 1,2-selenazoles have been described by Renson[15].

(ii) Isoselenazolium salts and (d)-condensed systems. *N*-Aryl-5-aryl-isoselenazolium salts were prepared by Liebscher and Hartmann[84] through the cyclization of *N,N*-dimethyl-3-chloro-3-aryl-2-chloropropeniminium salts with potassium selenocyanate. Reaction of benzisoselenazolinones (71) or *o*-methylselenobenzamides (72) with phosphorous pentachloride leads to 3-chloro-1,2-benzisoselenazolium salts (73)[85] (equation 80).

Treatment of the benzisoselenazolinone 71 ($R^1 = R^2 = H$) with ethyl chloroformate affords the corresponding *N*-ethoxycarbonylbenzisoselenazolium chloride[86].

(iii) Benzisoselenazolinones. In 1924, Lesser and Weiss[87] were the first to synthesize

$$(80)$$
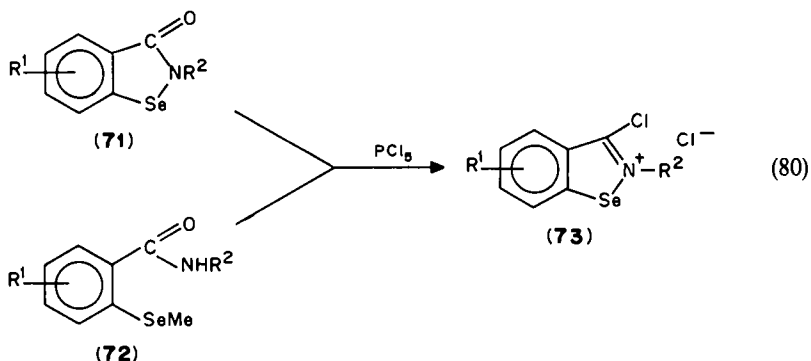
benzisoselenazolinone derivatives (75) by condensation of dichlorides (74) with ammonia or amines (equation 81).

$$(81)$$

$$R^1 = H; R^2 = H, Me, Et, Ph$$
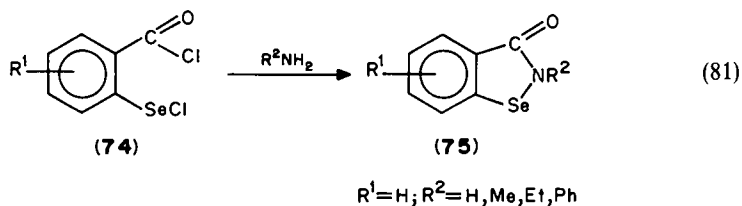
More recently, it has been shown that the hydrolysis of 3-chlorobenzisoselenazolium salts (73) or the reaction of o-methylselenobenzamides (72) with bromine in basic medium also leads to various benzisoselenazolinone derivatives. During the last five years, and owing to interest in the anti-inflammatory and glutathion peroxidase-like activities[88–92] of this class of compounds, their chemistry has been considerably investigated and patented[93–95]. It is not noteworthy that the sulphur analogues of 75 do not exhibit such pronounced activities. Important improvements in the synthesis of benzisoselenazolinones substituted in the benzene nucleus involve ortho-lithiation reactions[14,96], which afford faster chemical pathways[97,98] to some starting materials as shown in equation 82.

$$(82)$$
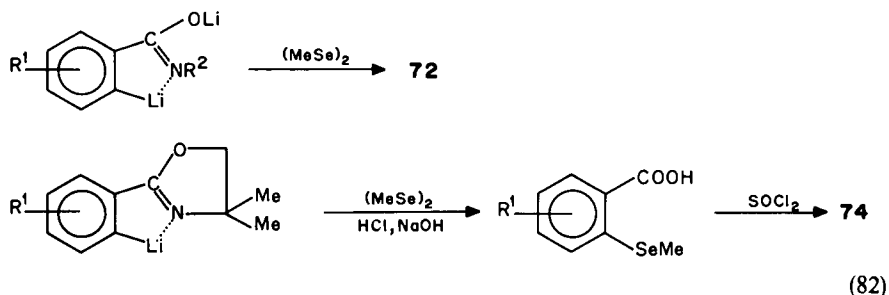
Various substituents were introduced into the benzene ring or on the nitrogen atom of 75 to try to improve the activity of the so-called PZ 51 or Ebselen 75 ($R^1 = H; R^2 = Ph$). The variations of the nature of R^2 in 75 included alkyl, aryl, heteroaryl and amino acid groups[98]. Other (d)-condensed isoselenazolinone systems (naphtho, thieno, furo and pyrido) were also obtained[99].

b. Properties. (i) 1,2-Selenazoles and (*d*)-condensed systems. Electrophilic substitution of isoselenazole occurs, as with isothiazole, at positions 4 and 5[15]. Recently, several methyl-substituted isoselenazoles were oxidized by SeO_2 to the corresponding acids in low yields[100].

The chemical and physicochemical properties of isoselenazole and its benzo-condensed derivatives have been described particularly their reaction with lithium carbanions[15]. [77]Se chemical shifts are specific for such heterocyclic systems and range around 1000–1050 ppm downfield from dimethyl selenide[101,102].

(ii) Benzisoselenazolinones. *N*-Acetylbenzisoselenazolinone (76a) reacts[103] with potassium acetate and acetic anhydride following three different pathways (equation 83). The benzo(*b*)selenophene derivatives 77, 78, 79 and 80 were separated from the reaction products. The mechanism has been discussed[103].

$$(a)\ R = COMe$$
$$(b)\ R = Me \tag{83}$$
$$(c)\ R = COOEt$$
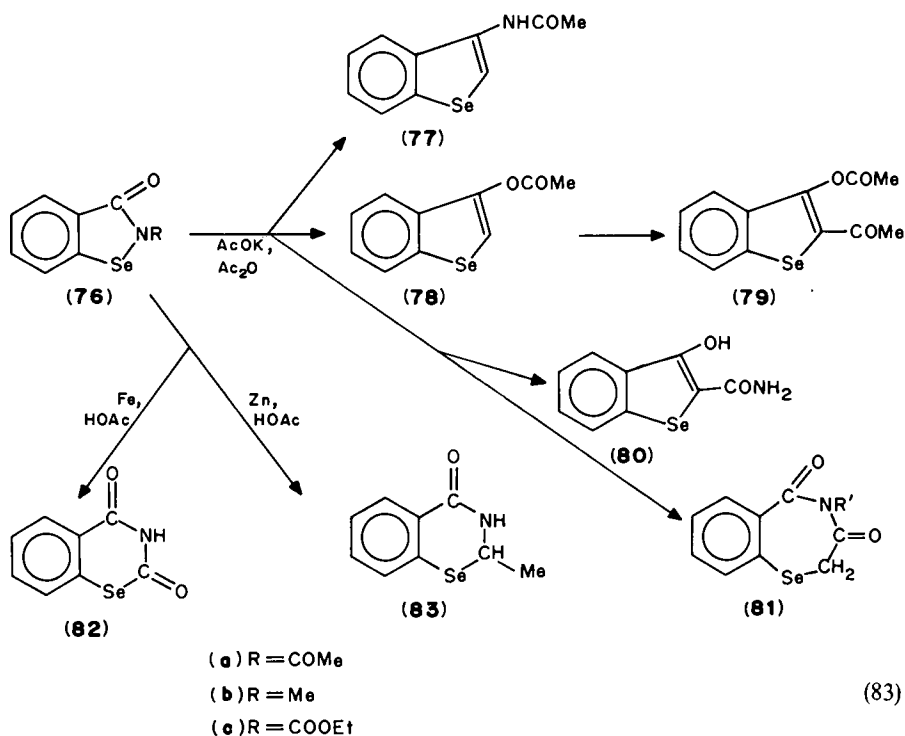
Compound 80 is probably formed through the intermediate 81 ($R' = H$). The fact that with 76b the intermediate 4-methyl-2*H*,4*H*-3,5-dioxobenzo(*b*)selenazepine (81, $R' = Me$) can be isolated is taken as a proof of the mechanism.

Ring expansion[86] of 76a or 76c leads to the 1,3-benzoselenazine derivatives 83 and 82. With diazomethane, 82 is regioselectively methylated on the nitrogen atom.

2. *(c)-Condensed 1,2-selenazoles*

SeO_2 oxidation of 5-amino-6-methyl-3-phenyl-4-(2*H*)-pyrimidone (84) (equation 84) leads to isoselenazolo[4,3-*d*]pyrimidine (85), the only known (*c*)-condensed 1,2-

selenazole[104,105a,b]. Unlike the analogous benzo[c]isothiazoles, several attempts to synthesize benzo[c]isoselenazoles were unsuccessful[99].

(84)

(84) **(85)**
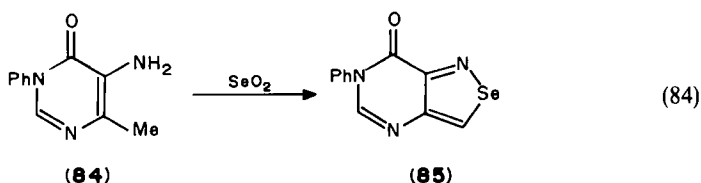
Attempted ring closures of o-toluidine with electrophilic selenium reagents ($SeOCl_2$, $SeCl_4$, $SeBr_4$, SeO_2, Se_2Cl_2) and the oxidation of o-aminoselenobenzamide or selenol benzoate did not lead to the desired products.

B. One Se—N Bond with One Other Heteroatom in the Ring

So far now no derivative of oxaselenazole has been described.

1. Thiaselenazoles, diselenazoles and derivatives

Benzo-condensed systems (1,2,3-benzodichalcogenazolium salts are the only known derivatives. They were reviewed by Renson (Ref. 15, pp. 462–463).

2. 1,2,3-Selenadiazoles and derivatives[79]

a. Synthesis. The chemistry of 1,2,3-selenadiazoles has been extensively studied since 1969, when Lalezari and coworkers proved that these heterocycles are easily obtained by SeO_2 oxidation of semicarbazones[106] (equation 85), and later showed their usefulness as synthons for access to alkynes[79].

(85)

(86) **(87)**
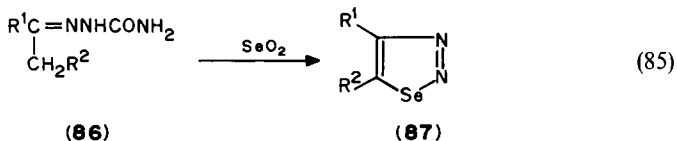
The mechanism of the SeO_2 oxidation of the semicarbazones **86** to yield 1,2,3-selenadiazoles **(87)**[106] has been proved[79] and the regioselectivity of the oxidative ring closure has been studied[107].

$^{75}SeO_2$ oxidation[108,109] has also been performed, affording ^{75}Se-labelled 1,2,3-selenadiazoles. ^{14}C-Labelled[110] and deuteriated[112] derivatives are known. Treatment of 7-hydroxycycloocteno-1,2,3-selenadiazole affords a condensed 1,2,3-selenadiazoline as rearrangement product[113].

Aromatic condensed 1,2,3-selenadiazoles cannot be obtained by the reaction pathway of equation 85. It has been shown[15,114] that the diazotization of o-aminoselenophenols **(88)** leads to 1,2,3-benzo[d]selenadiazoles **(89)** (equation 86).

(86)

(88) **(89)**

In our experience, diazotization of o-aminophenyl tellurides gives immediate evolution of nitrogen, and no derivative of 1, 2, 3-benzo[d]telluradiazole can be isolated[115].

b. Properties. The most important use of 1, 2, 3-selenadiazoles in organic syntheses is based on their thermal instability (this behaviour is different from that of 1, 2, 3-thiadiazoles, which are thermally more stable). Indeed, when heated, they decompose with the formation of nitrogen, elemental selenium and of acetylenes (**91**), diselenins (**92**) and selenophenes (**93**) (equation 87). The proportions of the various products are generally dependent on the nature of the substrate, the concentration, the temperature and the medium[15].

$$\text{(90)} \qquad \text{(91)} \qquad \text{(92)} \qquad \text{(93)} \qquad (87)$$

The mechanism of this reaction has been studied[116] and alkyneselenol, selenoketone and diselenetane[15,117] were recognized as intermediate or products of the reaction. 1, 2, 3-Benzoselenadiazole undergoes a thermal ring cleavage leading to 6-fulvene selenone[118]. In vacuum flash thermolysis, cyclopenta[d]-1, 2, 3-selenadiazole decomposes through propadiene selone to a selenopropargyl aldehyde derivative[119], whereas higher rings give tetrahydrofulvene selone derivatives[120]. For eight and higher membered cycloalkeno-1, 2, 3-selenadiazoles, the reaction may be considered as the method of choice for the transformation of a ketonic to an acetylenic function[121].

Cycloalkeno-1, 2, 3-selenadiazoles with smaller than six-membered rings give unstable acetylenes which can be trapped with tetraphenylcyclopentadienone[122,123] or with α-pyrone derivatives[124], in the latter case affording a new general method for benzoannellation. An analogous synthesis has been developed with 1, 4-quinone complexes[125].

In other cases, dimerization occurs, leading to **92**, and subsequent loss of a selenium atom leads finally to **93**. In this way, a mixture of 2, 4- and 2, 5-diarylselenophenes is obtained by thermolysis of 4-aryl-1, 2, 3-selenadiazole. 1, 2, 3-Selenadiazoles also undergo photolysis, leading to alkynes and small amounts of diselenafulvalenes through alkyne-selenols and selenoketenes, which have been identified as intermediates in the reaction (ref. 15, p. 463).

The behaviour of 1, 2, 3-selenadiazoles towards bases also illustrates the synthetic utility of these heterocycles. It has been shown that the abstraction of the 5-proton in 4-substituted 1, 2, 3-selenadiazole is followed by ring opening and leads to an alkyne selenolate (**94**) (equation 88).

Alkyne selenolates (**94**) are versatile synthons and allow the synthesis of a wide variety of molecules[15]. In acidic media, **94** can dimerize through nucleophilic addition and give diselenafulvene derivatives (**96**). Intermediates **94** also undergo carbon disulphide or diselenide cycloaddition, affording key molecules for the preparation of 'organic metals' (Ref. 15, p. 448). Alkyne selenolates react in dilute solutions with amines or alcohols, leading to selenoamides (**97**) or selenoesters (**98**)[15,126]. Cycloaddition with acetylene derivatives yields substituted selenophenes (**99**)[15].

The nucleophilic character of the selenolates **94** has been used in other condensations with ω-halo acids[127], acyl isothio(seleno)cyanates[128] and aryl isothiocyanates[129,130]. Recently, ring opening of 4, 5-dimethyl-1, 2, 3-selenadiazole by tin(IV) derivatives also afforded precursors of 'organic metal'[132]. PMR data for some 1, 2, 3-selenadiazoles have been reported[131] and more recently a detailed NMR study of 36 derivatives of the parent heterocycle has been performed using ^1H, ^{13}C and ^{77}Se resonances[130].

Photoelectronic and mass spectrometric spectra were also analysed for simple compounds[133]. Complexes with pentacarbonyl metals which are stable in air are available

$$(88)$$

with $Cr(CO)_5$[134], $W(CO)_5$[134] or $Fe(CO)_3$[135,136,137]. Some derivatives of 1, 2, 3-selenadiazoles exhibit antibacterial and antifungal activity[15,138].

3. 1,2,4-Selenadiazoles

The first synthesis of 1, 2, 4-selenadiazole derivatives was published in 1904[139a] and developed later by Cohen[139b].

Iodine oxidation of the arylselenoamide **100** affords an unstable intermediate which immediately cyclizes, with loss of H_2Se, to give 3, 5-diaryl-1, 2, 4-selenadiazoles (**101**) (equation 89).

$$(89)$$
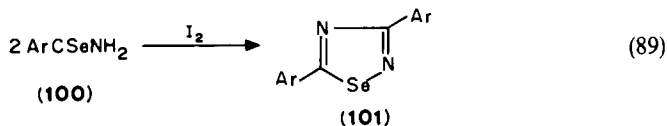
Analogously to the synthesis of 1, 2, 4-thiadiazoles, potassium selenocyanate reacts with N-haloamidines and gives 5-amino-3-substituted-1, 2, 4-selenadiazoles[139c].

C. One Se—N Bond with Two Other Heteroatoms in the Ring

1. 1,2,3,4-Selenatriazole

1, 2, 3, 4-Selenatriazole is the only five-membered ring system, (relevant to this chapter) known with four heteroatoms. Some of its derivatives (**104**) have recently been obtained[140] through condensation of 4, 4-dialkylselenosemicarbazides (**102**) with nitrous acid or with an aza transfer reagent (equation 90). Reaction of the diselenides **103** with azide anion affords a similar result.

$$(90)$$
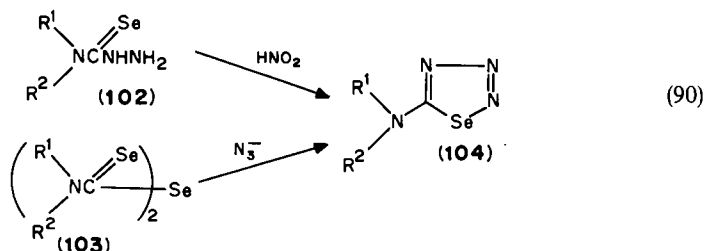
Compound **104** ($R^1 = R^2 = Et$) is unstable and light sensitive. Its decomposition furnishes disubstituted cyanamides, elemental selenium and nitrogen. If $R^1 = H$ and $R^2 = Et$ in **104**, decomposition affords hydrazoic acid and an isoselenocyanate.

D. Two Se—N Bonds

1. 1,2,5-Selenadiazoles and derivatives

a. Synthesis. The first non-condensed derivative of this series was obtained in 1967 by degradation of the pyrimidine ring of 1,2,5-selenadiazolo[3,4-*d*]pyrimidine-7(6*H*)-6-one[141].

A more general synthesis of 1,2,5-selenadiazoles (**107**) consists in the reaction of SeO_2 or Se_2Cl_2 with ethylenediamine derivatives (**105**) (equation 91)[15].

$$(91)$$
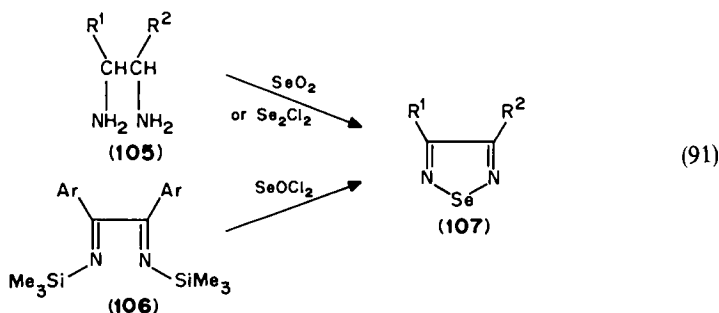
Two similar reactions starting from bis(trimethylsilyl)imines (**106**) and $SeOCl_2$[142] or from unprotected imines and $SeCl_2$[143] have also been used for the synthesis of **107**.

The chemistry of (*c*)-condensed 1,2,5-selenadiazoles is much better documented and a recent review[144] has been devoted to them. 2,1,3-Benzoselenadiazole (**109**) (piaselenole or piazselenole) is one of the oldest known organoselenium compounds. It was synthesized in 1889[145] by reaction of *o*-phenylenediamine (**108**) with SeO_2 (equation 92). Owing to the high reproducibility and the quantitative yields furnished by this reaction, it has been extensively used (ref. 15, p. 465).

$$(92)$$
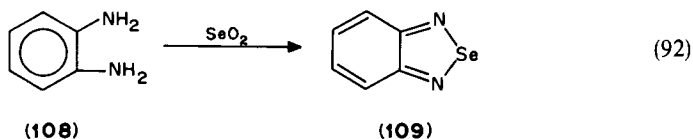
1,2,5-Selenadiazolohalogeno[3,4-*b*]- and -[3,4-*c*]-pyridine[146], 9-tosyl-hydrazononaphtho[2,3-*c*]-1,2,5-selenadiazol-4-one[147], 4,7-diphenyl-1,2,5-selena-diazolo[3,4-*c*]pyridines[148], 1,2,5-selenadiazolo[3,4-*c*]quinoline[149] and 2,1,3-benzoselenadiazolo[4,5-*c*:6,7-*c'*]bis-1,2,5-thiadiazole[150] have also been described.

b. Properties. Oxidation by SeO_2 of methyl-substituted 1,2,5-selenadiazoles affords the corresponding acids in low yields[100]. The chemical properties of 1,2,5-selenadiazoles have been reviewed[15]. Catalytic amination of **109** with NH_2OH–V_2O_5 affords 4-amino-2,1,3-benzoselenadiazole[151]. Pyrolysis of **109** *N*-oxide generates **109** and benzofuroxan[152], whereas, under similar conditions, the 1,3-dimethyl bis-quaternary salt gives

benzimidazole and its 1-methyl derivative[153]. Photolysis of **107** derivatives leads to nitrile selenide as the initial product[154,155], which is further decomposed to nitrile and elemental selenium. Owing to the easy access to (c)-condensed 1, 2, 5-selenadiazoles, these molecules have been exhaustively examined by physical and analytical methods. Theoretical calculations (MO, LCAO and PPP) have been carried out on the parent compound and its benzo derivatives[156]. Polarized electronic and electric field spectra of **107** have also been reported[157]. The parent heterocycle **107** ($R^1 = R^2 = H$) has been studied by photoelectron spectroscopy[158]. Several ^1H NMR studies have been reported. The effect of substituents on the coupling constants in the benzene ring of **109** has been described[159].

It has been shown that the electron-donating ability follows the order NMe > O > S or Se in N-quaternized 2, 1, 3-benzoselenadiazoles and their analogues[160]. A conformational study of 3-phenyl-1, 2, 5-selenadiazole in the nematic phase at 100 MHz was reported[161]. The structures of the parent compound[162] **107** and of its benzo derivative **109**[163] were determined under similar conditions on the basis of ^1H, ^{13}C and ^{77}Se NMR resonances. ^{13}C chemical shifts and $^{13}C-H$ coupling constants in 2, 1, 3-benzoselenadiazole are also available[164]. Weak solvent effects, detected in the ^{13}C NMR[164] and ^{15}N NMR spectra, were described[165] for **109** and its other chalcogeno analogues. Magnetic circular dichroism and electronic spectra of piazselenole have been reported[166]. UV spectra[167] and pK_a determinations by UV–visible techniques were described[168]. Selenium-containing radicals, derived from 1, 2, 5-selenadiazoles, were investigated by ESR techniques[169]. The behaviour of theses heterocycles under electronic impact showed an important loss of the corresponding nitrile and chalcogen extrusion (Se > S $\gg$ O)[170,171]. Meisenheimer complexes[172] and metal carbonyl derivatives[173] were investigated. Sher-mann and coworkers discussed the redox behaviour of 2, 1, 3-benzoselenadiazole[174] and the polarographic reduction of (c)-condensed 1, 2, 3-selenadiazoles was studied[175,176]. The investigation of **109** by electrical dipole moment measurements allowed the determination of the importance of its mesomeric forms[177] and the increase in mesomeric charge transfer from oxygen to selenium has been confirmed recently[178]. Complexes with tetracyano-quinodimethane (TCNQ) have been studied[179].

Kinetic data for the formation of (c)-condensed selenadiazoles have been repor-ted[180,181] and allow the use of this reaction for the determination of Se^{IV} derivatives (even in trace amounts) or of o-diamines[182-184]. Quantitative removal of chlorine or bromine from air streams is possible with piazselenole[185], and the complex so obtained can be thermally regenerated[186a]. The pH-dependent stability of Pd^{2+} complexes with 2, 1, 3-benzoselenadiazolyl-α-amino acids has been studied[186b].

E. Two Se—N Bonds with Two Other Heteroatoms in the Ring

1. 1,2,3,5-Selenatriazole

Reaction of 1, 2-diamino-5-phenylimidazoles with SeO_2[187a] affords 5-phenyl-imidazolo[1, 2-c]-1, 2, 3, 5-selenatriazole derivatives (equation 93). Benzimidazolo[1, 2-c]-1, 2, 3, 5-selenatriazole is obtained similarly.

$$ (93) $$

(110)   (111)
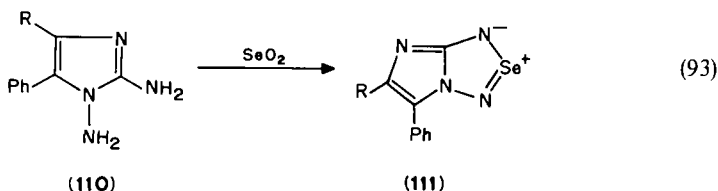
F. One Te—N Bond

1. 1,2-Tellurazole (isotellurazole) and derivatives

3-Substituted isotellurazoles were obtained recently in 5–10% yields by reaction of α, β-acetylenic ketones with hydroxylamine-θ-sulphonic acid derivatives and K_2Te[187b]. This method is analogous to that one used in the Se series[81] but fails for the preparation of the unsubstituted heterocycle.

Benzisotellurazole (**114**) was first obtained in 1978[188] by the reaction of o-bromotellurobenzaldehyde (**112**) with ammonia or the polyphosphoric acid (PPA) ring closure of o-butyltellurobenzaldoxime (**113**) (equation 94).

(112)

(113)

(114)

(94)
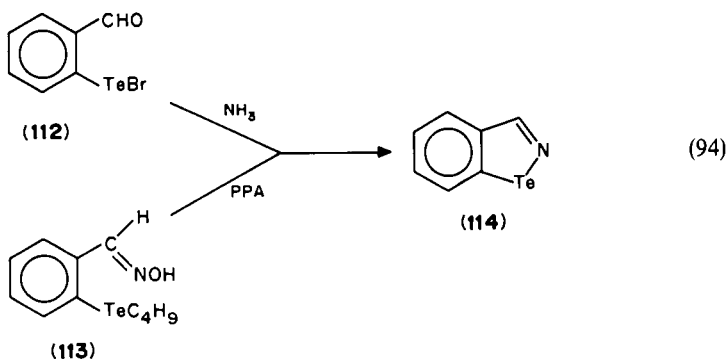
Thienoisotellurazoles could not be obtained by this method, the corresponding ditellurides being formed. Benzisotellurazole reacts with MeI to give N-methylbenzisotellurazolium iodide[188]. X-ray analysis[189] of the structure of 114 shows very short Te $\cdots$ N intermolecular contacts (2.4 Å), explaining its higher melting point and its lower solubility compared with the selenium analogue.

G. Two Te—N Bonds

1. 1,2,5-Telluradiazole and derivatives

In 1982, Bertini and coworkers[190,191] described the synthesis of the first examples of 1, 2, 5-telluradiazoles (**116**) (equation 95). The ring-opening reaction of 1, 2, 5-thiadiazoles (or better their selenium analogue) affords an intermediate dimetalloaldimine (**115**), which can be trapped with $TeCl_4$ in the presence of Et_3N to give **116**.

(115)
+
R_2Se

(116)

(95)
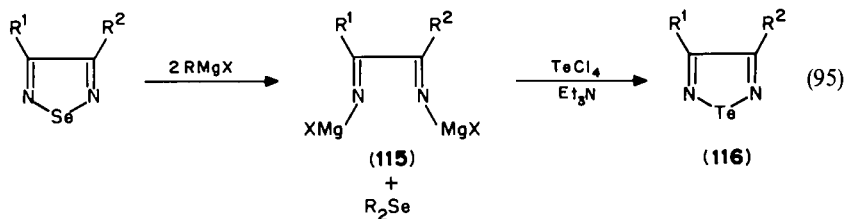
As for benzisotellurazole (**114**), X-ray analysis of the structure of 116 also confirms the presence of close intermolecular quasi-polymeric contacts[192], explaining the large

difference between the melting points of **116** ($R^1 = R^2 = H$; 185–188 °C) and its Se analogue (21 °C). Compound **116** and its derivatives are stable in air and water and are weak bases. They are unstable to light and are hydrolysed by acids to α-diketones, $NH_4{}^+$, Te and H_2TeO_3. Elemental tellurium reacts with o-chloromercuridiazobenzene to give a compound reducible to di(o-aminophenyl) ditelluride, the X-ray data for which are in agreement with a quasi 1-chloro-1, 2, 5-telluradiazole ring system[193].

X. SIX-MEMBERED RINGS

A. One Se—N Bond with One Oxygen in the Ring

Only derivatives of 5, 6-dihydro-1, 4, 3-oxaselenazine (**117**) are available[194–197] through 1, 4-dipolar cycloaddition of styrene (equation 96).

$$X = Ph, Cl; \quad Y = Ph$$

(96)

(**117**)
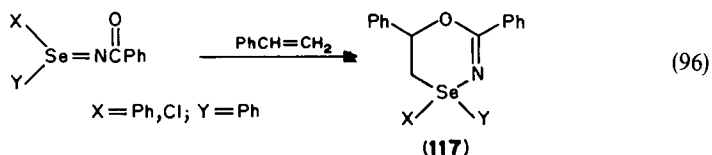
B. One Se—N Bond with One Sulphur in the Ring

Recently, ring expansion of 2-azido-2-ethylthio-1, 3-thiaselenols (**118**) afforded 2-ethylthio-1, 4, 3-thiaselenazine (**119**) derivatives with good yields[198] (equation 97).

(**118**)   (**119**)

(97)
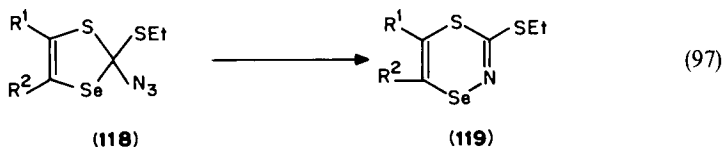
These new heterocyclic systems were well characterized by the usual techniques. They are thermally unstable and react with HI to give 2-amino-1, 3-thiaselenolium iodides.

C. One Se—N Bond with One Other Nitrogen in the Ring

3-Thioxo-6-chloromethyl-1, 2, 4-perhydroselenadiazine is produced by the reaction of allylthiourea with Se_2Cl_2[199]. Condensation[200] of benzeneselenenyl chloride with **120** leads to an ylid (**121**), which can be thermolysed to the benzoselenadiazine derivative **122** (equation 98).

(**120**)   (**121**)   (**122**)

(98)
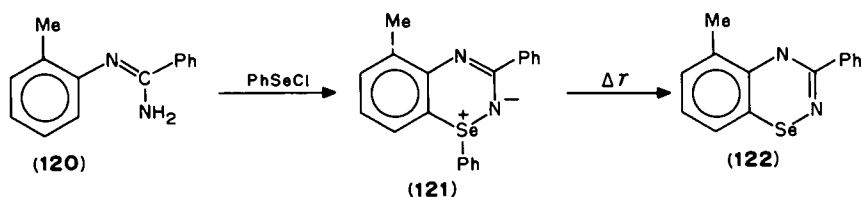
D. Two Se—N Bonds

As with *o*-phenylenediamine, the reaction of 1,8-diaminonaphthalene with SeO_2 affords $1H,3H$-naphtho[1,8-*c,d*]-1,2,6-selenadiazine[201,202]. This reaction was irreproducible but, by reaction with $SeOCl_2$, the corresponding selenoxide could be isolated in 51% yield. The same methodology was applied to 1,4,5,8-tetraaminonaphthalene and afforded naphtho[1,8-*c,d*:4,5-*c',d'*]bis-(1,2,6-selenadiazine)[15]. Its electronic structure has been studied by ESCA and theoretical calculations[203].

XI. LARGER RINGS

Condensation of $SeOCl_2$ (or Se_2Cl_2) with lithium trisilylamide affords eight- and fifteen-membered rings. They have been isolated and characterized by physicochemical methods and by X-ray diffraction[204].

XII. MISCELLANEOUS: AZASELENAPENTALENES

Only a few derivatives of azaselenapentalene are known. Bisarylhydrazones (123) react with SeO_2 and give the tetraazaselenapentalene 124 (equation 99)[205].

$$(99)$$
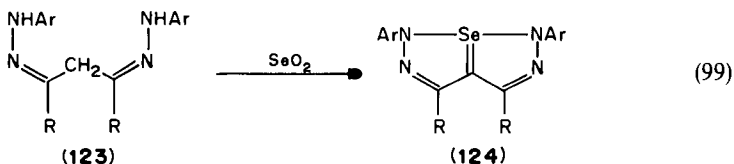
3-Methylene-1,2-diselenolylium cations (125) react with arenediazonium salts[206] and lead to diselenadiazapentalene (126) (equation 100). These compounds have been studied by mass spectrometry[111].

$$(100)$$
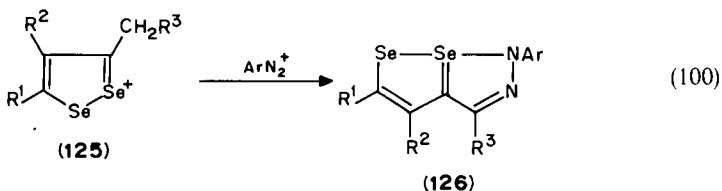
NOTE ADDED IN PROOF

Since this chapter was written, a book on selenium reagents that gives some synthetic applications of Se—N derivatives has been published[207].

XIII. REFERENCES

1. H. Rheinholt, in *Houben Weyl, Methoden der Organischen Chemie, Schwefel-, Selen-, Tellurverbindungen*, Vol. IX, Georg Thieme, Stuttgart, 1955, pp. 1124–1180.
2. E. Painter, *Chem. Rev.*, **28**, 200 (1941).
3. T. Campbell, H. Walker and G. Coppinger, *Chem. Rev.*, **50**, 279 (1952).
4. D. Klaymann and W. H. H. Gunther (Eds.), *Organic Selenium Compounds: Their Chemistry and Biology*, Wiley, New York, 1973.
5. R. A. Zingaro and W. Cooper, *Selenium*, Van Nostrand Reinhold, New York, 1974.

6. K. Irgolic, *The Organic Chemistry of Tellurium*, Gordon and Breach, New York, 1974.
7. W. Cooper, *Tellurium*, Van Nostrand Reinhold, New York, 1977.
8. K. Irgolic, *J. Organomet. Chem.*, **103**, 91 (1975); **130**, 411 (1977); **158**, 269 (1978); **189**, 65 (1980); **203**, 367 (1980).
9. G. Pattenden, *Saturated Heterocyclic Chemistry*, Chemical Society, London, 1973–78.
10. C. Bird and G. Cheeseman, *Aromatic and Heteroaromatic Chemistry*, Vols. 1–5, Chemical Society, London, 1973–77.
11. H. Suschitzky and O. Meth-Cohn, *Aromatic and Hetercoaromatic Chemistry*, Vols. 6 and 7, Chemical Society, London, 1978–79.
12. D. Reid, *Organic Compounds of Sulphur, Selenium and Tellurium*, Vols. 1–6, Chemical Society, London, 1970–81.
13. H. Suschitzky and O. Meth-Cohn, *Heterocyclic Chemistry*, Chemical Society, London, 1980.
14. L. Christiaens, in *Proceedings of the Third International Symposium on Organic Selenium and Tellurium Compounds* (eds. D. Cagniant and G. Kirsch), University of Metz, Metz, 1979, pp. 69–118.
15. M. Renson, in *The Chemistry of Organic Selenium and Tellurium Compounds* (Eds. S. Patai and Z. Rappoport), Vol. 1, Wiley, Chichester, 1986, pp. 399–516.
16. (a) H. J. Reich and J. M. Renga, *J. Org. Chem.*, **40**, 3313 (1975); (b) H. J. Reich, *Acc. Chem. Res.*, **12**, 22 (1979); (c) S. Tomoda, Y. Takeuchi and Y. Nomura, *Synthesis*, 212 (1985).
17. T. Hori and K. B. Sharpless, *J. Org. Chem.*, **44**, 4208 (1979).
18. P. T. Southwellkelly, F. L. Johnstone and E. R. Cole, *Phosphorus Sulfur*, **1**, 261 (1976).
19. (a) M. Jefson and J. Meinwald, *Tetrahedron Lett.*, **22**, 3561 (1981); (b) C. Paulmier and P. Lerouge, *Tetrahedron Lett.*, **23**, 1557 (1982).
20. H. J. Reich, J. M. Renga and J. E. Trend, *Tetrahedron Lett.*, 2217 (1976).
21. C. O. Meese, W. Walter and H. Schmidt, *Tetrahedron Lett.*, 3133 (1976).
22. C. O. Meese, *Dissertation*, University of Hamburg, 1978.
23. P. A. Grieco, Y. Yokuyama and E. Williams, *J. Org. Chem.*, **43**, 1283 (1978).
24. T. G. Back and D. J. McPhee *J. Org. Chem.*, **49**, 3842 (1984).
25. (a) K. C. Nicolaou, D. A. Claremon, W. E. Barnette and S. P. Seitz, *J. Am. Chem. Soc.*, **101**, 3704 (1979); (b) S. V. Ley and B. Lygo, *Tetrahedron Lett.*, 4625 (1982); (c) T. Toru, S. Fujita and E. Maekawa, *J. Chem. Soc., Chem. Commun.*, 1082 (1985); (d) R. R. Webb, II, and S. Danishefsky, *Tetrahedron Lett.*, 1357 (1983).
26. P. A. Grieco, D. Y. Jaw, D. A. Claremon and K. C. Nicolaou, *J. Org. Chem.*, **46**, 1215 (1981).
27. T. Toru, M. Nischigaki, T. Seko, T. Kanefusa and E. Maekawa, *Synthesis*, 878 (1985).
28. N. Ya. Derkach, T. V. Lyapina and E. S. Levchenko, *Zh. Org. Khim.*, **14**, 280 (1978); *J. Org. Chem. USSR*, **14**, 256 (1978).
29. K. Dostal and M. Sochorkowa, *Z. Chem.*, **12**, 46 (1972).
30. K. Dostal, Z. Zak and A. Haba, *Collect. Czech. Chem. Commun.*, **42**, 1466 (1977).
31. F. A. Davis and E. W. Kluger, *J. Am. Chem. Soc.*, **98**, 302 (1976).
32. D. H. R. Barton, A. G. Brewster, S. V. Ley and M. N. Rosenfeld, *J. Chem. Soc., Chem. Commun.*, 147 (1977).
33. D. Hellwinckel and G. Fahrbach, *Justus Liebigs Ann. Chem.*, **715**, 68 (1962).
34. N. Ya. Derkach, T. V. Lyapina and N. A. Pasmurtseva, *Zh. Org. Khim.*, **10**, 807 (1974); *J. Org. Chem. USSR*, **10**, 810 (1974).
35. S. Tamagaki, S. Oae and K. Sakaki, *Tetrahedron Lett.*, 649 (1975).
36. M. Hori, T. Kataoka, H. Shimizu and K. Tomimatsu, *Tetrahedron Lett.*, 901 (1982); *Phosphorus Sulfur*, **16**, 97 (1983).
37. S. Oae, M. Fukumura and N. Furukawa, *Phosphorus Sulfur*, **10**, 153 (1981).
38. N. Ya Derkach, N. P. Tischenko, and V. G. Volonchuk, *Zh. Org. Khim.*, **14**, 958 (1978); *J. Org. Chem. USSR*, **14**, 896 (1978).
39. V. P. Krasnov, V. I. Naddaka and V. I. Minkin, *Zh. Org. Khim.*, **17**, 445 (1981); *Chem. Abstr.*, **95**, 42551x.
40. R. Appel and G. Buchler, *Z. Anorg. Allg. Chem.*, **348**, 175 (1966).
41. V. I. Naddaka, V. P. Gar'kin, I. D. Sadekov, V. P. Krasnov and V. I. Minkin, *Zh. Org. Khim.*, **15**, 896 (1979); *J. Org. Chem. USSR*, **15**, 804 (1979).
42. V. I. Naddaka, L. L. Popova, and V. I. Minkin, *Zh. Org. Khim.*, **18**, 259 (1982); *J. Org. Chem. USSR*, **18**, 226 (1982).

43. N. Ya. Derkach, N. A. Pasmurtseva and E. S. Levchenko, *Zh. Org. Khim.*, 7, 1543 (1971); *J. Org. Chem. USSR*, 7, 1600 (1971).
44. N. Ya. Derkach, N. A. Pasmurtseva, T. V. Lyapina and E. S. Levchenko *Zh. Org. Khim.*, 10, 1873 (1974); *J. Org. Chem. USSR*, 10, 1884 (1974).
45. N. Ya. Derkach, T. V. Lyapina and E. S. Levchenko, *Zh. Org. Khim.*, 16, 33 (1980); *J. Org. Chem. USSR*, 16, 31 (1980).
46. V. Horn and R. Paetzold, *Z. Anorg. Allg. Chem.*, 404, 213 (1974).
47. N. Ya. Derkach, T. V. Lyapina and E.S. Levchenko, *Zh. Org. Khim.*, 17, 622 (1981); *J. Org. Chem. USSR*, 17, 536 (1981).
48. N. Ya. Derkach, N. A. Pasmurtseva and E. S. Levchenko, *Zh. Obsch. Khim.*, 42, 1652 (1972); *J. Gen. Chem. USSR*, 42, 1646 (1972).
49. N. Ya. Derkach, T. V. Lyapina and N. A. Pasmurtseva, *Zh. Org. Khim.*, 10, 807 (1974); *J. Org. Chem. USSR*, 10, 810 (1974).
50. A. Baroni, *Atti R. Accad. Naz. Lincei Mem. Cl. Sci. Fis. Mat. Nat.*, 6, 255 (1932); *Chem. Abstr.*, 27, 1870 (1933).
51. K. B. Sharpless, T. Hori, L. K. Truesdale and C. O. Dietrich, *J. Am. Chem. Soc.*, 98, 269 (1976).
52. N. Ya. Derkach and G. G. Barashenkov, *Zh. Org. Khim.*, 12, 2484 (1976); *J. Org. Chem. USSR*, 12, 2408 (1976).
53. N. Ya. Derkach, G. G. Barashenkov and E. S. Levchenko, *Zh. Org. Khim.*, 18, 964 (1982); *J. Org. Chem. USSR*, 18, 837 (1982).
54. G. Kresze and W. Wucherpfennig, *Angew. Chem., Int. Ed. Engl.*, 6, 149 (1967).
55. N. Ya. Derkach, G. G. Barashenkov and E. I. Slyusarenko, *Zh. Org. Khim.*, 18, 70 (1982); *J. Org. Chem. USSR*, 18, 60 (1982).
56. Ya. G. Balton and E. S. Levchenko, *Zh. Org. Khim.*, 3, 772 (1967); *J. Org. Chem. USSR*, 3, 742 (1967).
57. N. Ya. Derkach and N. A. Pasmurtseva, *Zh. Org. Khim.*, 9, 1414 (1973); *J. Org. Chem. USSR*, 9, 1443 (1973).
58. N. Ya. Derkach, T. V. Lyapina, and E. S. Levchenko, *Zh. Org. Khim.*, 10, 139 (1974); *J. Org. Chem. USSR*, 10, 145 (1974).
59. N. Ya. Derkach, T. V. Lyapina, and E. S. Levchenko, *Zh. Org. Khim.*, 14, 280 (1978); *J. Org. Chem. USSR*, 14, 256 (1978).
60. G. Hopf and R. Paetzold, *Z. Anorg. Allg. Chem.*, 401, 179 (1973).
61. G. G. Barashenkov and N. Ya. Derkach, *Z. Obshch. Khim.*, 48, 1110 (1978); *J. Gen. Chem. USSR*, 48, 1012 (1978).
62. O. Foss and V. Janickis, *J. Chem. Soc., Dalton Trans.*, 620 (1980).
63. D. Hellwinckel and G. Fahrbach, *Justus Liebigs Ann. Chem.*, 712, 1 (1968).
64. V. I. Naddaka, V. P. Gar'kin, I. D. Sadekov and V. I. Minkin, *Zh. Org. Khim.*, 13, 220 (1977); *J. Org. Chem. USSR*, 13, 202 (1977).
65. V. I. Naddaka, V. P. Gar'kin, A. A. Maksimenko and I. D. Sadekov, *Zh. Org. Khim.*, 16, 2581 (1980); *J. Org. Chem. USSR*, 16, 2210 (1980).
66. V. I. Naddaka and V. P. Gar'kin, *Zh. Org. Khim.*, 17, 401 (1981); *J. Org. Chem. USSR*, 17, 341 (1981).
67. H. Suzuki, S. Takeda and Y. Hanazaki, *Chem. Lett.*, 679 (1985).
68. V. I. Naddaka, V. P. Gar'kin, K. V. Obayan and V. I. Minkin, *Zh. Org. Khim.*, 17, 669 (1981); *J. Org. Chem. USSR*, 17, 579 (1981).
69. V. I. Naddaka, V. P. Gar'kin and V. I. Minkin, *Zh. Org. Khim.*, 16, 2619 (1980); *Chem. Abstr.*, 94, 208474f.
70. V. I. Naddaka, V. P. Gar'kin, K. V. Obayan and V. I. Minkin, *Zh. Org. Khim.*, 17, 883 (1981); *J. Org. Chem. USSR*, 17, 777 (1981).
71. V. I. Naddaka, V. P. Gar'kin and K. V. Obayan, *Zh. Org. Khim.*, 17, 2020 (1981); *J. Org. Chem. USSR*, 17, 1803 (1981).
72. E. A. Stukalo, A. A. Kisilenko and L. N. Markowski, *Zh. Org. Khim.*, 16, 2554 (1980); *J. Org. Chem. USSR*, 16, 2184 (1980).
73. L. N. Markovski, E. A. Stukalo and G. P. Kunitskaya, *Zh. Org. Khim.*, 13, 2055 (1977); *J. Org. Chem. USSR*, 13, 1911 (1977).
74. L. N. Markovski, E. A. Stukalo and G. P. Kunitskaya, *Zh. Org. Khim.*, 13, 2514 (1977); *J. Org. Chem. USSR*, 13, 2360 (1977).

75. V. I. Naddaka, V. P. Krasnov and V. I. Minkin, *Zh. Org. Khim.*, **19**, 2632 (1983); *J. Org. Chem. USSR*, **19**, 2314 (1983).
76. D. Black and K. Watson, *Aust. J. Chem.*, **26**, 2167 (1973).
77. S. Tamagaki, K. Sakaki and S. Oae, *Heterocycles*, **2**, 39 (1974).
78. H. Roesky and K. Ambrosius, *Z. Naturforsch., Teil B*, **33**, 759 (1978).
79. I. Lalezari, A. Shafiee and M. Yalpani, *Adv. Heterocycl. Chem.* (Ed. A. R. Katritzky), **24**, 109–150, Academic Press, Orlando (1979).
80. F. Wille, A. Ascherl, G. Kaupp and L. Capeller, *Angew. Chem.*, **74**, 753 (1962).
81. F. Lucchesini, V. Bertini and A. De Munno, *Tetrahedron*, **40**, 931 (1984).
82. N. Onyamboko, R. Weber, A. Fauconnier and M. Renson, *Bull. Soc. Chim. Belg.*, **92**, 53 (1983).
83. D. Ames, A. Singh and W. Smyth, *Tetrahedron*, **39**, 831 (1983).
84. J. Liebscher and H. Hartmann, *Synthesis*, 273 (1976).
85. R. Weber and M. Renson, *Bull. Soc. Chim. Fr.*, 1124 (1976).
86. M. M'Buyi, *Doctoral Thesis*, University of Liège, 1983.
87. R. Lesser and R. Weiss, *Chem. Ber.*, **57**, 1079 (1924).
88. A. Muller, E. Cadenas, P. Graf and H. Sies, *Biochem. Pharmacol.*, **33**, 3235 (1984).
89. R. Reiter and A. Wendel, *Biochem. Pharmacol.*, **33**, 1923 (1984).
90. M. Parnham and S. Kindt, *Biochem. Pharmacol.*, **33**, 3247 (1984).
91. A. Muller, H. Gabriel and H. Sies, *Biochem. Pharmacol.*, **34**, 1185 (1985).
92. P. Kuhl, H. Borbe, A. Romer, H. Fischer and M. Parnham, Paper presented at the 7th European Workshop on Inflammation, Capri, Italy, 1985.
93. A. Welter, L. Christiaens and P. Wirtz, *Eur. Pat. Appl.*, EP 44453; *Chem. Abstr.*, **96**, 199699v (1982).
94. A. Welter, S. Leyck and E. Etschenberg, *Ger. Offen.*, DE 3226286; *Chem. Abstr.*, **100**, 191883f (1984).
95. A. Welter, S. Leyck and E. Etschenberg, *Ger. Offen.*, DE 3226284; *Chem. Abstr.*, **101**, 38454t (1984).
96. H. Gschwend and H. Rodriguez, *Org. React.*, **26**, 1–360, Wiley, New York (1979).
97. L. Christiaens, A. Luxen, M. Evers, Ph. Thibaut, M. M'Buyi and A. Welter, *Chem. Scr.*, **24**, 178 (1984).
98. C. Lambert, University of Liège, unpublished results, 1986.
99. R. Weber, *Doctoral Thesis*, University of Liège, 1975.
100. F. Lucchesini, V. Bertini and A. De Munno, *Heterocycles*, **23**, 127 (1985).
101. L. Christiaens, J.-L. Piette, L. Laitem, M. Baiwir, J. Denoel and G. Llabres, *Org. Magn. Reson.*, **8**, 354 (1976).
102. N. Onyamboko, M. Renson, S. Chapelle and P. Granger, *Org. Magn. Reason.*, **19**, 74 (1982).
103 R. Weber and M. Renson, *Bull. Soc. R. Sci. Liège*, **48**, 146 (1979).
104. T. Ueda, Y. Shibata, J. Sakakibara, M. Indue and T. Ishida, *Chem. Pharm. Bull.*, **30**, 3424 (1982).
105. (a) H. Ito, J. Sakakibara and T. Veda, *Cancer Lett.*, **28**, 61 (1985); (b) T. Veda, Y. Shibata and J. Sakakibara, *Chem. Pharm. Bull.*, **33**, 3065 (1985).
106. I. Lalezari, A. Shafiee and M. Yalpani, *Tetrahedron Lett.*, **10**, 5105 (1969).
107. O. Zimmer and H. Meier, *Chem. Ber.*, **114**, 2938 (1981).
108. R. Hanson and M. Davis, *J. Labelled Compd. Radiopharm.*, **16**, 31 (1979).
109. R. Hanson and M. Davis, *J. Pharm. Sci.*, **70**, 91 (1981).
110. S. Dhawan and J. Kagan, *J. Labelled Compd. Radiopharm.*, **19**, 331 (1982).
111. J. Moller, R. Christie, C. Pedersen and D. Reid, *Acta Chem. Scand., Ser. B*, **30**, 600 (1976).
112. B. Bak, O. Nielsen, H. Svanholt and A. Holm, *Chem. Phys. Lett.*, **55**, 36 (1978).
113. H. Petersen and H. Meier, *Chem. Ber.*, **111**, 3423 (1978).
114. H. Spencer, M. Lakshmilkantham, M. Cava and A. Garito, *J. Chem. Soc., Chem. Commun.*, 867 (1975).
115. L. Christiaens, unpublished results.
116. M. Ghandehari, D. Davalian, M. Yalpani and M. Partovi, *J. Org. Chem.*, **39**, 3906 (1974).
117. A. Holm, C. Berg, C. Bjerre, B. Bak and H. Svanholt, *J. Chem. Soc., Chem. Commun.*, 99 (1979).
118. H. Bock, S. Aygen and B. Solouki, *Z. Naturforsch., Teil B*, **38**, 611 (1983).
119. W. Sander and O. Chapman, *J. Org. Chem.*, **50**, 543 (1985).
120. (a) R. Schulz and A. Schweig, *Z. Naturforsch., Teil B*, **39**, 1536 (1984); (b) R. Schulz and A. Schweig, *Tetrahedron Lett.*, **25**, 2337 (1984).

121. A. Shafiee, S. Toghraie, F. Aria and G. Mortezaei-Zandjani, *J. Heterocycl. Chem.*, **19**, 1305 (1982).
122. H. Meier, M. Layer and A. Zetzeke, *Chem. Ztg.*, **98**, 460 (1975).
123. H. Meier, N. Hanold and H. Kolshorn, *Angew. Chem., Int. Ed. Engl.*, **21**, 66 (1982).
124. H. Meier, T. Molz, U. Mekle, T. Echter and M. Loreh, *Justus Liebigs Ann. Chem.*, 914 (1982).
125. E. Muller and G. Odenigbo, *Justus Liebigs Ann. Chem.*, 1435 (1975).
126. F. Malek-Yazdi and M. Yalpani, *J. Org. Chem.*, **41**, 729 (1976).
127. I. Lalezari, *Synthesis*, 660 (1984).
128. A. Shafiee and G. Fanaii, *Synthesis*, 512 (1984).
129. V. Laishev, M. Petrov and A. Petrov, *Zh. Org. Khim.*, **18**, 514 (1982).
130. H. Meier, J. Zountsas and O. Zimmer, *Z. Naturforsch., Teil B*, **36**, 1017 (1981),
131. A. Caplin, *J. Chem. Soc., Perkin Trans. 1*, 30 (1974).
132. R. Arad-Yellin and F. Wudl, *J. Organomet. Chem.*, **280**, 197 (1985).
133. H. Boek, S. Aygen, P. Rosmus and B. Solouki, *Chem. Ber.*, **113**, 3187 (1980).
134. N. Batzel and R. Boese, *Z. Naturforsch., Teil B*, **36**, 172 (1981).
135. P. Mente and C. Rees, *J. Chem. Soc., Chem. Commun.*, 418 (1972).
136. T. Gilchrist, P. Mente and C. Rees, *J. Chem. Soc., Perkin Trans. 1*, 2165 (1972).
137. G. Schrauzer and H. Kisch, *J. Am. Chem. Soc.*, **95**, 2501 (1973).
138. A. Eid and A. Salama, *Egypt. J. Pharm. Sci.*, **20**, 41 (1979); *Chem. Abstr.*, **98**, 143332u (1983).
139. (a) W. Becker and J. Meyer, *Chem. Ber.*, **37**, 2550 (1904); (b) V. Cohen, *Synthesis*, 768 (1978); (c) J. Goerdeler, D. Gross and H. Klinke, *Chem. Ber.*, **96**, 1289 (1963).
140. M. Jacobsen, L. Henriksen and A. Holm, *Acta Chem. Scand., Ser. B*, **37**, 585 (1983).
141. Y. Shealy and J. Clayton, *J. Heterocycl. Chem.*, **4**, 96 (1967).
142. H. Buchwald and K. Ruhlmann, *J. Organomet. Chem.*, **166**, 25 (1979).
143. H. Roesky and H. Hofmann, *Z. Naturforsch., Teil B*, **39**, 1315 (1984).
144. W. Sliwa and A. Thomas, *Heterocycles*, **20**, 71 (1983).
145. O. Hinsberg, *Chem. Ber.*, **22**, 862, 2895 (1889).
146. A. Thomas and W. Sliwa, *Heterocycles*, **20**, 1043 (1983).
147. R. Neidlein, D. Droste-Tran-Viet, A. Gieren, M. Kokkinidis, R. Wilckens, H. Geserich and W. Ruppel, *Helv. Chim. Acta*, **67**, 574 (1984).
148. S. Mataka, K. Takahashi, T. Imura and M. Tashiro, *J. Heterocycl. Chem.*, **19**, 1481 (1982).
149. K. Sharma, R. Singh and S. Kumari, *Synthesis*, 581 (1983).
150. A. Komin and M. Carmack, *J. Heterocycl. Chem.*, **12**, 829 (1975).
151. V. Sergeev, V. Pesin and N. Notikova, *Khim. Geterotsikl. Soedin.*, 328 (1972).
152. C. Pedersen, *Tetrahedron Lett.*, **20**, 745 (1979).
153. G. Eremeeva, Y. Akulin, T. Timofeeva, B. Strelets and L. Efros, *Khim. Geterotsikl. Soedin.*, 1129 (1982).
159. C. Pedersen, H. Harrit, M. Poliakoff and I. Dunkin, *Acta Chem. Scand., Ser B*, **31**, 848 (1977).
155. C. Pedersen and N. Hacker, *Tetrahedron Lett.*, **17**, 3981 (1977).
156. A. Gyul'maliev, I. Stenkevich and Z. Todres, *Khim. Geterotsikl. Soedin.*, 1055 (1975).
157. T. Lin and J. Braun, *Chem. Phys.*, **26**, 403 (1977).
158. H. Bock, B. Solouki, S. Aygen, T. Hirabayashi, S. Mohmada, P. Rosmus and J. Wittmann, *J. Mol. Struct.*, **60**, 31 (1980).
159. A. Katritzky and Y. Takeuchi, *J. Chem. Soc., Perkin Trans. 2*, 1682 (1972).
160. M. Davis, L. Deady and E. Homfeld, *J. Heterocycl. Chem.*, **11**, 1011 (1974).
161. C. Veracini, A. De Munno, V. Bertini, M. Congeri and G. Chidichimo, *J. Chem. Soc., Perkin Trans. 2*, 561 (1977).
162. G. Chidichimo, F. Lelj, P. Barili and C. Veracini, *Chem. Phys. Lett.*, **55**, 519 (1978).
163. C. Khetrapal and A. Kunwar, *J. Mol. Struct.*, **74**, 343 (1981).
164. G. Cheeseman and C. Turner, *Org. Magn. Reson.*, **6**, 430 (1974).
165. I. Yavari, R. Botto and J. Roberts, *J. Org. Chem.*, **43**, 2542 (1978).
166. H. Yamaguchi, A. Uchida, F. Yoneda and H. Baumann, *J. Chem. Soc., Faraday Trans. 2*, **77**, 947 (1981).
167. R. D. Gordon, *Spectrochim. Acta, Part A*, **36**, 1089 (1980).
168. J. Neve, M. Hanocq and L. Molle, *Talanta*, **26**, 15 (1979).
169. M. Chiu and B. Gilbert, *J. Chem. Soc., Perkin Trans. 2*, 258 (1973).
170. C. Pedersen and J. Moeller, *Acta Chem. Scand., Ser. B*, **29**, 483 (1975).
171. M. Arshadi, *Org. Mass. Spectrom.*, **13**, 379 (1978).

172. C. Deicha and F. Terrier, *J. Chem. Res. (S)*, 312 (1981).
173. K. Pannell, A. Mayr, R. Hoggard, J. McKennis and J. Dawson, *Chem. Ber.*, **116**, 230 (1983).
174. E. Shermann, S. Lambert and K. Pilgram, *J. Heterocycl. Chem.*, **11**, 763 (1974).
175. V. Tsveniashvili, L. Tskalobadze and V. Gaprindashvili, *Soobsheh, Akad. Nauk Gruz. SSSR*, **71**, 625 (1973); *Chem. Abstr.*, **80**, 70049 (1974).
176. V. Tsveniashvili, M. Malashkhiya, N. Khavtasi and V. Gaprindashvili, *Zh. Obshch. Khim.*, **53**, 1851 (1983).
177. F. Tobiason, L. Huestis, C. Chandler, S. Pedersen and P. Peters, *J. Heterocycl. Chem.*, **10**, 773 (1973).
178. A. Gieren, H. Betz, T. Hubner, V. Lamm, R. Neillein and D. Droste, *Z. Naturforsch., Teil B*, **39**, 485 (1984).
179. H. Singh, W. McWhinnie, R. Ziolo and C. Jones, *J. Chem. Soc., Dalton Trans.*, 1267 (1984).
180. J. Neve, M. Hanocq and L. Molle, *Talanta*, **26**, 1173 (1979).
181. J. Neve, M. Hanocq and L. Molle, *Mikrochim. Acta*, 41 (1980).
182. G. Schwedt, *Fresenius. Anal. Chem.*, **288**, 50 (1977).
183. A. Montiel, *Analusis*, **9**, 102 (1981).
184. Y. Shibata, M. Morita and K. Fuwa, *Anal. Chem.*, **56**, 1527 (1984).
185. J. Blaha, W. Brittain and C. Meloan, *Anal. Lett.*, 1391 (1980).
186. (a) J. Blaha, W. Brittain, C. Meloan and W. Fateley, *Appl. Spectrosc.*, **34**, 636 (1980); (b) S. D'yachenko, M. Bureneva, M. Papirnik, V. Pesin, N. Ostashkova and A. Stetsenko, *Z. Obshch. Khim.*, **51**, 1912 (1981).
187. (a) K. Potts, R. Cody and R. Dennis, *J. Org. Chem.*, **46**, 4065 (1981); (b) F. Lucchesini and V. Bertini, Synthesis, 824 (1983).
188. R. Weber, J.-L. Piette and M. Renson, *J. Heterocycl. Chem.*, **15**, 865 (1978).
189. H. Campsteyn, L. Dupont, J. Lamotte-Brasseur and M. Vermeire, *J. Heterocycl. Chem.*, **15**, 745 (1978).
190. V. Bertini, F. Lucchesini and A. De Munno, *Synthesis*, 681 (1982).
191. M. Muniz-Miranda, G. Sbrana, V. Bertini, F. Lucchesini, E. Benedetti and A. De Munno, *Spectrochim. Acta, Part A*, **40**, 847 (1984).
192. V. Bertini, P. Dapporto, F. Lucchesini, A. Sega and A. De Munno, *Acta Crystallog., Sect. C*, **40**, 653 (1984).
193. R. Cobbledick, F. Enstein, W. McWhinnie and F. Musa, *J. Chem. Res. (S)*, 145 (1979).
194. N. Derkach, T. Lyapina and G. Barashenkov, *Zh. Org. Khim.*, **15**, 788 (1979).
195. N. Derkach, T. Lyapina and G. Barshenkov, *Zh. Org. Khim.*, **16**, 33 (1980).
196. N. Derkach, G. Barashenkov and E. Levchenko, *Zh. Org. Khim.*, **19**, 1622 (1983).
197. N. Derkach, T. Krasnyanskaya, E. Levchenko and T. Zabolotnaya, *Zh. Org. Khim.*, **20**, 2377 (1984).
198. H. Poleschner, J. Bottger and F. Franghanel, *Synthesis*, 667 (1984).
199. M. Apostolescu, *Bull. Inst. Politech. Iasi*, **20**, 9 (1974); *Chem. Abstr.*, **82**, 112049x (1975).
200. T. Gilchrist, C. Rees and D. Vaughan, *J. Chem. Soc., Perkin Trans. 1*, 55 (1983).
201. F. Sachs, *Justus Liebigs Ann. Chem.*, **365**, 142 (1909).
202. M. Kaplan, R. Haddon, F. Schilling, J. Marshall and F. Bramwell, *J. Am. Chem. Soc.*, **101**, 3306 (1979).
203. J.-P. Boutique, J. Riga, J. Verbist, J. Delhalle, J. Fripiat, J.-M. Andre, R. Haddon and M. Kaplan, *J. Am. Chem. Soc.*, **104**, 2691 (1982).
204. H. Roesky, K. Weber and J. Bats, *Chem. Ber.*, **117**, 2686 (1984).
205. M. Perrier and J. Vialle, *Bull. Soc. Chim. Fr.*, **II**, 205 (1979).
206. M. Renson, in *The Chemistry of Organic Selenuim and Tellurium Compounds* (Eds. S. Patai and Z. Rappoport), Vol. 1, Wiley, Chichester, 1986, pp. 467–468.
207. C. Paulmier, *Selenium Reagents and Intermediates in Organic Synthesis*, Pergamon Press, Oxford, 1986.

CHAPTER **12**

Synthesis of organic conductors containing selenium and tellurium

D. COWAN and A. KINI*

The Johns Hopkins University, Baltimore, Maryland, USA

I. INTRODUCTION

A. What Are Organic Metals?

The electrical conductivity (σ) of solids is a physical property with a range of values greater than 20 orders of magnitude. It is usually determined by a four-probe measurement

---

*Present address: Argonne National Laboratory, Argonne, Illinois 60439, USA.
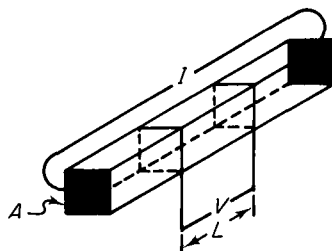
FIGURE 1. Arrangement of four
probes for electrical conductivity mea-
surements on single crystals

depicted in Figure 1. This type of measurement minimizes any error due to contact
resistance since little current flows in the voltage measuring circuit. The electrical
conductivity is then calculated from the known or measured current (I), the voltage drop
(V) and the sample dimensions (A and L) (equation 1).

$$\sigma = (1/R)(L/A) = (I/V)(L/A)\Omega^{-1}cm^{-1} \tag{1}$$

The best insulators such as PTFE have room temperature conductivities of about
10^{-16} to $10^{-20}\Omega^{-1}cm^{-1}$, whereas semiconductors such as silicon have conductivities in
the range 10^{-2}–$10^{-8}\Omega^{-1}cm^{-1}$ and metals such as copper and silver have conductivities
that approach $10^6\Omega^{-1}cm^{-1}$. Materials such as mercury that become superconducting at
low temperatures have no resistance below the critical temperature (T_c) and therefore have
infinite conductivity.

Even more characteristic than the magnitude of the conductivity is the temperature
dependence of the conductivity. As the temperature is increased, the conductivity increases
for insulators and semiconductors (see equation 2, where σ_0, E_g, k and Δ are constants)

$$\sigma = \sigma_0 e^{-Eg/kT} = \sigma_0 e^{-\Delta/T} \tag{2}$$

while the conductivity of metals decreases as the temperature increases (see equation 3,
where ρ is the resistivity and ρ_0, B and γ are constants).

$$\rho = 1/\sigma = \rho_0 + BT^\gamma \tag{3}$$

Since the electrical conductivity of a solid is determined by its electronic structure, an
elementary band description is presented. This model will be shown to be valid for many of
the organic conductors later in the chapter. On bringing together two atomic p orbitals on
adjacent atoms or molecular fragments, a π bonding and a π^* anti-bonding set of
molecular orbitals are formed. If there is one electron per basis function, the π bonding
molecular orbital is filled and the π^* anti-bonding molecular orbital is empty. Now, if we
bring together or stack two of these molecules, the π bonding level is split into two new
molecular orbitals and the π^* anti-bonding level is also split into two new orbitals. Since
there are two electrons per bonding π orbital, both of the new π levels are filled and the π^*
unfilled. If n of the molecules are stacked as in a crystal, then we will form one band from
the π orbital (HOMO) and one from the π^* orbital (LUMO). Each band will contain n
states or levels. Since there are $2n$ electrons in the band formed from the HOMO, this band
will be completely filled while the band from the LUMO will be completely empty—there
were no electrons associated with the π^* basis functions. The width of the band will be
determined by the extent to which the orbitals overlap (see Figure 2). This band picture
describes most insulators and semiconductors. As the temperature is increased, electrons
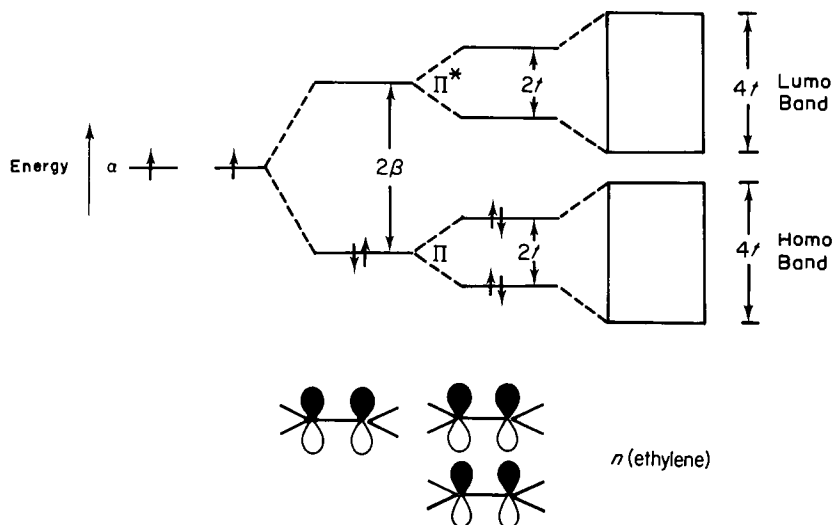
FIGURE 2. Formation of electronic bands from a stack of ethylene molecules. The band width is given by the value of $4t$ and is approximately twice the value of the dimer splitting

are thermally excited from the filled to empty band. Both the electrons in the LUMO and holes in the HOMO band can contribute to the electrical conductivity. Intrinsic conductivity is then largely controlled by the band gap (E_g, see equation 2).

If it is possible to change the electronic structure by adding electrons to the band formed from the LUMO or remove electrons from the band formed from the HOMO, then a metal should result. The metallic structure is a consequence of the fact that it is possible in an incompletely filled band to shift some of the electrons to infinitesimally higher energy states within the band, giving rise to a net velocity or conductivity. This conductivity in metals (and also in semiconductors) is determined by the concentration and the mobility of the charge carriers. Unlike semiconductors, there is no energy or band gap in metals, and therefore the temperature dependence of the conductivity is dominated by the mobility term, which depends on the scattering of the electrons caused by interactions with the lattice vibrations. As the temperature is reduced, the amplitude of the lattice vibrations is diminished and the mobility and conductivity increase. Figure 3 provides a schematic drawing for insulators, semiconductors, metals and semimetals. The semimetals result from band overlaps which produce incompletely filled bands. It is obvious that to form either a semimetal or metal we need incompletely filled bands, and this translates into the need for stable organic radicals. The other obvious feature is that these radicals must be planar molecules with delocalized π molecular orbitals to allow stacking. The production of a stable radical by steric protection will not allow effective interaction of the radical species in the solid state. These stacks of planar radical species are quasi-one-dimensional in character since the strong interaction is along the stack direction. This results in a structure that is subject to phase transitions which convert metals into semiconductors. In order to increase the interchain interaction (more 2D character) and suppress these transitions, heteroatoms (S, Se, Te) have been added to the ring. The heteroatoms have three other beneficial effects: 1, because of their polarizability they stabilize radical (cation)
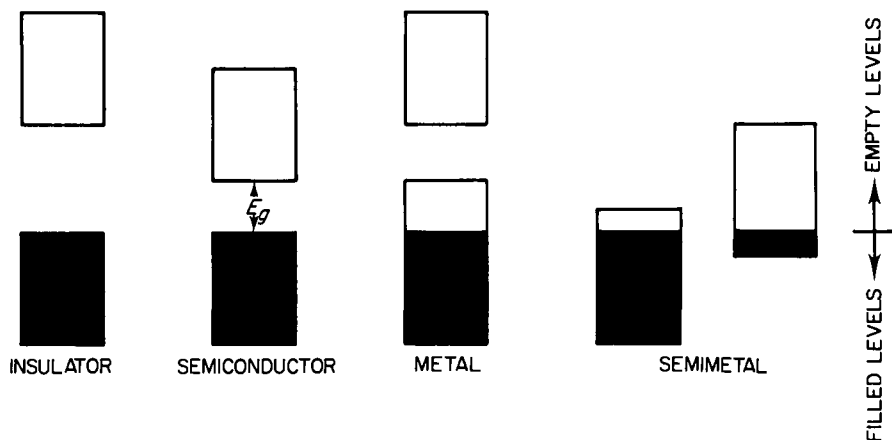
FIGURE 3. Schematic band structures of solids. The boxes indicate the allowed energy states and the shaded areas indicate the regions filled with electrons

species; 2, again because of their polarizability they help to stabilize a stack of like-charged species; and 3, because their p orbitals extend further in space than those centered on carbon there is greater orbital overlap in the stacking direction producing wider bands (a solid which is more metallic in nature). In 1976, we proposed a set of design constraints for the preparation of good organic conductors[1,2]. These constraints with a few modifications which we made in 1982 are as follows[3]:

1. Stable open-shell (free radical) species in order to form a partially filled band.
2. Planar molecules with delocalized π-molecular orbitals so that effective overlap of HOMO and/or LUMO can occur.
3. Inhomogeneous charge and spin distribution to reduce the repulsion when like charged molecules are stacked.
4. Segregated stacks of radical species—regardless of charge transfer, a mixed stack will always have a completely filled band.
5. No periodic distortion which opens a gap at the Fermi level (uniform stacks).
6. Little or no disorder (symmetric radicals and/or radical anions and cations)—disorder tends to produce a potential which localizes the wave function.
7. Molecular components of similar size.
8. Fractional charge (mixed-valence)—by adjusting the charge, it is possible to minimize the on-site Coulomb repulsion (U_{eff}), which should be small compared with the band width ($4t$).
9. Relatively strong interchain coupling to suppress phase transitions.
10. Cation and/or anion nominally divalent—unless the molecular components can support doubly charged species, only a correlated type of conductivity is possible.
11. Polarizable species.

More detailed descriptions of the solid-state chemistry and physics can be found in a number of recent reviews[4-6].

B. Sulfur-, Selenium- and Tellurium-based Organic Metals

Table 1 gives a list of some of the most conducting organic compounds and Figure 4 shows their structures. One of the striking features of this list is that so many are formed

TABLE I. Organic metals

Compound[a]	z^b	σ_{RT} $(\Omega^{-1}cm^{-1})$	σ_{max} $(\Omega^{-1}cm^{-1})$	$T_{max}{}^c(K)$	Ref.
TTF–TCNQ	0.59	500	2×10^4	59	7–13
TMTTF–TCNQ	0.65	350	5×10^3	60	1, 2, 14, 15
HMTTF–TCNQ	0.72	500	2×10^3	75	16
TSF–TCNQ	0.63	800	1×10^4	40	17–20
TMTSF–TCNQ	0.57	1200	7×10^3	61	1, 2, 21
HMTSF–TCNQ	0.74	2000	7×10^3	(32)	1, 2, 22, 23
HMTTeF–TCNQ	—	550	9×10^2	(73)	24, 25
HMTTeF–DMTCNQ	—	460	1×10^3	(83)	24, 25
HMTSF–TNAP	—	2900	2×10^4	50	1, 2, 26, 27
$(TTT)_2I_3$	0.5	1000	3×10^3	(60)	28, 29
$(TSeT)_2I$	0.5	1500	1×10^4	(35)	30, 31
$(TSeT)_2Cl$	0.5	2100	2×10^4	(26)	32–36
$(TMTSF)_2PF_6$	0.5	550	7×10^4	(18)	37–44
$(TMTSF)_2ClO_4$	0.5	650	5×10^5	(6)	45, 47
$(BEDT-TTF)_2I_3$	0.5	30	1.5×10^4	(4.2)	48–51
$(Perylene)_2(PF_6)_{1.1}$	0.55	900	1×10^3	200	52–54

[a]For structures see Figure 4.
[b]$z \equiv$ fractional charge per cation; see Ref. 2 and references cited therein.
[c]Parentheses indicate a broad conductivity maximum.

from sulfur and selenium heterocycles. We expect that this list will grow to include more tellurium compounds as more work is done on these materials. As a rule, the selenium compounds tend to be more conducting than the sulfur compounds and stay metallic to lower temperatures.

From the magnitude of the electrical conductivity and the crystal structure, it is possible to calculate the effective mean free path of the carriers. For TTF–TCNQ, the mean free path at room temperature is almost one lattice spacing and at 59 K it is about ten lattice spacings (40 Å). For comparison, the mean free path in Pb at 60 K is about 28 lattice spacings (100 Å). While a band picture is consistent with all of the experimental evidence on organic metals, it is clear that a hopping model is not adequate to explain the conductivity of these materials at low temperatures. To date, the only superconducting organic compounds have been salts prepared from TMTSF [for example, $(TMTSF)_2ClO_4$ where $T_c = 1.2$ K] and BEDT-TTF [for example, $(BEDT-TTF)_2I_3$ where $T_c = 1.4$ K].

II. SYNTHESIS

A. Heterofulvalene Donors

Heterofulvalene donors containing four chalcogen atoms (1) are the most widely studied class of compounds in the realm of organic conductors. Tetrathiafulvalene (TTF, 1a) has provided much of the impetus for the later developments in organic synthesis and in physics with the discovery that its charge-transfer salt with TCNQ displays metal-like electrical behaviour[7–13]. In addition, TTF represents a prototype structure, ripe for structural and elemental modifications, thus providing a fertile ground for synthetic organic chemists to explore new methodologies. The selenium and tellurium analogs, TSF (1b) and TTeF (1c) respectively, are widely sought-after compounds since the charge-transfer solids derived from them are expected to be even better electrical conductors. So
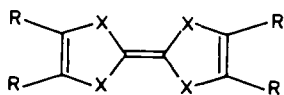
R	X	Compound
H	S	TTF
H	Se	TSF
CH$_3$	S	TMTTF
CH$_3$	Se	TMTSF
—CH$_2$CH$_2$CH$_2$—	S	HMTTF
—CH$_2$CH$_2$CH$_2$—	Se	HMTSF
—CH$_2$CH$_2$CH$_2$—	Te	HMTTeF
— SCH$_2$CH$_2$S—	S	BEDT—TTF
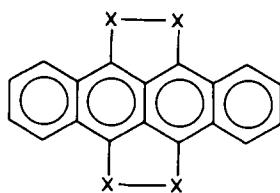
X = S   TTT
X = Se   TST
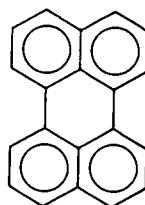
Perylene
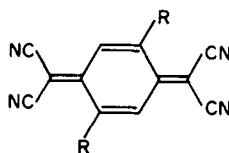
R = H   TCNQ
R = Me   DMTCNQ
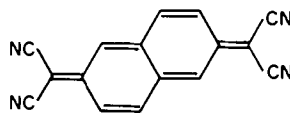
TNAP

FIGURE 4. Structures of compounds in Table 1

far, TSF, its derivatives and some derivatives of TTeF have been prepared. The parent tellurium compound, TTeF, has remained elusive.
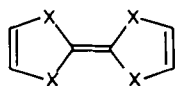
(1a) X = S   TTF

(1b) X = Se   TSF

(1c) X = Te   TTeF

To a large measure, the synthetic activity has focused on various methods for the synthesis for TMTSF and HMTSF. This is primarily due to the superconducting property[37–47] of salts $(TMTSF)_2X$ where $X = PF_6$, ClO_4 and the absence of a metal-to-insulator transition in HMTSF–TCNQ as the temperature approaches zero[22,23].

1. Selenium donors

Tetraselenafulvalene and its derivatives, owing to their symmetry (D_{2h}), are conveniently constructed by coupling appropriate 1,3-diselenole units wherein the tetraselenoalkene bond is formed in the last step. A widely employed strategy consists in coupling 1,3-diselenole-2-one, -thione or -selone with a trivalent phosphorus reagent, Ph_3P or $(MeO)_3P$ (Scheme 1).

While the exact mechanistic details of the coupling reaction are yet to be unravelled, a general pathway can be written as in Scheme 2. Some of the intermediates shown have been either isolated[55,56] or trapped[57] from the coupling reaction. In spite of the lack of understanding of the mechanism, some empirical guidelines for successful coupling with phosphorus reagents have emerged:

1. Selones, in general, can be coupled under milder conditions than and with superior yields to their thio or oxo counterparts. Exceptions seem to be the compounds with electron-withdrawing substituents (e.g. tetracyano-TTF[58]) and BEDS-TSF[110]; in these cases the oxo precursors couple more efficiently.
2. Selones usually do not yield products with chalcogen scrambling. For example, certain 1,3-diselenole-2-thiones were found to give triselenathiafulvalenes as a by-product (R = Me) and as the only product (R = CF_3, COOMe) (Scheme 3)[59]. Such scrambling was not observed for 1,3-dithiole-2-selones.
3. Triarylphosphines are superior to trialkylphosphites since the latter can undergo an Arbuzov-type reaction with thiones[55].

X = O, S, Se

(1b) $R^1 = R^2 = H$ TSF

(2) $R^1 = R^2 = Me$ TMTSF

(3) $R^1 = R^2 = -(CH_2)_3-$HMTSF

(4) $R^1 + R^2 =$ benzo   DBTSF

(5) $R^1 = R^2 = COOMe$

SCHEME 1

SCHEME 2

R = Me	85%	15%
R = CF$_3$	—	100%
R = COOMe	—	100%
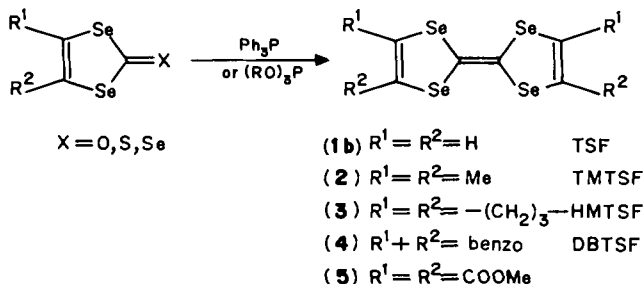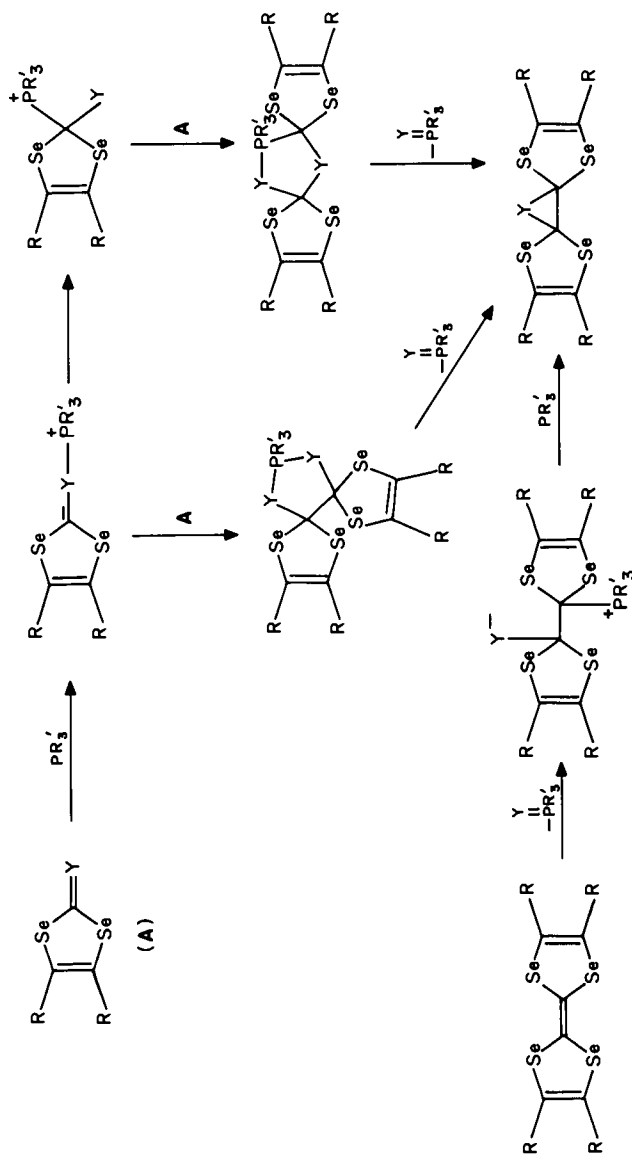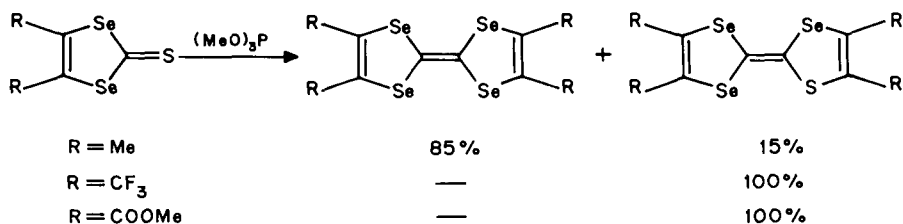
SCHEME 3

In practice, however, experimentation with different phosphorus reagents, solvents and substrates (oxo, thioxo, selenoxo) is often necessary to determine the optimum combination that yields the desired heterofulvalene.

Deprotonation of the 1,3-dithiolium ion 7, generated by peracid treatment of 1,3-dithiole-2-thione (6), has been known to give the corresponding TTF derivative via a carbene intermediate (Scheme 4)[60-62]. An analogous approach in the case of 1,3-diselenole-2-thione, however, was unsuccessful (Scheme 5)[63,66].

A recently described[93] non-coupling synthesis of HMTSF has the potential of being applicable to other TSF derivatives. Here, the 1,2-diselenol dianion is reacted with tetrachloroethylene to give HMTSF (Scheme 6).

The next section will describe various reported methods of synthesizing the 1,3-diselenole-2-thiones and the 1,3-diselenole-2-selones.
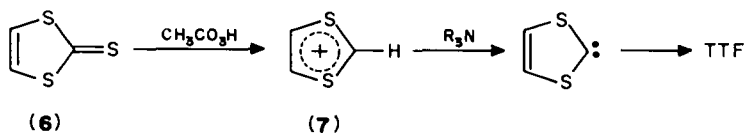
SCHEME 4
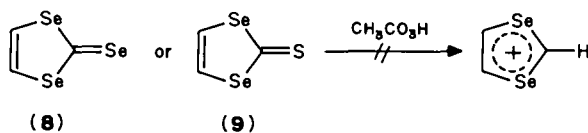
SCHEME 5
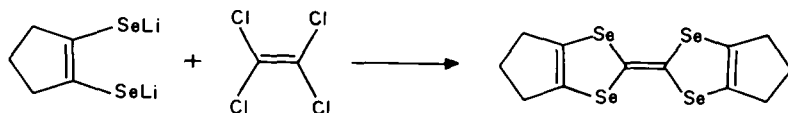
SCHEME 6

a. Engler's tetraselenafulvalene synthesis. Engler and Patel[63] were the first to report the synthesis of TSF; their methodology consists in treating sodium acetylide with elemental selenium and carbon diselenide in diethyl ether. Subsequent acidification and workup provided 1,3-diselenole-2-selone (**8**) in low (15–25%) yield. TSF was obtained in 70–80% yield by triphenylphosphine coupling[63]. As the mechanism (Scheme 7) suggests, the method is limited to the synthesis of unsubstituted or monosubstituted TSF[63,64]. The reaction is general inasmuch as any combination of sulfur/selenium and carbon disulfide/carbon diselenide can be employed to obtain the corresponding heterocycles. However, sulfur/carbon diselenide and selenium/carbon disulfide combinations result in extensive scrambling (see Table 2)[65].

Coupling of 1,3-thiaselenole-2-selone (**12**) with trimethyl phosphite yielded a mixture of *cis*- and *trans*-dithiadiselenafulvalene (**13**). The lower symmetry and the presence of cis/trans isomers in DSDTF (**13**) causes a structural disorder in the TCNQ salt. It was expected that its conductivity would be much lower than that of either TTF–TCNQ or TSF–TCNQ. However, neither the room temperature conductivities nor the
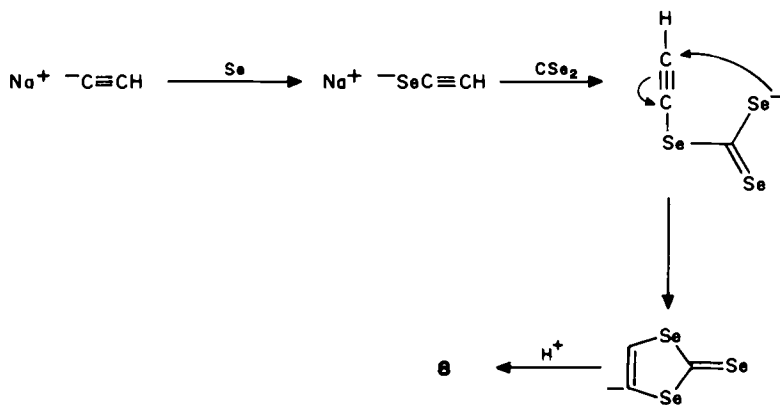
SCHEME 7

TABLE 2. Product composition in the reaction of sodium acetylide with chalcogen (X) and carbon dichalcogenide (CY$_2$)

NaC≡CH $\xrightarrow{X, CY_2}$	Products					
	6	**8**	**9**	**10**	**11**	**12**
X = Y = S	Only	—	—	—	—	—
X = Y = Se	—	Only	—	—	—	—
X = S; Y = Se	1	50	8	1	15	25
X = Se; Y = S	22	0	1	70	5	2

conductivity–temperature profiles were dramatically different for the three salts. Thus, it was concluded that intramolecular structural disorder plays an important but not dominant role in the solid-state electrical properties[67].
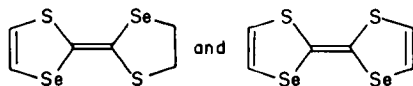
(**13**)DSDTF

b. Selenocarbamate route. This has been one of the most widely used synthetic strategies for the construction of TSF derivatives[66]. As described in Scheme 8, it involves the intermediacy of 2-oxoalkyl -*N*, *N*-dialkyldiselenocarbamate (**15**), which is generated by the nucleophilic attack of *N*, *N*-dialkyldiselenocarbamate ion (**14**)[68] on an appropriate α-haloketone. H_2SO_4-catalysed cyclization of **15** was followed by anion exchange with $HClO_4$ or HBF_4 (for stability reasons) to provide the 2-imminium-1, 3-diselenole salt **16**. Conversion of **16** to 1, 3-diselenole-2-selone (**17**) or -thione (**18**) was achieved by bubbling H_2Se or H_2S into a methanolic solution of **16**. The selone or the thione was then coupled in the usual manner [Ph_3P or $(MeO)_3P$] to obtain the corresponding TSF derivative[66].

A large number of di- and tetra-substituted TSF derivatives have been prepared by this method (Table 3).

Various synthetic approaches to the *N*, *N*-dialkyldiselenocarbamate ion (**14**) have been investigated owing to the experimental difficulties associated with the use of carbon diselenide, which is toxic, very expensive, extremely fetid and ill-ventable.

(**14**)

(**15**)

(**16**)

(**17**) X = Se
(**18**) X = S
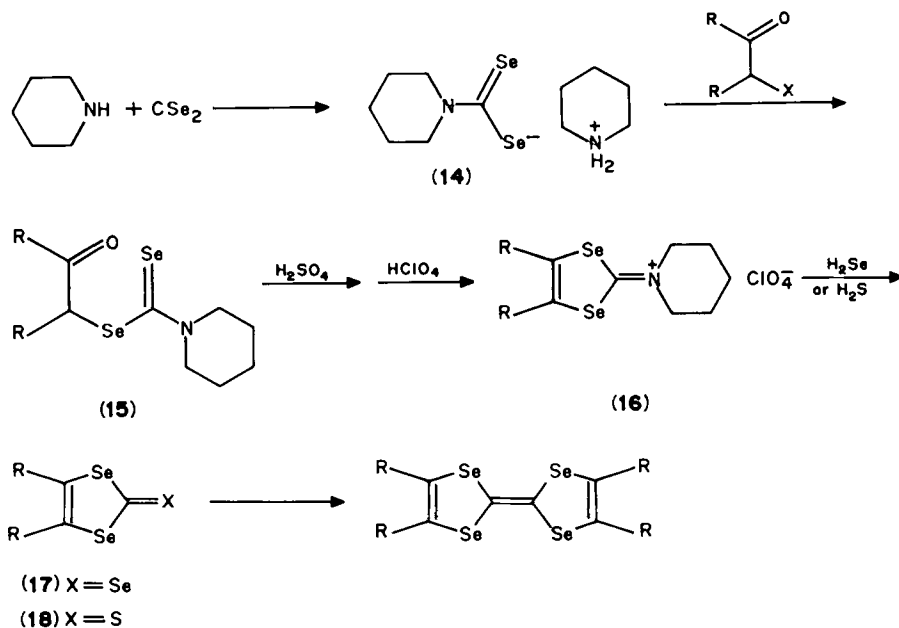
SCHEME 8

TABLE 3. Various TSF derivatives synthesized by the diselenocarba-
mate route

R_1	R_2	Product	Ref.
CH_3	H	DMTSF(19)	66
CH_3	CH_3	TMTSF (2)	66, 74
CD_3	CD_3	TMTSF-d_{12}(20)	69
Ph	H	DPTSF(21)	66
Ph	Ph	TPTSF(22)	66
	—$(CH_2)_3$—	HMTSF(3)	66, 74
	—$(CH_2)_4$—	OMTSF	Unpublished
	—CH_2CH_2S—	α-DTTSeF	77

Shu et al.[70] reported the use of thio- and seleno-urea for the synthesis of diselenadithia-
fulvalene (DSDTF) and TSF derivatives (Scheme 9). Here, the α-haloketone was reacted
with thio- or seleno-urea in perchloric acid to obtain the corresponding thio- or seleno-
uronium salt (23). Treatment of thiouronium salt 23a with H_2Se gave 2-oxoalkyl-N, N-
dimethylthioselenocarbamate (24) in 75% yield. Further elaboration, as described in
Scheme 7, furnished DSDTF in ca. 40% overall yield. The selenouronium salt (23b),
however, yielded 2-oxoalkyl-N, N-dimethyldiselenocarbamate (15) as a minor product.
The major reaction pathway was the elimination of 2-oxoalkylselenide ion (25).

A further refinement for the generation of the diselenocarbamate ion, avoiding the use
of CSe_2, came independently and simultaneously from the groups of Wudl[71] and Cowan[72].
As shown in Scheme 10, hydrogen selenide was reacted with phosgene imminium chloride
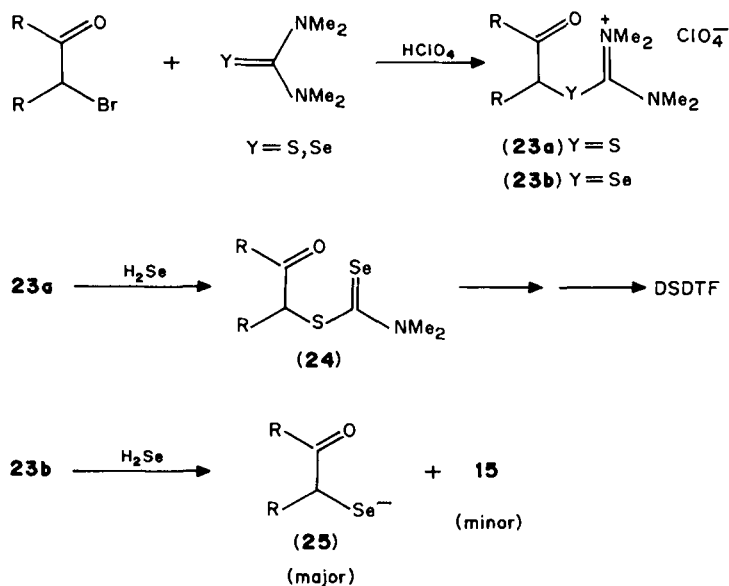
SCHEME 9
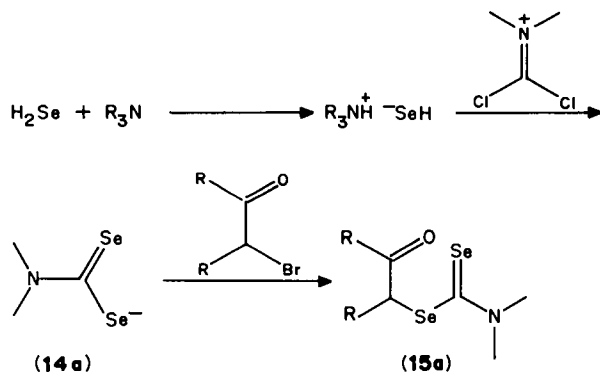
SCHEME 10

in the presence of a di- or tri-alkylamine to give the dialkyldiselenocarbamate ion **14a**; the latter was then treated with an α-haloketone to form the key intermediate 2-oxoalkyl-N,N-dialkyldiselenocarbamate (**15a**).

Moradpour et al.[73] reported a slight modification to the Wudl–Cowan route which avoids the use of gaseous selenium reagents, thus making the synthesis of TSF derivatives much less hazardous. In this method, sodium selenide (generated in situ from elemental selenium and NaBH$_4$ in DMF) was partially acidified with t-BuOH and the resulting NaSeH was allowed to react with phosgene imminium chloride. The product, N,N-dimethyldiselenocarbamate ion (**14a**), was converted to the 2-imminium-1,3-diselenole salt **16a** in the usual manner and treated with NaSeH in EtOH (instead of bubbling in H$_2$Se) to give 1,3-diselenole-2-selone (**17a**) in good yield (Scheme 11).

Notably absent among the selenafulvalene donors synthesized by the selenocarbamate route is TSF. There are several reasons for this. First, α-haloacetaldehyde is extremely unstable. Second, neither α-haloacetaldehyde nor its acetal (which is stable and commercially available) have been shown to react with the diselenocarbamate ion **14** to form the key intermediate, diselenocarbamate ester.

Johannsen et al.[75] reported a novel acid-catalysed exchange reaction between diselenides and bis(N,N-dialkylselenocarbamoyl)selenide, which furnished the key carbamate ester in near quantitative yield (Scheme 12). Chloroacetaldehyde diethylacetal (**26**),
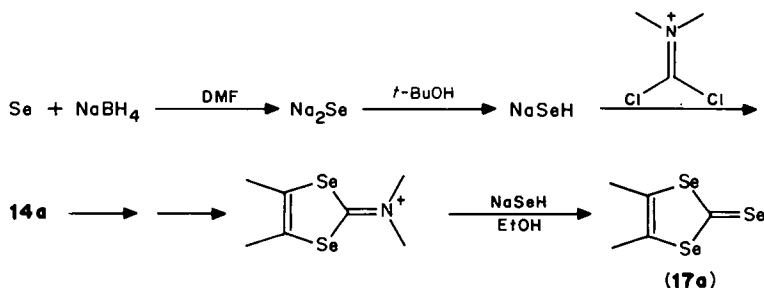
SCHEME 11
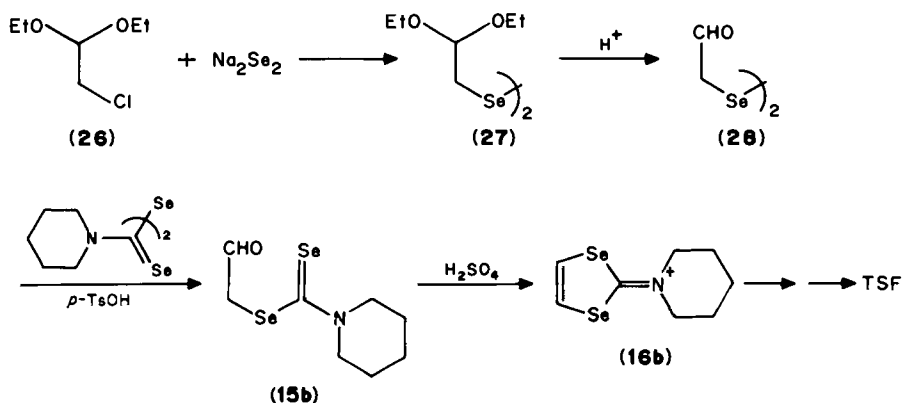
SCHEME 12

while inert to diselenocarbamate ion **14**, reacts smoothly with sodium diselenide, which is significantly more nucleophilic. The resultant bis(diethoxyethyl)diselenide (**27**) was hydrolysed to bis(2-oxoethyl)diselenide (**28**) in 85% yield. Then, following the method of Henriksen[76], **28** was reacted with bis(*N*, *N*-dialkylselenocarbamoyl)selenide in a 2:3 molar ratio (with acid catalysis) to obtain the desired diselenocarbamate ester **15b**. Cyclization of **15b** within strong acid furnished the 2-imminium-1, 3-diselenole salt **16b** in 65% yield. This salt could be transformed to TSF via known procedures. This method represents the most efficient synthetic route to TSF.

c. Addition of CSe₂ to acetylenes. Certain substituted tetraselenafulvalenes and diselenadithiafulvalenes can be synthesized in a one-step procedure. Okamoto and his group found that CSe₂ adds to acetylenes bearing at least one electron-withdrawing group under high pressure (ca. 5–10 kbar)[78]. The addition is believed to result in a carbene (via a dipolar intermediate **29**), which then dimerizes to the corresponding TSF derivative (Scheme 13)[78–80].

$(5)R^1 = R^2 = COOMe$

$(31)R^1 = R^2 = SiMe_3$

$(32) R^1 = R^2 = CONH_2$

$(33) R^1 = H; R^2 = COOMe$

$(34) R^1 = H; R^2 = SiMe_3$

$(35) R^1 = H; R^2 = COOH$

$(36) R^1 = H; R^2 = CONH_2$
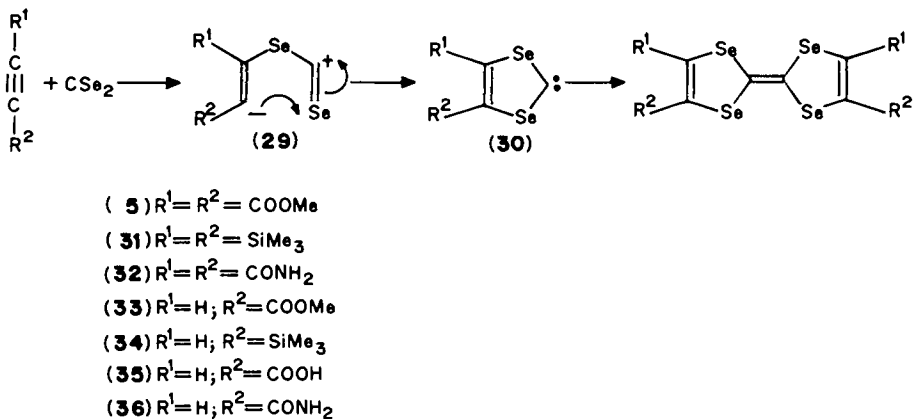
SCHEME 13

Failure of unsubstituted acetylene to react in this manner (to give TSF) supports the formation of the dipolar intermediate **29**. The reaction is general in scope since DSDTF and TTF derivatives can similarly be obtained from CSSe[79] and CS$_2$[78-81], respectively. TSF could be indirectly obtained by this method since Lakshmikantam and Cava[85] converted tetrakis(carbomethoxy)TSF (**5**) to TSF by the action LiBr in HMPA. However, the yield in this latter reaction is more subject to the whims of nature than are most reactions.

d. Triselenocarbonate–acetylene route. Easton and Leaver[82] reported in 1965 that when ethylene trithiocarbonate and dimethyl acetylenedicarboxylate were refluxed in toluene, an exchange of the trithiocarbonate unit giving ethylene and 4,5-dicarbomethoxy-1,3-dithiole-2-thione (**37**) had occurred (Scheme 14). The reaction appears to involve a dipolar addition and fails in the case of mixed sulfur–oxygen analogs of ethylene trithiocarbonate[83].

A successful extension of the above reaction to the selenium analog was subsequently reported by Cava's group[84,85]. While 1,3-diselenolane-2-thione (**38**) gave the 1,3-thiaselenole-2-selone derivative, a precursor to DSDTF derivative[84], the corresponding 1,3-diselenolane-2-selone **39** gave the 1,3-diselenole-2-selone derivative (Scheme 15)[84,85]. Again, the presence of at least one electron-withdrawing group on acetylene is essential.

e. Selenadiazole route. Thermolysis of 1,2,3-selenadiazoles in the presence of either CS$_2$ or CSe$_2$ is a direct route to 1,3-thiaselenole-2-thione or 1,3-diselenole-2-selone. Cava

SCHEME 14

(**38**) X = S
(**39**) X = Se

(**5**) R^1 = R^2 = COOMe
(**40**) R^1 = R^2 = CN
(**33**) R^1 = H; R^2 = COOMe
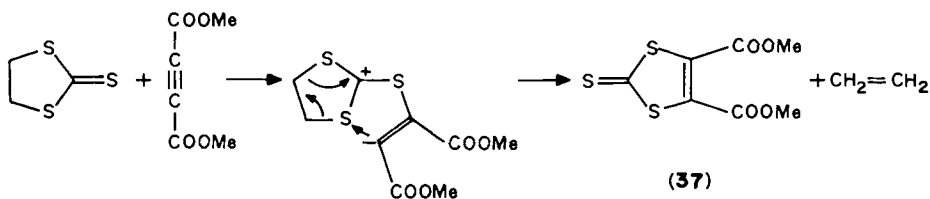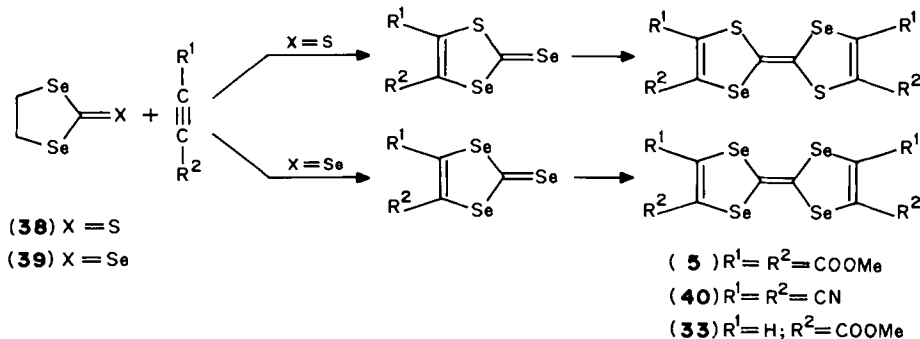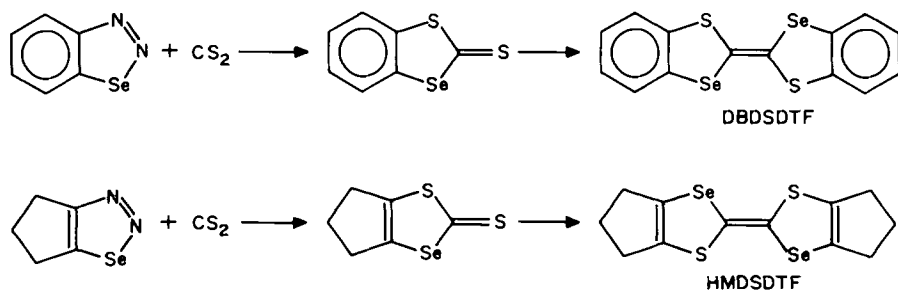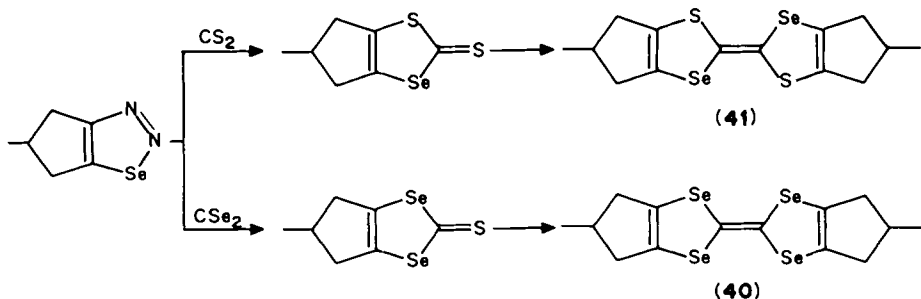
SCHEME 15

SCHEME 16

SCHEME 17

and coworkers first reported this unique extrusion–insertion process and successfully applied it to the syntheses of dibenzodiselenadithiafulvalene (DBDSDTF) and hexamethylenediselenadithiafulvalene (HMDSDTF) (Scheme 16)[86].

Engler et al.[77] extended this methodology to the synthesis of dimethyl HMTSF (40) and dimethyl HMDSDTF (41) (Scheme 17).

Other examples of the successful use of the selenadiazole route can be found in the formation of di(2,5-dihydrothieno)TSF (42)[87] and DBTSF (4)[88].

(42)
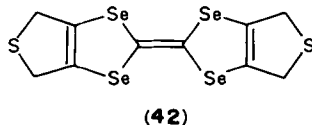
f. Selenium insertion route. The reaction of organometallic compounds (RLi, RMgX) with elemental sulfur, selenium or tellurium usually produces chalcogenates in good yield.
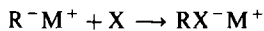
$$R^-M^+ + X \longrightarrow RX^-M^+$$
$$M = Na, Li, K, Mg, Etc.$$
$$X = S, Se, Te$$
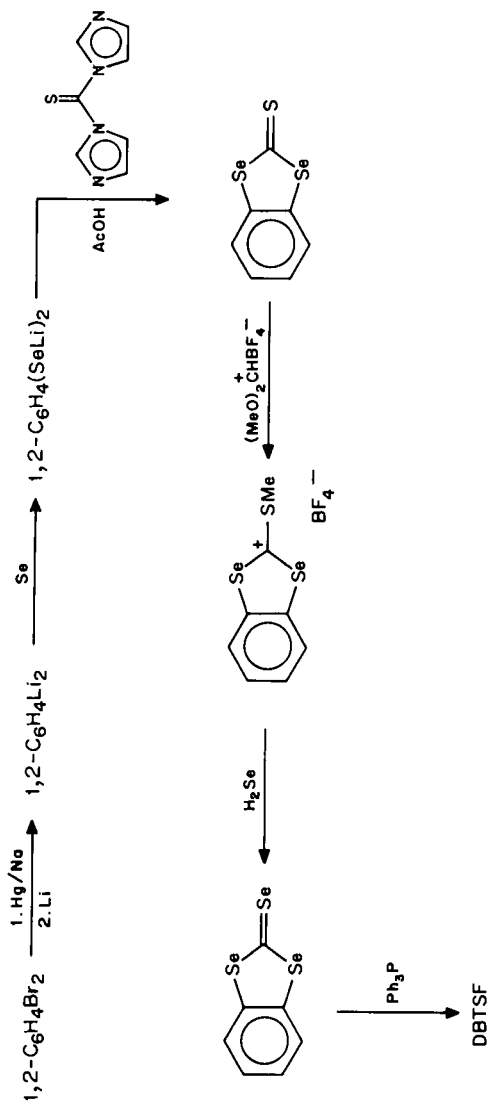
SCHEME 18

It has been used with great success in the syntheses of several heterocycles and TSF precursors. Synthesis of DBTSF (**4**) is a representative example (Scheme 18)[89]. *o*-Dilithiobenzene, generated by the method of Wittig via the mercury compound, was treated with elemental Se and then the 1, 2-diselenol dianion was protonated and treated with thiocarbonyldiimidazole to obtain benzo-1, 3-diselenole-2-thione. The corresponding selone was then obtained by methylation of the thione with dimethoxycarbenium tetrafluoborate followed by treatment with H_2Se. Conversion of the thione to selone was found necessary for the success of Ph_3P-induced coupling to obtain DBTSF.

With a similar synthetic strategy, starting from 3,4-dibromothiophene and 2,5-dimethyl-3- 4-dibromothiophene, Cowan and coworkers have reported the synthesis of thieno[3, 4-*d*]-1, 3-diselenole-2-selone (**43a**)[90] and its dimethyl derivative **43b**[91], respectively. Generation of diselenol dianion was found to be feasible by two consecutive metal–halogen exchange/selenium insertion sequences.

Triphenylphosphine coupling to obtain the TSF derivative was, however, possible only with the dimethyl compound **43b**, perhaps owing to its favorable solubility characteristics (Scheme 19)[91]. More recently, Ketcham *et al.*[92] have provided the synthesis of bis(selenopheno)TTF (**44**) employing 3, 4-dibromoselenophene as the starting compound (Scheme 20).

The interest in these heterofulvalene donors with peripheral chalcogen atoms stems from the possibility of enhanced interchain interactions in their charge-transfer solids. Such interchain interactions are expected to suppress the Peierls' instability commonly associated with the low-dimensional conductors.

Two reports have appeared recently on methods that circumvent several steps involved in converting the diselenol dianion (obtained by selenium insertion) to the TSF derivatives. McCullough and Cowan[93] found that the cyclopentene-1, 2-diselenol dianion can be treated with tetrachloroethylene to obtain HMTSF in a one-pot reaction (Scheme 21). Although the tetrachloroethylene reaction was successfully employed earlier for sulfur (DBTTF)[94,95] and tellurium (HMTTeF[96], DBTTeF[97], BDMT-TTeF[98]) donors, the apparent inability of diselenol dianions to follow suit was puzzling. The critical factors for the success were the purity of 1, 2-dibromocyclopentene, the temperature at which the second equivalent of selenium is added and the temperature at which tetrachloroethylene is allowed to react with diselenol dianion[93].

(**43a**) R = H

(**43b**) R = Me

BDMT−TSF
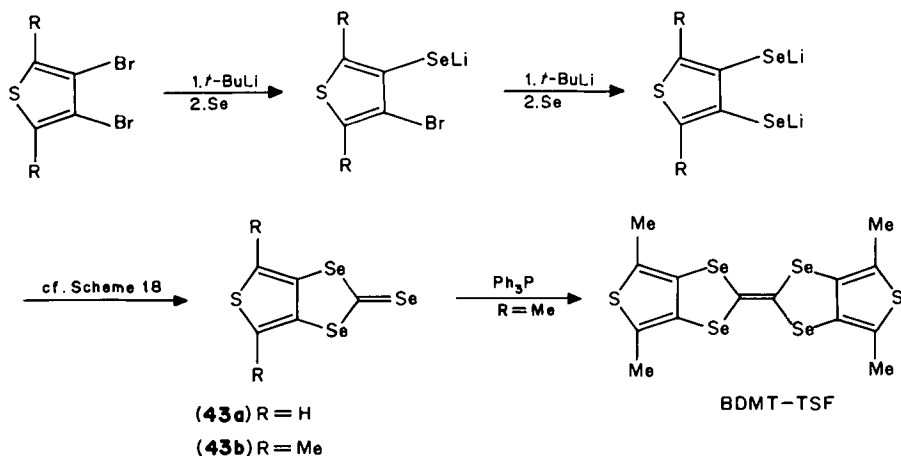
SCHEME 19

SCHEME 20

R = H
R = Me
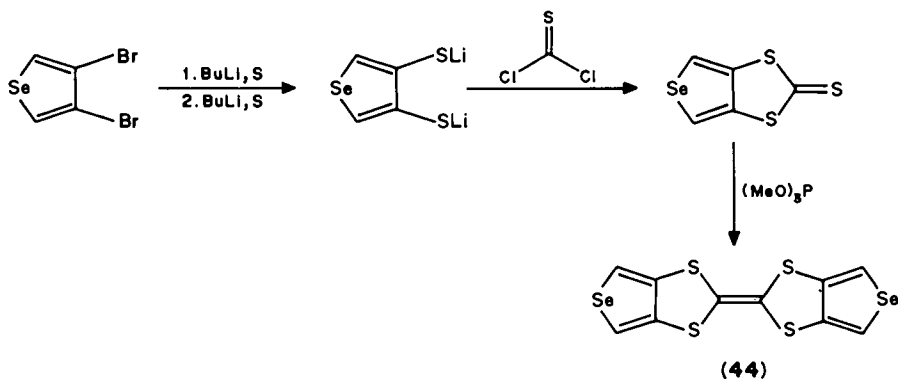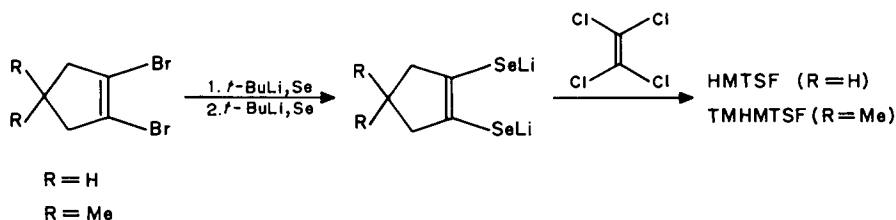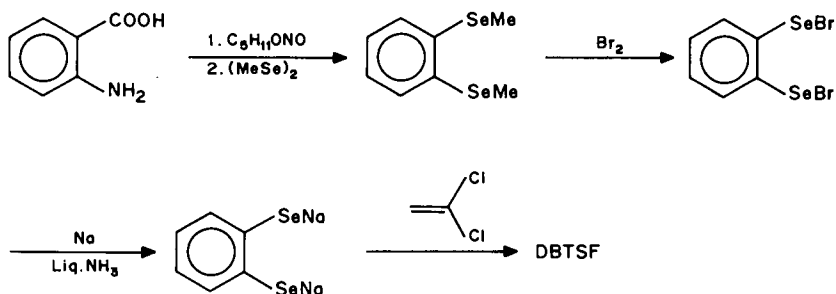
SCHEME 21

SCHEME 22

In a close structural analogy to the above reaction, Lambert and Christiaens[99] have developed a synthesis of DBTSF. As shown in Scheme 22, it involved the addition of dimethyl diselenide to benzyne to obtain bis(methylseleno)benzene, which was converted to diselenol dianion via bromination and treatment with sodium–liquid NH_3. The disodium salt of benzene-1,2-diselenol thus generated was reacted with vinylidene

SCHEME 23
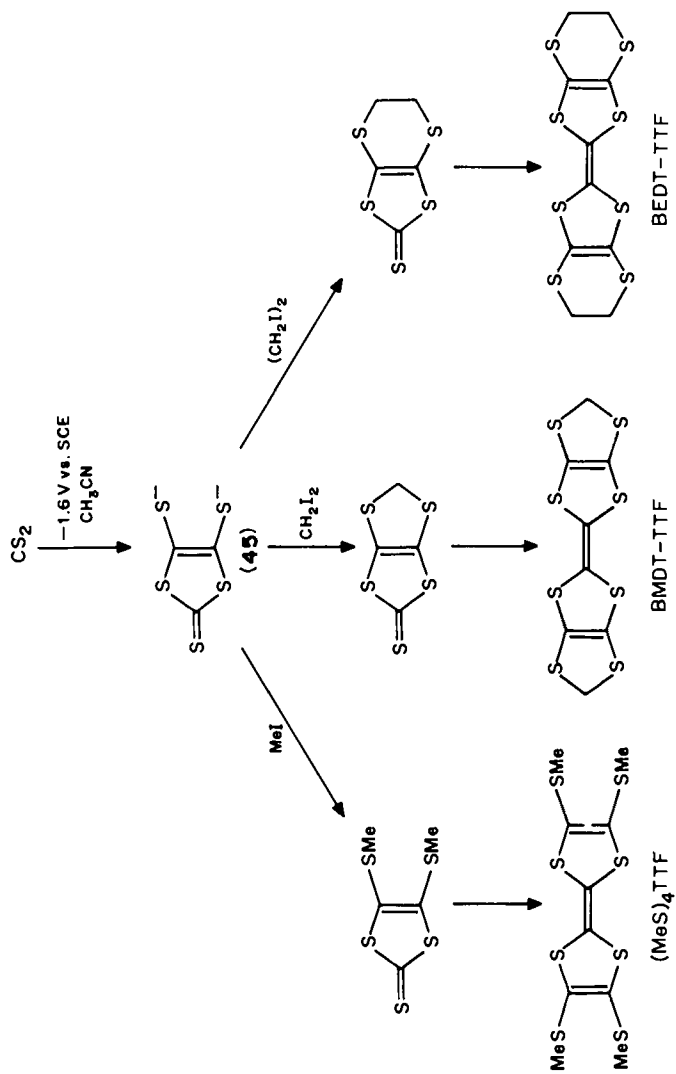
dichloride to obtain DBTSF. An unspecified acetylenic intermediate was postulated by these authors[99].

g. Electrochemical reduction of CSe_2. Carbon disulfide has been known to undergo electrochemical reduction (CH_3CN, -1.6 V vs SCE) to give the dithiol dianion **45**[100,101]. With this common intermediate, various sulfur-rich TTF derivatives, tetrakis(thiomethoxy)TTF[102], BMDT-TTF[1,103] and BEDT-TTF[104,105] were prepared as shown in Scheme 23. Interest in these TTF derivatives, BEDT-TTF in particular, has mounted recently owing to the observation of high electrical conductivity in two dimensions and the consequent suppression of the metal–insulator transition in (BEDT-TTF)$_2$ClO$_4$[106]. Furthermore, superconductivity has been discovered at 7 Kbar in (BEDT-TTF)$_2$ReO$_4$ at 1.5 K[107]. More recently, ambient pressure superconductivity was observed in (BEDT-TTF)$_2$I$_3$ at 1.4 K[48-51]. Changing the anion from I_3^- to AuI_2^- increased T_c to 5 K[108]. These developments, naturally, have focused attention on the selenium analog, BEDS-TSF.

In fact, electrochemical reduction of CSe_2 (DMF, -1.35 V vs. SCE, 40 °C)[109,110] followed a close parallel to CS_2 reduction and 1, 3-diselenole-2-selone-4, 5-diselenol dianion (**46**) was indeed formed (Scheme 24). The reduction could also be effected chemically with potassium naphthalide in THF[110]. The intermediate **46** was then alkylated with 1, 2-dibromoethane to 4, 5-ethylenediseleno-1, 3-diselenole-2-selone (**47**). Since the direct coupling of **47** to BEDS-TSF was unsuccessful, it had first to be transformed to the oxo analog **48**, which was smoothly coupled to the desired selenium donor[110].

BEDS–TSF
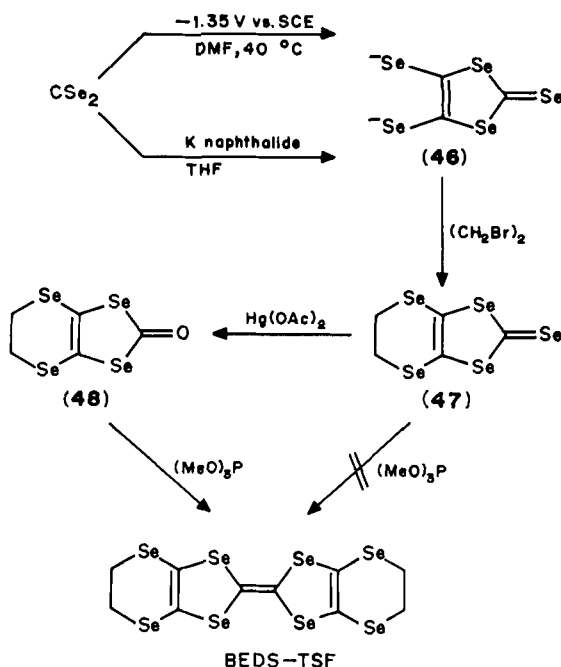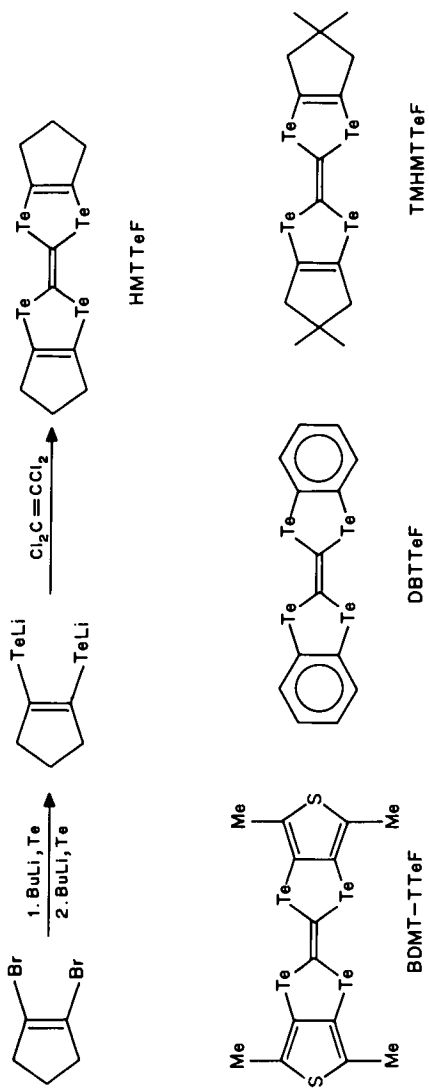
SCHEME 24

SCHEME 25

2. Tellurium donors

Unlike their selenium counterparts, very few tetratellurafulvalenes are known and the parent compound TTeF has not been prepared. The only known tellurafulvalenes to date are HMTTeF[96], DBTTeF[97], BDMT-TTeF[98] and TMHMTTeF[111].

All four compounds share a common synthetic procedure—tellurium insertion into a carbon—lithium bond and subsequent reaction of ditellurolate with tetrachloroethylene. Synthesis of HMTTeF is shown in Scheme 25 as a representative example.

B. Other Selenium/Tellurium Donors

Electrical conductivity in organic solids is not limited to those comprising hetero-fulvalene donors discussed in Section II.A. Other sulfur, selenium and tellurium hetero-cyclic donors and polycyclic aromatic hydrocarbons have also been found to be excellent molecular components of good electrical conductors. Their charge-transfer salts and cation-radical salts have been widely investigated. In this section, the synthetic methods employed in their preparation are presented.

1. Tetraseleno- and tetratelluro-polyacenes

Reports of high metal-like conductivity in salts derived from TTT (51a)[28,29] and TTN (49a)[112] stimulated synthetic efforts on the selenium and tellurium counterparts. In addition, tetrachalcogenoanthracenes (50a–c) were envisaged by Endres *et al.*[113] to be perylene-like and were expected to yield solids with enhanced conductivity properties compared with those derived from perylene itself[52–54,114,130]. The presence of peripheral chalcogen atoms bound to each other, a distinctly different structural feature from the heterofulvalenes, was expected to result in higher dimensionality and stabilization of the metallic state.
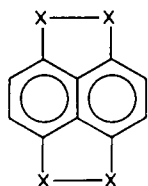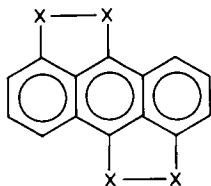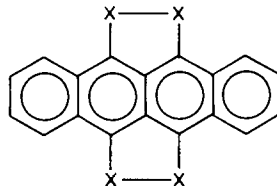
(49a) X = S TTN	(50a) TTA	(51a) TTT
(49b) X = Se TSeN	(50b) TSeA	(51b) TSeT
(49c) X = Te TTeN	(50c) TTeA	(51c) TTeT

Tetrachalcogenopolyacenes are prepared by a general method which involves reacting the corresponding tetrachloro aromatic compound with an alkali metal dichalcogenide in a dipolar aprotic solvent (Scheme 26). To date, TSeN[115,116], TSeA[113], TSeT[117] and TTeT[118] have been prepared by the above method.

Delhaes *et al.*[30] have also reported the synthesis of TSeT by the reaction of selenium with 5,11-dichlorotetracene in boiling Dowtherm (a eutectic of biphenyl and diphenyl ether, b.p. ca. 260 °C) (Scheme 27).

2. Dichalcogenopyranylidenes

Dichalcogenopyranylidenes are isoelectronic with tetrachalcogenafulvalenes and consequently form stable cation radical salts. Once again, the discovery of electrical
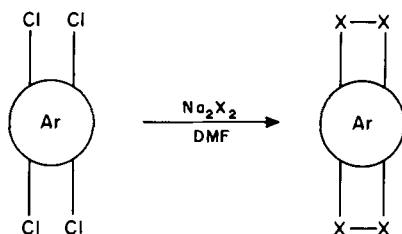
SCHEME 26
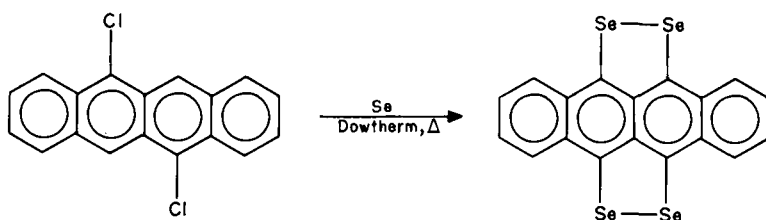
SCHEME 27

conductivity in charge-transfer salts derived from 4,4'-bithiopyranylidene (52a)[119-121] and its derivatives[120,122] spurred the interest in the synthesis of the selenium/tellurium analogs.
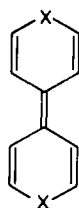
(52a) X = S   BTP
(52b) X = Se   BSeP
(52c) X = Te   BTeP

Unlike BTP, the unsubstituted compounds BSeP and BTeP are at present unknown; however, several of their derivatives have been synthesized recently.

Tetraphenyl and tetramethyl derivatives of BSeP were first prepared by Mollier and co-workers according to Scheme 28[123,124]. An appropriately substituted acetylene was first converted to a penta-1,4-diyne-3-one derivative (53). Addition of H_2Se in a double Michael fashion gave the selenopyranone 54, which was converted to the thione 55 by boron sulfide. Coupling of 55 with copper powder in xylene afforded the BSeP derivatives 56 and 57 in good yield.

An alternative method, reported by the same authors, consisted of coupling selenopyry-
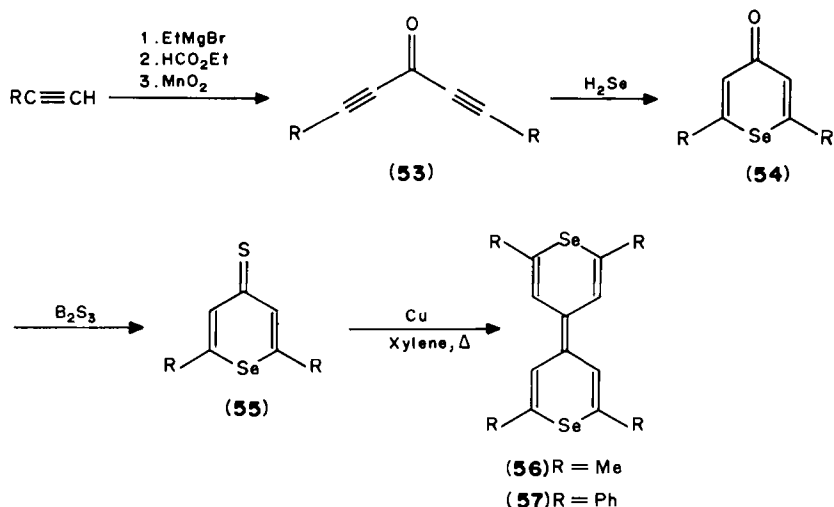
SCHEME 28
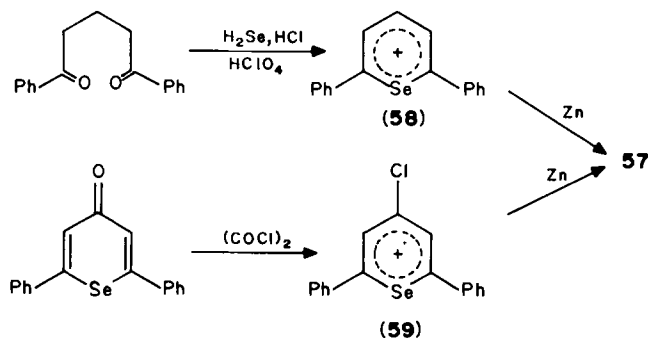
SCHEME 29

lium salts (**58** or **59**) with Zn or TiCl$_3$ (Scheme 29)[124]. The selenopyrylium salt **58** was derived from 1,5-diphenylpentane-1,5-dione and H$_2$Se under acidic conditions, while treatment of the selenopyranone **54** with oxalyl chloride provided the chloro derivative **59**.

Tetraphenyl-BSeP (**57**) forms a 1:1 complex with TCNQ that has a conductivity of 0.5 Ω^{-1} cm^{-1} (compacted powder), which is comparable to that of TTF–TCNQ[124,125].

Synthesis of tellurium compounds in this series was first reported in 1982 with a synthetic sequence that closely parallels the route to selenium compounds (Scheme 30)[126,127]. The only modifications were the use of lithium telluride (generated from tellurium and lithium triethylborohydride) instead of hydrogen chalcogenide and carrying out the reaction under basic conditions (with added NaOEt). These modifications were found to be essential to suppress the formation of the so-called 'anti-Michael' adduct **61** and to facilitate the isolation of desired telluropyranone **60** in high yield[128]. Thionation
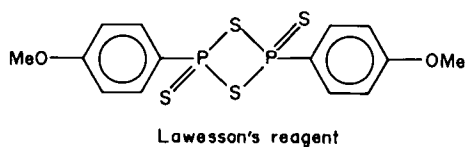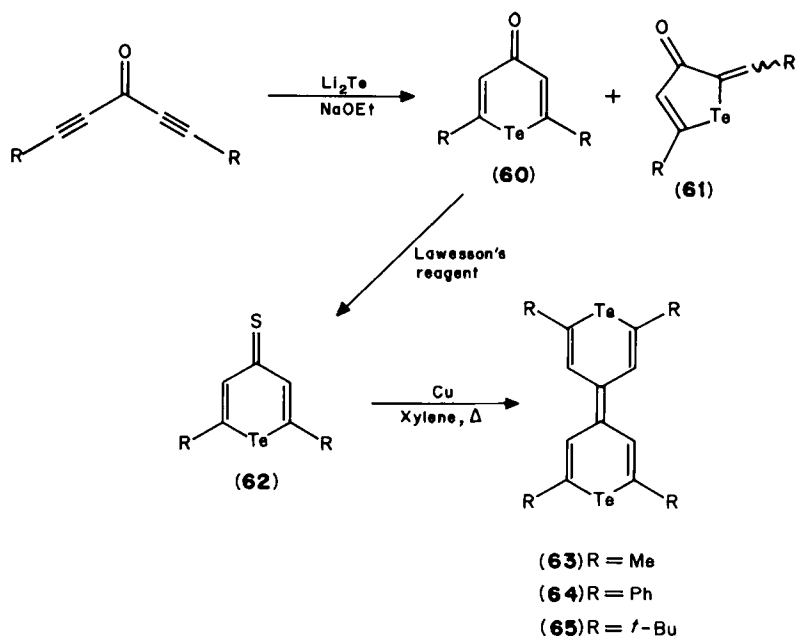
SCHEME 30

with Lawesson's reagent [2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide] converted **60** to the telluropyran-4-thione **62**, which when refluxed with copper powder in xylene culminated in BTeP derivatives. The dibenzo BTeP derivative **66** was also prepared[127].

(66)
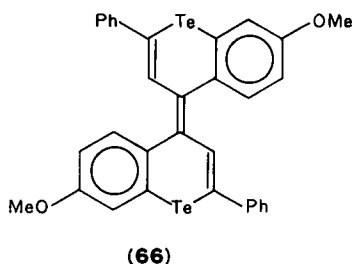
3. Miscellaneous selenium/tellurium donors

In this section, syntheses of donors that do not fall into the previous categories are discussed. The major thrust of the search for new, novel donors is the striking discovery that aromatic hydrocarbons (perylene, pyrene, etc.) yield cation radical salts, similar to the Bechgaard salts [(TMTSF)$_2$X], and these salts can be highly conducting[52-54,113,114]. In fact, these salts were discovered much earlier[129,130] than the Bechgaard salts. They are typically represented as $(D^+X^-)_aD_b$ where D and X are a donor and an inorganic diamagnetic ion, respectively, and $a = b = 1$. Thus, the importance of studying diverse classes of compounds has been clearly recognized and has prompted investigations towards that end.

Incorporation of chalcogen atoms in aromatic carbon frameworks offers an attractive avenue of research. Trichalcogenatriphenylenes (67) and dichalcogenapyrenes (68) represent two sets of donors examined in that context.
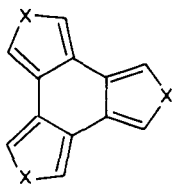
(67a) X = S   BTT

(67b) X = Se   BTSe

(67c) X = Te   BTTe
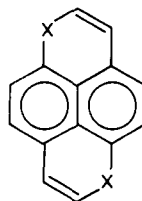
(68a) DTP

(68b) DSeP

(68c) DTeP

Benzotrithiophene (BTT, 67a) was first reported by Hart and Sasaoka[131] as a model sulfur-bridged hexaradialene. The donor properties of BTT were evident from its ability to form charge-transfer complexes with electron acceptors (TCNQ, DDQ) and radical cation salts with Lewis acids (SbCl$_5$, FeCl$_3$). Subsequently the 1:1 complexes BTT–TCNQ and BTT–TCNQF$_4$ were prepared and both were found to be insulators[3]. Since the nitrile stretching frequencies in these complexes indicated partial charge transfer[132], a requirement for high electrical conductivity[133], the crystals of the complexes were inferred to be of mixed-stack type.

The selenium analog BTSe (67b) was synthesized as shown in Scheme 31[3]. However, the reaction of lithium telluride with hexakis(bromomethyl)benzene to obtain hexahydro-BTTe (70) proved to be difficult. Precipitation of elemental tellurium on mixing the reactants was the typical outcome, although in a few instances small amounts of 70 were isolated. Its propensity to form hexaradialene was evident in the mass spectral fragmentation pattern.

Bechgaard recently reported an improved synthesis of DTP (68a) and the electrical properties of DTP–TCNQ[134]. The salt is very one-dimensional and stays metallic down to 1.2 K. This result is interesting because it supports the prediction that a 'purely' one-dimensional system is not subject to Peierls' distortion[135]. (Peierls' distortion is a lattice distortion commonly encountered in quasi-one-dimensional solids resulting in a band gap. Its chemical analog is the well known Jahn–Teller distortion).

The selenium and tellurium analogs DSeP (68b) and DTeP (68c) are at present unknown.
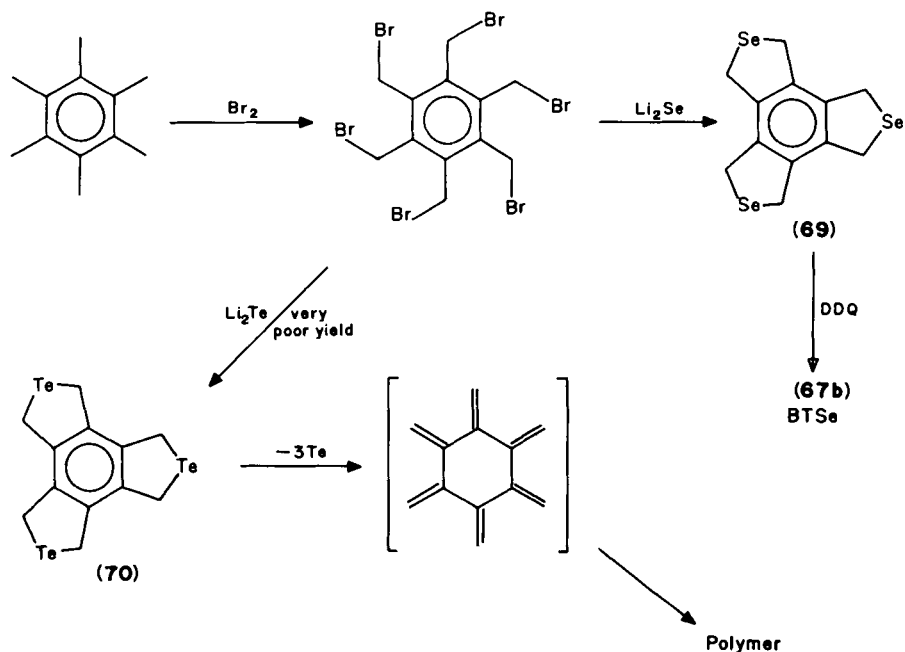
SCHEME 31

III. ABBREVIATIONS USED

BDMT-TSF	Bis(2, 5-dimethylthieno)tetraselenafulvalene
BDMT-TTF	Bis(2, 5-dimethylthieno)tetrathiafulvalene
BDMT-TTeF	Bis(2, 5-dimethylthieno)tetratellurafulvalene
BEDS-TSF	Bis(ethylenediseleno)tetraselenafulvalene
BEDT-TTF	Bis(ethylenedithio)tetrathiafulvalene
BMDT-TTF	Bis(methylenedithio)tetrathiafulvalene
BSeP	4, 4'-Biselenopyranylidene
BTP	4, 4'-Bithiopyranylidene
BTSe	Benzotriselenophene
BTT	Benzotrithiophene
BTTe	Benzotritellurophene
BTeP	4, 4'-Bitelluropyranylidene
DBDSDTF	Dibenzodiselenadithiafulvalene
DBTSF	Dibenzotetraselenafulvalene
DBTTF	Dibenzotetrathiafulvalene
DBTTeF	Dibenzotetratellurafulvalene
DDQ	2, 3-Dichloro-5, 6-dicyanoquinone
DMTCNQ	2, 5-Dimethyltetracyanoquinodimethane
DMTSF	Dimethyltetraselenafulvalene
DPTSF	Diphenyltetraselenafulvalene
DSDTF	Diselenadithiafulvalene

DSeP	1,6-Diselenapyrene
DTP	1,6-Dithiapyrene
DTeP	1,6-Ditellurapyrene
HMDSDTF	Hexamethylenediselenadithiafulvalene
HMTSF	Hexamethylenetetraselenafulvalene
HMTTF	Hexamethylenetetrathiafulvalene
HMTTeF	Hexamethylenetetratellurafulvalene
OMTSF	Octamethylenetetraselenafulvalene
TCNQ	Tetracyanoquinodimethane
TCNQF$_4$	Tetrafluorotetracyanoquinodimethane
TMHMTTeF	Tetramethylhexamethylenetetratellurafulvalene
TMTSF	Tetramethyltetraselenafulvalene
TMTTF	Tetramethyltetrathiafulvalene
TNAP	Tetracyano-2,6-naphthoquinodimethane
TPTSF	Tetraphenyltetraselenafulvalene
TSF	Tetraselenafulvalene
TSeA	Tetraselenoanthracene
TSeN	Tetraselenonaphthalene
TSeT	Tetraselenotetracene
TTA	Tetrathioanthracene
TTF	Tetrathiafulvalene
TTN	Tetrathionaphthalene
TTT	Tetrathiotetracene
TTeA	Tetratelluroanthracene
TTeF	Tetratellurafulvalene
TTeN	Tetratelluronaphthalene
TTeT	Tetratellurotetracene

IV. ACKNOWLEDGEMENTS

V. REFERENCES

1. D. Cowan, P. Shu, C. Hu, W. Krug, T. Carruthers, T. Poehler and A. Bloch, *Chemistry and Physics of One-Dimensional Metals* (Ed. H. J. Keller), Plenum Press, New York, 1977, pp. 25–46.
2. A. N. Bloch, T. F. Carruthers, T. O. Poehler and D. O. Cowan, *Chemistry and Physics of One-Dimensional Metals* (Ed. H. J. Keller), Plenum Press, New York, 1977, pp. 47–85.
3. D. O. Cowan, A. Kini, L.-Y. Chiang, K. Lerstrup, D. Talham, T. Poehler and A. Bloch, *Mol. Cryst. Liq. Cryst.*, **86**, 1 (1982); D. O. Cowan and F. M. Wiygul, *Chem. Eng. News*, **64**(29), 28 (1986).
4. D. Jerome and H. J. Schulz, *Adv. Phys.*, **31**, 299 (1982).
5. A. J. Berlinsky, *Contemp. Phys.*, **17**, 331 (1976).
6. R. L. Greene and P. M. Chaikin, *Physica*, **B126**, 431 (1984).
7. J. H. Perlstein, J. P. Ferraris, V. W. Walatka, D. O. Cowan and G. A. Candela, *AIP Conf. Proc. (Magnetism and Magnetic Materials)*, **10**, 1494 (1972).
8. J. Ferraris, D. O. Cowan, V. Walatka and J. Perlstein, *J. Am. Chem. Soc.*, **95**, 948 (1973).
9. A. N. Bloch, J. P. Ferraris, D. O. Cowan and T. O. Poehler, *Solid State Commun.*, **13**, 753 (1973).
10. L. B. Coleman, J. M. Cohen, D. J. Sandman, F. G. Yamagishi, A. F. Garito and A. J. Heeger, *Solid State Commun.*, **12**, 1125 (1973).
11. D. E. Schafter, F. Wudl, G. A. Thomas, J. P. Ferraris and D. O. Cowan, *Solid State Commun.*, **14**, 347 (1974).

12. G. A. Thomas *et al.*, *Phys. Rev. B*, **13**, 5105 (1976).
13. R. V. Gemmer, D. O. Cowan, T. O. Poehler, A. N. Bloch, R. E. Pyle and R. H. Banks, *J. Org. Chem.*, **40**, 3544 (1975).
14. J. P. Ferraris, T. O. Poehler, A. N. Bloch and D. O. Cowan, *Tetrahedron Lett.*, 2553 (1973).
15. T. Ishiguro, H. Sumi, S. Kagoshima, K. Kajimura and H. Anzai, *J. Phys. Soc. Jpn.*, **48**, 456 (1980).
16. R. L. Greene, J. J. Mayerle, R. R. Schumaker, G. Castro, P. M. Chaikin, S. Etemad and S. J. LaPlaca, *Solid State Commun.*, **20**, 943 (1976).
17. E. M. Engler and V. V. Patel, *J. Am. Chem. Soc.*, **96**, 7376 (1974).
18. S. Etemad, T. Penney, E. M. Engler, B. A. Scott and P. E. Seiden, *Phys. Rev. Lett.*, **34**, 741 (1975).
19. S. Etemad, *Phys. Rev. B*, **13**, 2254 (1976).
20. E. M. Engler, B. A. Scott, S. Etemad, T. Penney and V. V. Patel, *J. Am. Chem. Soc.*, **99**, 5909 (1977).
21. K. Bechgaard, D. O. Cowan and A. N. Bloch, *Chem. Commun.*, 937 (1974).
22. A. N. Bloch, D. O. Cowan, K. Bechgaard, R. E. Pyle, R. H. Banks and T. O. Poehler, *Phys. Rev. Lett.*, **34**, 1561 (1975).
23. J. R. Cooper, M. Weger, D. Jerome, D. Lefur, K. Bechgaard, A. N. Bloch and D. O. Cowan, *Solid State Commun.*, **19**, 749 (1976).
24. D. O. Cowan, M. Mays, M. Lee, R. McCullough, A. Bailey, K. Lerstrup, F. Wiygul, T. Kistenmacher, T. Poehler and L. -Y. Chiang, *Mol. Cryst. Liq. Cryst.*, **125**, 191 (1985).
25. G. Saito, H. Kumogai, J. Tanaka, T. Enoki and H. Inokuchi, *Mol. Cryst. Liq. Cryst.*, **120**, 337 (1985).
26. K. Bechgaard, C. S. Jacobsen and N. Hessel Andersen, *Solid State Commun.*, **25**, 875 (1978).
27. B. Mogensen, R. H. Friend, D. Jerome, K. Bechgaard and K. Carneiro, *Solid State Commun.*, **26**, 919 (1978).
28. G. Mihaly, A. Janossy and G. Gruner, *Solid State Commun.*, **22**, 771 (1977).
29. L. C. Isett and E. A. Perez-Albuerne, *Solid State Commun.*, **21**, 433 (1977).
30. B. Hilti, C. W. Mayer and G. Rihs, *Helv. Chim. Acta*, **61**, 1462 (1978).
31. P. Delhaes, C. Coulon, S. Flandrois, H. Hilti, C. W. Mayer and G. Rihs, *J. Chem. Phys.*, **73**, 1452 (1980).
32. S. P. Zolotukhin, V. F. Kaminskii, A. I. Kotov, R. B. Lyubovskii, M. L. Khidekel, R. P. Shibaeva, I. F. Shchegolev and E. B. Yagubskii, *Piśma Zh. Eksp. Teor. Fiz.*, **25**, 480 (1977); *JETP Lett.*, **25**, 451 (1977).
33. V. N. Laukhin, A. I. Katov, M. L. Khidekel, I. F. Shchegolev, and E. B. Yagubskii, *Piśma Zh. Eksp. Teor. Fiz.*, **28**, 284 (1978).
34. S. P. Zolotukhin, Y. S. Karimov and I. F. Shchegolev, *Sov. Phys. JETP*, **49**, 192 (1979).
35. V. B. Ginodman, L. N. Zherikhina and E. E. Yurchakevich, *JETP Lett.*, **30**, 268 (1980).
36. V. N. Laukhin and I. F. Shchegolev, *Sov. Phys. JETP*, **51**, 1170 (1980).
37. D. Jerome, A. Mazaud, M. Ribault and K. Bechgaard, *J. Phys. Lett.*, **41**, L95 (1980).
38. M. Ribault, G. Benedek, D. Jerome and K. Bechgaard, *J. Phys. Lett.*, **41**, 397 (1980).
39. K. Andres, F. Wudl, D. B. McWhan, G. A. Thomas, D. Nalewajek and A. L. Stevens, *Phys. Rev. Lett.*, **45**, 1449 (1980).
40. R. L. Greene and E. M. Engler, *Phys. Rev. Lett.*, **45**, 1587 (1980).
41. H. J. Schulz, D. Jerome, M. Ribault, A. Mazaud and K. Bechgaard, *J. Phys. Lett.*, **42**, 51 (1981).
42. D. Jerome, *Chem. Scr.*, **17**, 13 (1981).
43. F. Wudl, K. Andres, D. B. McWhan, G. A. Thomas, D. Nalewajek, W. M. Walsh, Jr., L. W. Rupp, Jr., F. J. DiSalvo, J. V. Wazczak and A. I. Stevens, *Chem. Scr.*, **17**, 19 (1981).
44. C. S. Jacobsen, K. Mortensen, N. Thorup, D. B. Tanner, M. Weger and K. Bechgaard, *Chem. Scr.*, **17**, 103 (1981).
45. K. Bechgaard, K. Carneiro, M. Olsen, F. Rasmussen and C. S. Jacobsen, *Phys. Rev. Lett.*, **46**, 852 (1981).
46. K. Bechgaard, K. Carneiro, F. Rasmussen, M. Olsen, G. Rindorf, C. S. Jacobsen, H. J. Pedersen and J. C. Scott, *J. Am. Chem. Soc.*, **103**, 2440 (1981).
47. D. U. Gubser, W. W. Fuller, T. O. Poehler, D. O. Cowan, M. Lee, R. S. Potember, L. -Y. Chiang and A. N. Bloch, *Phys. Rev. B*, **24**, 478 (1981).
48. E. B. Yagubskii, I. F. Shchegolev, V. N. Laukhin, P. A. Kononovich, M. V. Karatsovnik, A. V. Zvarykina and L. I. Buravov, *JETP Lett.*, **39**, 12 (1984).
49. V. F. Kaminskii, T. G. Prokhorova, R. P. Shibaeva and E. B. Yagubskii, *JETP Lett.*, **39**, 17 (1984).

50. G. W. Crabtree, K. D. Carlson, L. N. Hall, T. Copps, H. H. Wang, T. J. Emge, M. A. Beno and J. Williams, *Phys. Rev. B*, **30**, 2958 (1984).
51. T. Emge, P. Leung, M. Beno, A. Schultz, A. Wang, L. Sowa and J. Williams, *Phys. Rev. B*, **30**, 6780 (1984).
52. H. J. Keller, D. Nothe, H. Pritzkow, D. Wehne, M. Werner, P. Koch and D. Schweitzer, *Mol. Cryst. Liq. Cryst.*, **62**, 181 (1980).
53. H. J. Keller, D. Nothe, H. Pritzkow, D. Dehe, M. Werner, R. H. Harms, P. Koch and D. Schweitzer, *Chem. Scr.*, **17**, 101 (1981).
54. L. Alcacer, D. Chasseau and J. Gaultier, *Solid State Commun.*, **35**, 945 (1980).
55. S. Yoneda, T. Kawase, M. Inaba and Z. Yoshida, *J. Org. Chem.*, **43**, 595 (1978).
56. Z. Yoshida, T. Kawase and S. Yondea, *Tetrahedron Lett.*, 331 (1975).
57. G. Scherowsky and J. Weiland, *Chem. Ber.*, **107**, 3155 (1974).
58. M. G. Miles, J. D. Wilson, D. J. Dahn and J. H. Wagenknecht, *J. Chem. Soc., Chem. Commun.*, 751 (1974).
59. E. M. Engler, V. V. Patel and R. R. Schumaker, *J. Chem. Soc., Chem. Commun.*, 835 (1977).
60. E. Klingbserg, *J. Am. Chem. Soc.*, **84**, 3410 (1962).
61. D. Leaver, W. A. H. Robertson and D. M. McKinnon, *J. Chem. Soc.*, 5104 (1962).
62. H. Prinzbach, H. Berger and A. Luttinghaus, *Angew. Chem.*, **77**, 453 (1965).
63. E. M. Engler and V. V. Patel, *J. Am. Chem. Soc.*, **96**, 7376 (1974).
64. H. Poleschner and E. Fanghänel, *J. Prakt. Chem.*, **324**, 691 (1982).
65. E. M. Engler and V. V. Patel, *J. Org. Chem.*, **40**, 487 (1975).
66. K. Bechgaard, D. O. Cowan, A. N. Bloch and L. Henriksen, *J. Org. Chem.*, **40**, 746 (1975).
67. E. M. Engler and V. V. Patel, *J. Chem. Soc., Chem. Commun.*, 672 (1975).
68. L. Henriksen and E. S. Kristiansen, *Int. J. Sulfur Chem., Part A*, **2**, 13 (1972).
69. F. Wudl, E. Aharon-Shalom and S. H. Bertz, *J. Org. Chem.*, **46**, 4612 (1981).
70. P. Shu, A. N. Bloch, T. F. Carruthers and D. O. Cowan, *J. Chem. Soc., Chem. Commun.*, 505 (1977).
71. F. Wudl and D. Nalewajek, *J. Chem. Soc., Chem. Commun.*, 866 (1980).
72. L. -Y. Chiang, T. O. Poehler, A. N. Bloch and D. O. Cowan, *J. Chem. Soc., Chem. Commun.*, 866 (1980).
73. A. Moradpour, V. Peyrussan, I. Johannsen and K. Bechgaard, *J. Org. Chem.*, **48**, 388 (1983).
74. L. -Y. Chiang, D. O. Cowan, T. O. Poehler and A. N. Bloch, *Mol. Cryst. Liq. Cryst.*, **86**, 27 (1982).
75. I. Johannsen, K. Lerstrup, L. Henriksen and K. Bechgaard, *J. Chem. Soc., Chem. Commun.*, 89 (1984).
76. L. Henriksen, *Synthesis*, 771 (1982).
77. E. M. Engler, V. V. Patel, J. R. Andersen, R. R. Schumaker and A. A. Fukushima, *J. Am. Chem. Soc.*, **100**, 3769 (1978).
78. Y. Okamoto and P. S. Wojciechowski, *J. Chem. Soc., Chem. Commun.*, 669 (1981).
79. J. E. Rice, P. Wojciechowski and Y. Okamoto, *Heterocycles*, **18**, 191 (1982).
80. Y. Okamoto, H. S. Lee and S. T. Attarwala, *J. Org. Chem.*, **50**, 2788 (1985).
81. H. D. Hartzler, *J. Am. Chem. Soc.*, **95**, 4374 (1973).
82. D. B. J. Easton and D. Leaver, *J. Chem. Soc., Chem. Commun.*, 585 (1965).
83. B. R. O. Connor and F. N. Jones, *J. Org. Chem.*, **35**, 2002 (1970).
84. M. V. Lakshmikantam, M. P. Cava and A. F. Garito, *J. Chem. Soc., Chem. Commun.*, 383 (1975).
85. M. V. Lakshmikantam and M. P. Cava, *J. Org. Chem.*, **41**, 882 (1976).
86. H. K. Spencer, M. V. Lakshmikantam, M. P. Cava and A. F. Garito, *J. Chem. Soc., Chem. Commun.*, 867 (1975).
87. C. Berg, K. Bechgaard, J. R. Andersen and C. S. Jacobsen, *Tetrahedron Lett.*, 1719 (1976).
88. I. Johannsen, K. Bechgaard, K. Mortensen and C. Jacobsen, *J. Chem. Soc., Chem. Commun.*, 295 (1983).
89. K. Lerstrup, M. Lee, F. M. Wiygul, T. J. Kistenmacher and D. O. Cowan, *J. Chem. Soc., Chem. Commun.*, 294 (1983).
90. L. -Y. Chiang, P. Shu, D. Holt and D. O. Cowan, *J. Org. Chem.*, **48**, 4713 (1983).
91. K. Lerstrup and D. O. Cowan, *J. Phys. (Paris) Colloq. C3*, 1247 (1983).
92. R. Ketcham, A. B. Hornfeldt and S. Gronowitz, *J. Org. Chem.*, **49**, 1117 (1984).
93. R. D. McCullough and D. O. Cowan, *J. Org. Chem.*, **50**, 4646 (1985).
94. W. R. H. Hurtley and S. Smiles, *J. Chem. Soc.*, 2263 (1926).

95. G. S. Bajwa, K. D. Berlin and H. A. Pohl, *J. Org. Chem.*, **41**, 145 (1976).
96. F. Wudl and E. Aharon-Shalom, *J. Am. Chem. Soc.*, **104**, 1154 (1982).
97. K. Lerstrup, D. Talham, A. Bloch, T. Poehler and D. Cowan, *J. Chem. Soc., Chem. Commun.*, 336 (1982).
98. K. Lerstrup, D. O. Cowan and T. J. Kistenmacher, *J. Am. Chem. Soc.*, **106**, 8303 (1984).
99. C. Lambert and L. Christiaens, *Tetrahedron Lett.*, 833 (1984).
100. S. Wawzonek and S. Heilmann, *J. Org. Chem.*, **39**, 511 (1974).
101. G. Bontempelli, F. Nago, G. Mazzochin and R. Seeber, *J. Electroanal. Chem. Interfacial Electrochem.*, **63**, 231 (1974).
102. P. R. Moses and J. Q. Chambers, *J. Am. Chem. Soc.*, **96**, 945 (1974).
103. W. P. Krug, A. N. Bloch, T. O. Poehler and D. O. Cowan, *Ann. N. Y. Acad. Sci.*, **313**, 366 (1978).
104. M. Mizuno, A. F. Garito and M. P. Cava, *J. Chem. Soc., Chem. Commun.*, 18 (1978).
105. W. Krug, *PhD Dissertation*, The Johns Hopkins University, Baltimore, 1977.
106. G. Saito, T. Enoki, K. Toriumi and H. Inokuchi, *Solid State Commun.*, **42**, 557 (1982).
107. S. S. P. Parkin, E. M. Engler, R. R. Schumaker, R. Lagier, V. Y. Lee, J. C. Scott and R. L. Greene, *Phys. Rev. Lett.*, **50**, 270 (1983).
108. H. H. Wang, M. A. Beno, U. Geiser, M. A. Firestone, K. S. Webb, L. Nunez, G. W. Crabtree, K. D. Carlson, J. M. Williams, L. J. Azvedo, J. F. Kwak and J. E. Schirber, *Inorg. Chem.*, **24**, 2465 (1985).
109. E. M. Engler, D. C. Green and J. Q. Chambers, *J. Chem. Soc., Chem. Commun.*, 148 (1976).
110. V. Y. Lee, E. M. Engler, R. R. Schumaker and S. S. P. Parkin, *J. Chem. Soc., Chem. Commun.*, 235 (1983).
111. D. Cowan, A. Bailey and K. Lerstrup, unpublished results.
112. F. Wudl, D. E. Shafer and B. Miller, *J. Am. Chem. Soc.*, **98**, 252 (1976).
113. H. Endres, H. J. Keller, J. Quekborner, J. Veigel and D. Schweitzer, *Mol. Cryst. Liq. Cryst.*, **86**, 1851 (1982).
114. C. Krohnke, V. Enkelman and G. Wegner, *Angew. Chem., Int. Ed. Engl.*, **19**, 912 (1980).
115. A. Yamahira, T. Nohami and H. Mikawa, *J. Chem. Soc., Chem. Commun.*, 904 (1983).
116. J. C. Stark, R. Reed, L. A. Acampora, D. J. Sandman, S. Jensen, M. T. Jones and B. M. Foxman, *Organometallics*, **3**, 732 (1984).
117. K. A. Balodis, A. D. Livdane, R. S. Medne and O. V. Neiland, *J. Org. Chem. USSR (Engl. Transl.)*, **15**, 343 (1979).
118. D. J. Sandman, J. C. Stark and B. M. Foxman, *Organometallics*, **1**, 739 (1982).
119. S. Hunig, B. J. Garner, G. Ruider and W. Schenk, *Justus Liebigs Ann. Chem.*, 1036 (1973).
120. J. H. Perlstein, J. A. Van Allen, L. C. Iset and G. A. Reynolds, *Ann. N. Y. Acad. Sci.*, **313**, 61 (1977).
121. D. J. Sandman, A. J. Epstein, T. J. Holmes, J.-S. Lee and D. D. Titus, *J. Chem. Soc., Perkin Trans. 2*, 1578 (1980).
122. H. Strezelecka and J. Rivory, *Mater. Res. Bull.*, **15**, 899 (1980).
123. S. Es-Seddiki, G. Le Coustumer, Y. Mollier and M. Davoud, *Tetrahedron Lett.*, 2771 (1981).
124. S. Es-Seddiki, G. Le Costumer, Y. Mollier and M. Davoud, *Mol. Cryst. Liq. Cryst.*, **86**, 1811 (1982).
125. J. Amzil, M. Brutus, G. LeCostumer, M. Hakiki, J. F. Hemidy, Y. Mollier, J. P. Sauve and M. Stavaux, *J. Phys. (Paris) Colloq. C*, 1249 (1983).
126. M. R. Detty, B. J. Murray and J. H. Perlstein, *Tetrahedron Lett.*, 539 (1983).
127. M. R. Detty and B. J. Murray, *J. Org. Chem.*, **47**, 1146 (1982).
128. M. R. Detty, B. J. Murray and M. D. Seidler, *J. Org. Chem.*, **47**, 1968 (1982).
129. T. C. Chiang, A. H. Reddock and D. F. Williams, *J. Chem. Phys.*, **54**, 2051 (1971).
130. H. Akamatu, H. Inokucki and Y. Matsunaga, *Nature (London)*, **173**, 168 (1954).
131. H. Hart and M. Sasaoka, *J. Am. Chem. Soc.*, **100**, 4326 (1978).
132. J. S. Chappell, A. N. Bloch, W. A. Bryden, M. Maxfield, T. O. Poehler and D. O. Cowan, *J. Am. Chem. Soc.*, **103**, 2442 (1981).
133. J. B. Torrance, *Acc. Chem. Res.*, **12**, 79 (1979).
134. K. Bechgaard, in *Proceedings of Symposium 'Horizons in the Chemistry and Properties of Low Dimensional Solids', Honolulu, Hawaii, December 16–21, 1984; Mol. Cryst. Liq. Cryst.*, **125**, 81 (1985).
135. R. E. Peierls, *Quantum Theory of Solids*, Oxford University Press, London, 1955, p. 108.

CHAPTER **13**

Organoselenium and organotellurium analogues of ethers and peroxides

WILLIAM R. McWHINNIE

Department of Molecular Sciences, Aston University, Aston Triangle, Birmingham B4 7ET, UK

I. INTRODUCTION

Diorganyl selenides and diorganyl tellurides, the selenium and tellurium analogues of the ethers, probably constitute the largest single class of known organic derivatives of the heavier chalcogens. The scope of this chapter could, therefore, by very great. To avoid a totally superficial coverage of a large bulk of material, some constraints will be introduced; thus most heterocyclic systems which could, strictly, be classified as examples of R_2E (E = Se, Te) will be omitted. This is sensible, particularly when, as with tellurophene for example, it is wise to consider reactions of the total ring system.

Diorganyl diselenides and diorganyl ditellurides present less classification problems since, although some dichalcogenide linkages appear as constituents of a heterocyclic ring, e.g. 1, the reactivity of such compounds is often dominated by the reactivity of the dichalcogenide linkage.
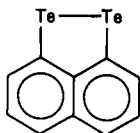
(1)

This chapter will cover the general methods of synthesis of R_2E and R_2E_2 (E = Se, Te), the structures of the compounds, the reactions they undergo and their spectroscopic properties. The objective under each heading will be to bring out the salient features rather

than to attempt a comprehensive coverage. The fact that interest in the compounds has been steadily growing over the past decade reflects amongst other things their growing importance in organic synthesis, their role in formulating novel materials of high electrical conductivity and their amenity to study by techniques such as X-ray crystallography and multinuclear NMR spectroscopy. Not surprisingly, therefore, a number of books[1-3], review articles and annual surveys[4-6] and the proceedings of three relevant international conferences[7-9] do, between them, provide a very comprehensive entrée to the literature. Further, the present series of texts will also provide specialist chapters relevant to topics covered here; consequently, in dealing with spectroscopic properties, for example, this chapter will confine attention to those data which provide extra chemical insight to the molecules R_2E and R_2E_2 and will not be concerned to elucidate the detailed theory of the techniques. Although, inevitably, some overlap with other chapters will occur, it is hoped that this contribution can stand alone as a helpful introduction to the chemistry of the title compounds.

II. SYNTHESIS

A. Symmetrical and Unsymmetrical Selenides

A variety of inorganic and organic selenium compounds may be employed as starting materials for the synthesis of selenides, R_2Se and $RR'Se$. Examples of synthetic methods are conveniently presented as a function of these various materials.

1. Elemental selenium

Selenium is normally converted to selenide. This may be achieved with a variety of reducing agents in aqueous or non-aqueous media. Typical examples are

$$Se \xrightarrow{\text{NaOH/H}_2\text{O}} Na_2Se \xrightarrow{\text{RX}} R_2Se \qquad \text{(Ref. 10)}$$

$$\text{e.g. R} = \text{alkyl}$$

and

$$Se \xrightarrow[\text{NH}_3(\text{liq.})]{\text{Na}} Na_2Se \xrightarrow{\text{RX}} R_2Se \qquad \text{(Ref. 11)}$$

$$\text{e.g. R} = \text{Me, Et}$$
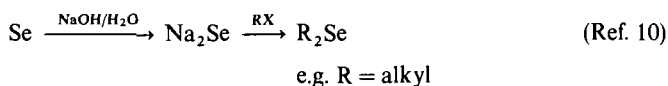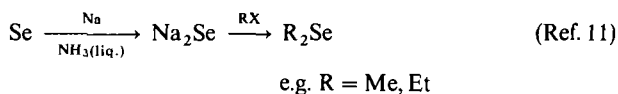
A recently developed procedure[12] uses DMF as a non-aqueous solvent for the reaction of sodium and elemental selenium. It is always advisable to work with solutions of selenide (and telluride) under a strictly inert atmosphere.

An interesting example of the use of the Se^{2-}/DMF reagent is provided by the synthesis of poly(p-phenylene selenide)[13,14]:

$$p\text{-BrC}_6\text{H}_4\text{Br} + Na_2Se \xrightarrow[120 - 140\,°C]{\text{DMF}} (C_6H_4Se)_n$$
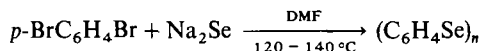
The experimental conditions were milder than those required for poly(p-phenylene sulphide) and it is believed that an $S_{RN}1$ mechanism is operative[14].

2. Selenium(IV) compounds

Selenium tetrachloride is readily available and reacts with a variety of organometallic compounds to give, under appropriate reaction conditions, diorganylselenium dichl-

orides, which may then be reduced to the selenide. In some cases reduction is not necessary since the selenide results directly. Appropriate organometallic compounds for the transmetallation reactions include Grignard reagents, organolithiums, organothalliums (e.g. R_2TlBr), organotins and organomercurides. Some examples are as follows:

$$SeCl_4 + RLi \longrightarrow RSeCl_3 \xrightarrow{RLi} R_2SeCl_2 \qquad \text{(Ref. 15)}$$

$$SeCl_4 + 4\,RMgBr \longrightarrow R_2Se + RR + 2\,MgCl_2 \rightarrow 2\,MgBr_2 \qquad \text{(Ref. 16)}$$

$$SeCl_4 + (F_5C_6)_2TlBr \longrightarrow (F_5C_6)_2SeCl_2 + TlCl_2Br \qquad \text{(Ref. 17)}$$

$$SeCl_4 + Ph_4Sn \longrightarrow Ph_2SeCl_2 + Ph_2SnCl_2 \qquad \text{(Ref. 18)}$$

$$SeBr_4 + 3\,Ph_2Hg \longrightarrow Ph_2Se + 3\,PhHgBr + PhBr \qquad \text{(Ref. 19)}$$
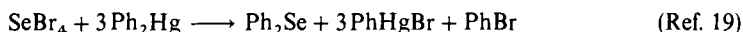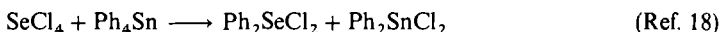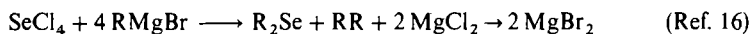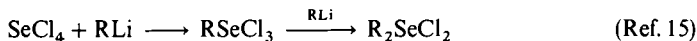
An alternative selenium(IV) compound is the dioxide; a neat example of its use involves a triorganyl hydroborate reagent[20]:

$$SeO_2\,(\text{suspension}) \xrightarrow[\text{THF}]{R_3BH^-} R_2Se$$
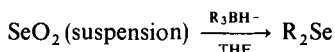
$$R = \text{allyl}$$

Selenium tetrachloride may also react directly with some organic compounds. Arylselenium compounds result from the direct reaction of $SeCl_4$ with those aromatic compounds which are activated to electrophilic attack, e.g.[21]

$$2\,EtOC_6H_5 + SeCl_4 \xrightarrow{CHCl_3} (p\text{-}EtOC_6H_4)_2SeCl_2 + 2\,HCl$$
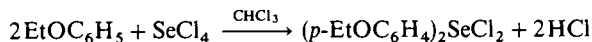
Carbon—carbon double bonds are also susceptible to attack; selenium tetrachloride adds across the bond to give a 2-chloroalkylselenium trichloride, which may then react with further alkene to give bis(2-chloroalkyl)selenium dichloride[22].

In many of the reactions illustrated above the product is a diorganylselenium dihalide which must be reduced to the selenide. A variety of reducing agents may be used but aqueous $Na_2S_2O_5$ and hydrazine are currently among the most popular, e.g.

$$R_2SeCl_2 \xrightarrow[\text{H}_2\text{O}]{Na_2S_2O_5} R_2Se$$
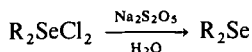
3. Selenium(II) compounds

The availability of organyl selenium compounds of the type RSeX (the tellurium analogues are much less convenient) make them all an excellent choice for the synthesis of unsymmetrical selenides. These compounds also play a prominent role in the application or organoselenium chemistry to organic synthesis[3,5,23]. The reactions of RSeX are illustrated for a variety of X groups; examples are taken from the more recent literature, earlier examples being well documented[1].

$$F_3CCH = CH_2 + PhSeCl \xrightarrow{-HCl} F_3CCH = CHSePh \xrightarrow{BuLi} PhSeBu \text{ (Ref. 26)}$$

$$RCH = CH_2 + PhSeBr \longrightarrow PhSeCHRCH_2Br \qquad \text{(Ref. 27)}$$
$$\text{(kinetic control)}$$

$$(R = C_1–C_4 \text{ alkyl}) \qquad RCHBrCH_2SePh$$
$$\text{(thermodynamic control)}$$

X = SiMe$_3$:

$$+ \text{ PhSeSiMe}_3 \xrightarrow{ZnI_2} PhSe(CH_2)_nCOOH$$

X = H:

$$2 \text{ RSeH } + \text{ Cu}_2\text{O} \longrightarrow 2 \text{ RSeCu } + \text{ H}_2\text{O}$$

$$\downarrow 2 \text{ R'I}$$

$$2 \text{ RR'Se } + \text{ Cu}_2\text{I}_2$$

X = CN:

$$RCH_2OH + ArSeCN \xrightarrow[Bu_3P]{THF \text{ or } Py} (Ar)(RCH_2)Se$$
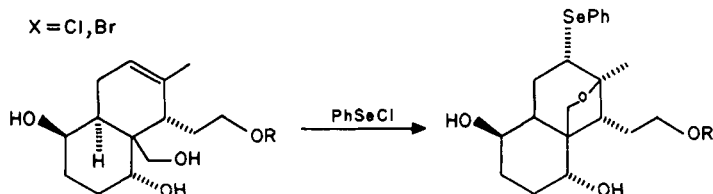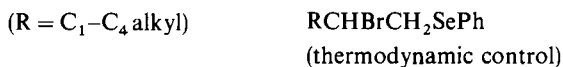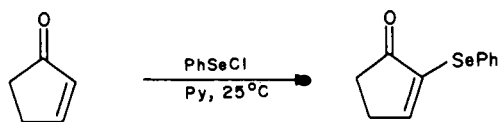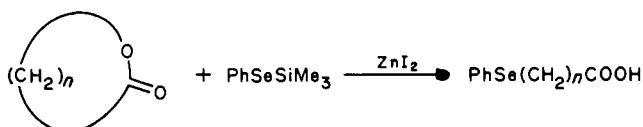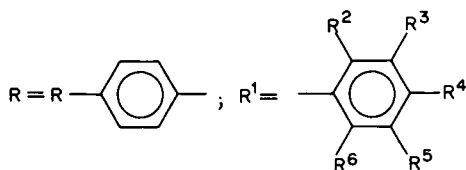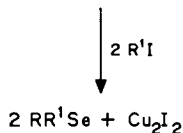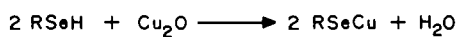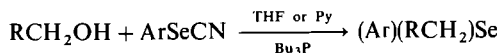
e.g. 1-dodecanol reacts with o-NO$_2$C$_6$H$_4$SeCN to give 94% selenide[30].

Organylselenium(II) halides will react with unsaturated organic molecules, e.g. Kataev and coworkers[31,32] employed this reaction for the synthesis of vinyl selenides:

$$p\text{-RC}_6H_4SeCl + C_2H_4 \longrightarrow p\text{-RC}_6H_4SeCH_2CH_2Cl$$

$$\xrightarrow[(Me_3COK)]{-HCl} p\text{-RC}_6H_4Se(CH = CH_2)$$
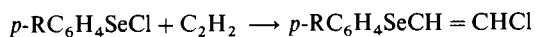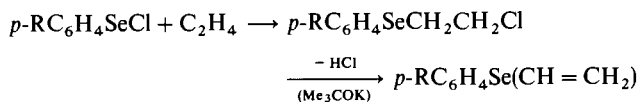
$$p\text{-RC}_6H_4SeCl + C_2H_2 \longrightarrow p\text{-RC}_6H_4SeCH = CHCl$$
$$R = MeO, Me, Cl, Br$$

4. Organyl selenides, RSe$^-$

These useful reagents may be prepared by reduction of diselenides, R_2Se_2, or of organylselenium(II) compounds, RSeX. They are good nucleophiles and will react with organic halides R'X to provide a convenient route to unsymmetrical selenides, RR'Se. An example of this reaction type which affords a potentially terdentate selenium ligand is[33]

$$(BrCH_2CH_2)_2Se + 2PhSe^- \longrightarrow (PhSeCH_2CH_2)_2Se$$
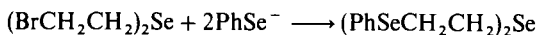
An interesting synthesis of unsymmetrical selenides from primary, secondary or tertiary amines with PhSe$^-$ over a ruthenium catalyst ($RuCl_3/K$) was recently reported[34], e.g.

$$R^1R^2R^3N + PhSeNa \xrightarrow[\text{2. H}_2\text{O}]{\text{1. Ru, diglyme, Ar}} R^1PhSe + R^2R^3NH$$
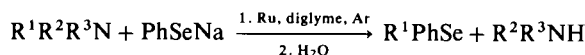
5. Selenides from diselenides

Some diselenides are photochemically unstable with respect to elimination of selenium, but these reactions will be dealt with in Section IV.D. Heating diselenides with Raney nickel is a standard method of conversion to selenide[35]. Diorganyl mercury compounds have also been used to convert diselenide to selenide, this route being useful for unsymmetrical selenides[36]:

$$Ph_2Se_2 + Bu_2Hg \xrightarrow[\text{reflux}]{\text{dioxane}} 2PhSeBu + Hg$$
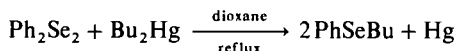
Mitchell[37] has prepared 2, 3, 12, 13-tetraselena(4, 4)metacyclophane in 8% yield using the following reaction and has also demonstrated the conversion to a bis-selenide on treatment with tris(diethylamino)phosphine:
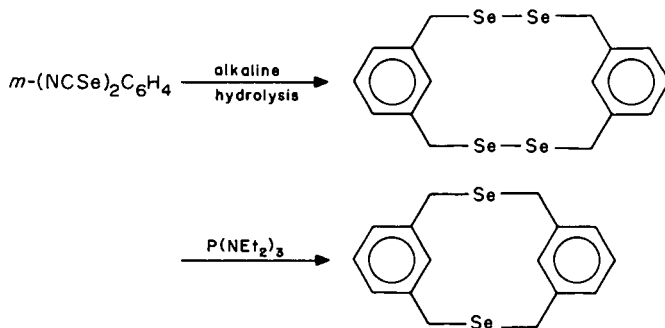
Diselenides may also provide a useful synthetic route to cyclic selenides[38], e.g.
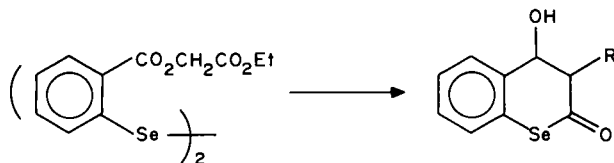
6. Miscellaneous

The above reactions represent the major synthetic pathways to selenides, but many other reactions of interest are in the literature. The following are almost random examples.

An attempted Wittig reaction of selenophosphoranes with ketones resulted in a general method for the synthesis of unsymmetrical selenides[39], e.g.
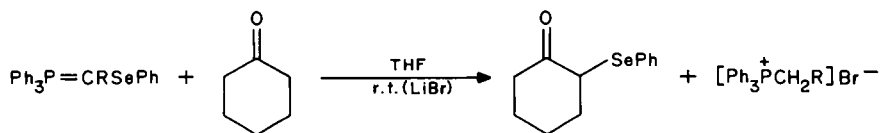
The mechanism of the reaction is believed to be as follows:
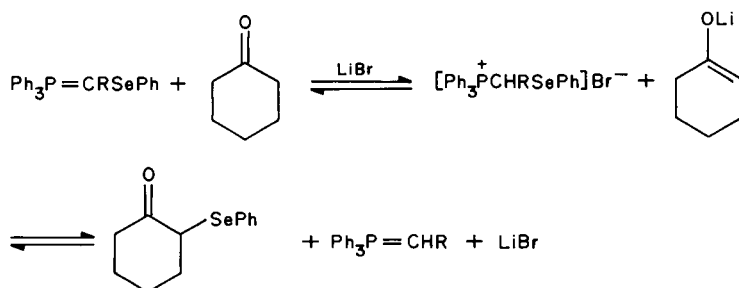
Polyselenides will react with halogens such as bromine in a complex reaction to give monomeric selenides[40], e.g.

$$(CH_2CHSe)_n + Br_2 \longrightarrow (BrCH_2)_2Se \xrightarrow[\text{excess}]{Br_2} (BrCH_2)_2SeBr_2$$
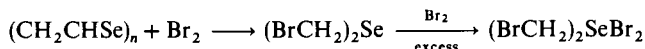
Selenium, $SeBr_4$ and dibromomethane are also formed in the reaction.

B. Symmetrical , Unsymmetrical and Cyclic Diselenides; Triselenides

Diselenides are the selenium analogues of the organic peroxides. They are yellow to orange–red in colour and, unless constrained in a small ring, are structurally analogous to hydrogen peroxide (see Section III). They are interesting compounds in their own right and are, as illustrated in Section II.A.5 above, useful synthetic intermediates in the synthesis of other organoselenium compounds.

1. Symmetrical diselenides

Standard methods of synthesis may be found in Ref. 1. Elemental selenium is a useful starting material since reduction with either sodium or rongalite ($HOCH_2OSO_2Na$) can give Se_2^{2-}, which can then react with various organic reagents to give the diselenide. Specific examples follow:

$$Na_2Se_2 + 2\,MeX \longrightarrow Me_2Se_2 + 2\,NaX \qquad \text{(Ref. 41)}$$
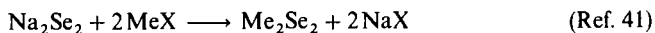
The diselenide may be formed in liquid ammonia solution using sodium as reductant or it may be prepared in aqueous solution using rongalite. The recent introduction of DMF as a convenient medium for the reaction of sodium and selenium[12] should greatly increase the utility of this reaction. Although it is generally true that aromatic halides will react with Se_2^{2-} only when activated by a nitro-group[42], there are exceptions when the Se^{2-}/DMF reagent is used as the following sequence illustrates[43].

+ 2 NaCl
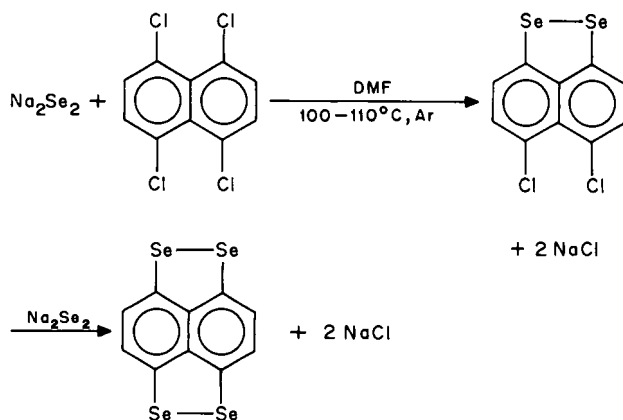
The reagent may also be used to give polymeric diselenides[44], thus:
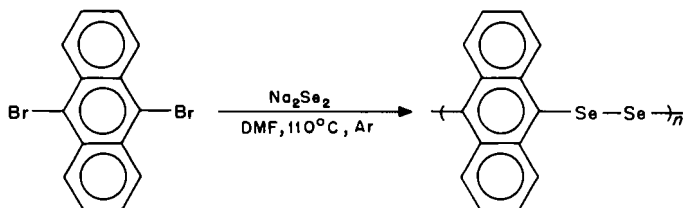
However, diazonium salts may be considered more standard reagents for the synthesis of diaryl diselenides, e.g.[45]

$$2R\overset{+}{N}_2Cl^- + Na_2Se_2 \longrightarrow R_2Se_2 + N_2 + 2NaCl$$
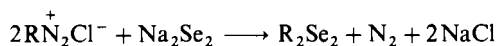
R = 2- and 4-carboxyphenyl

Two other inorganic selenium reagents that may be used for the synthesis of diselenides are Se_2Cl_2 and H_2Se. Diselenium dichloride will react with unsaturated organic compounds, e.g. alkynes[46]:

R = Et, CH_2OMe, CH_2Cl

20–42%
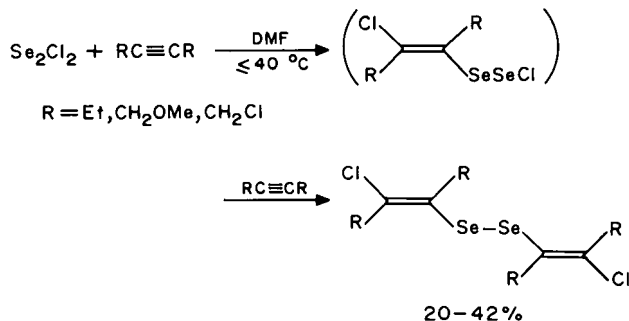
Complications may arise if phenylacetylenes, $PhC{\equiv}CR$, are used in that anything up to a 41% yield of a benzoselenophene may be obtained, viz.:
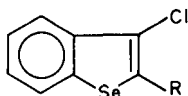
Aldehydes will react with H_2Se under reducing conditions to give diselenides[47], e.g.

$$ArCHO + H_2Se \xrightarrow[\text{2. NaBH}_4]{\text{1. base}} (ArOH_2\text{-}Se)_2$$

$$92\%$$
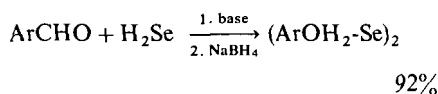
$$Ar = 1\text{-naphthyl}$$

Organic selenium compounds may also be used as precursors for diselenides. For example, the hydrolysis of organyl selenocyanates gives diorganyl diselenides[48] (see also Section II.A.5):

$$2\,RSeCN \xrightarrow[\text{H}_2\text{O or EtOH}]{\text{NaOH}} R_2Se_2$$
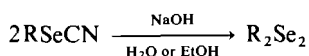
Grignard reagents are useful since selenium will insert into the C—Mg bond; hydrolysis of the reagent followed by oxidation with dioxygen then gives the diselenide, e.g.[49]

$$p\text{-ClC}_6\text{H}_4\text{MgBr} + Se \longrightarrow p\text{-ClC}_6\text{H}_4\text{SeMgBr} \xrightarrow[\text{2. O}_2]{\text{1. H}_2\text{O}} (p\text{-CLC}_6\text{H}_4)_2Se_2$$
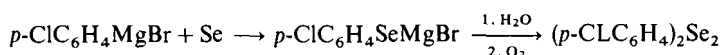
A variation on this theme, but involving organolithium compounds, has recently been claimed to give yields and purity for diselenides which are superior to other methods[50]:

$$RLi + Se \longrightarrow RSeLi \xrightarrow{\text{Me}_2\text{NC(S)Cl}} Me_2NC(S)SeR \xrightarrow[\text{Fe(CN)}_6{}^{3-}]{\text{OH}^-} R_2Se_2$$
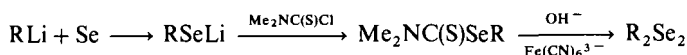
$$R = \text{aryl or heteroaryl}$$

The intermediate is readily crystallized and purified. Other workers[51] have also used an intermediate with a selenium—sulphur bond, e.g.
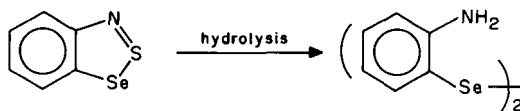
2. Unsymmetrical diselenides

Few compounds have been isolated, but the greater stability of RSeX and RSeH than their tellurium counterparts do provide synthetic pathways to unsymmetrical diselenides which are not available for ditellurides. The reaction generally used is[42,52]

$$RSeX + R^1SeH \longrightarrow RSeSeR^1 + HX$$

$$X = \text{halide, CN}$$
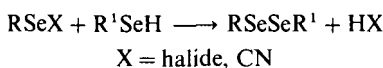
3. Cyclic diselenides

Naphtho[1,8-cd:4,5-c^1d^1]bis-1,2-diselenole has been considered in Section II.B.1, but there has been growing interest recently in cyclic diselenides and this has led to the publication of several papers describing their synthesis. *Peri*-bridged naphthalenes

were the first of their class to be reported. They were prepared by the reaction of 1,8-dilithionaphthalene with selenium[53].

An interesting cyclic diselenide arose as a by-product from a reaction designed to produce a new tetraselenafulvalene derivative[54]:
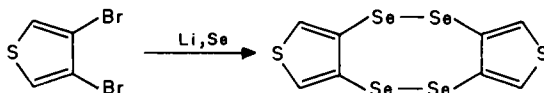
4. Triselenides and tetraselenides

Diethyl triselenide has been reported[42] and a number of aromatic triselenides are known[55]. A general method of preparation is

$$2RSeSeCN + 2EtSH \longrightarrow 2HCN + Se + Et_2S_2 + R_2Se_3$$

$$R = p\text{-}XC_6H_4, \text{ where } X = H, Me, Cl, Br, MeO, NO_2$$
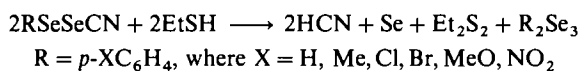
Other earlier examples will be found in Ref. 1. Foss and Janickis[56] heated piperidine or morpholine with selenium powder in the presence or red lead. The morpholine reaction gave di-, tri- and tetra-selenium dimorpholine whereas the piperidine gave the tetra-selenium compound.

A search for novel materials with high electrical conductivity led to an unexpected triselenide isolated as a complex with benzonitrile[57]:
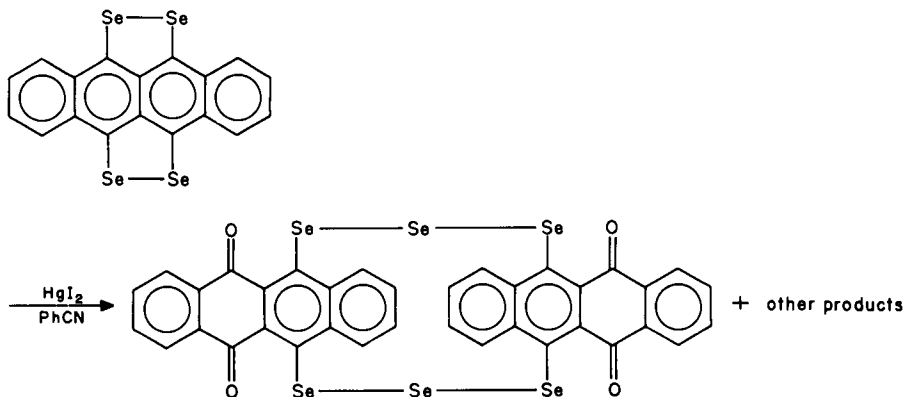
Another novel example of a triselenide based on ferrocene has been reported[58], namely
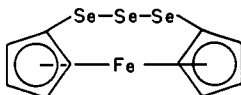
C. Symmetrical and Unsymmetrical Tellurides

Methods broadly similar to those used for diorganyl selenides may be used to synthesis diorganyl tellurides, but the sections are separated in this chapter for greater ease of reference. Some options available in selenium chemistry may be less convenient in tellurium chemistry. For example, organyl tellurenyl compounds, RTeX, are less

convenient than their Se analogues. Some may be prepared by careful addition of 1 mol of halogen to 1 mol of ditelluride (e.g. PhTeI, p-PhC$_6$H$_4$TeBr[59]), but the reaction is not general since RTeX tends to disproportionate to Te and R$_2$TeX$_2$. The isolation of stable, well defined examples of RTeX usually requires the presence of a coordinating group in the molecule, e.g. **2**[60].

(2)
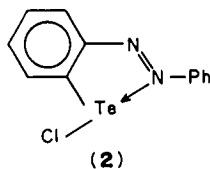
Thus, although the earlier literature contains several references to the use of 'TeX$_2$' (X = Cl, Br) as starting materials for the synthesis of R$_2$Te, it is now unusual for tellurium(II) compounds to be selected as the precursors of choice.

1. Elemental tellurium

Elemental tellurium is now a common starting material in organotellurium chemistry, particularly for the synthesis of more sophisticated tellurides. It may be used in one of two reaction types: prior reduction to telluride or insertion into a carbon—metal or carbon—halogen bond (see Section II.C).

The first organyl tellurium compound to be reported, Et$_2$Te, was prepared by reaction of potassium telluride with ethyl sulphate[61]; the telluride was prepared by an inconvenient route (Te + potassium hydrogen D-tartrate at red heat), but as Irgolic[2] suggests, another early use of a binary metal telluride by Natta[62] could repay further investigation and exploitation:

$$3Te + 2Al \longrightarrow Al_2Te_3 \xrightarrow[\text{ROH or R}_2\text{O}]{250-300\,°C} R_2Te$$
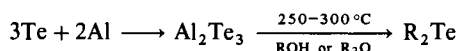
Usually the telluride is prepared *in situ* by reduction of elemental tellurium in aqueous on non-aqueous media. An example is[63]

$$Te + HOCH_2OSO_2Na \xrightarrow[\substack{\text{air-free} \\ 70-80\,°C}]{10\%\,\text{NaOH}} Na_2Te \xrightarrow{\text{PhCH}_2\text{Cl}} (PhCH_2)_2Te$$

('rongalite')
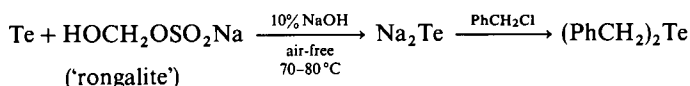
A recent variation[64,65] of this reaction has employed SnCl$_2$ as reducing agent: (the method will also work for selenium; thus divinylselenide may be prepared at ambient pressure[66]).

$$2\,CH_2 = CH_2 + Te \xrightarrow[\text{90-120}\,°C/10-15\,\text{atm}]{\text{SnCl}_2,\text{OH}^-/\text{H}_2\text{O}} (CH_2 = CH)_2Te$$
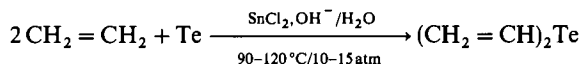
The reduction of tellurium in liquid ammonia is conveniently carried out with metallic sodium. The Na$_2$Te formed will react readily with aliphatic halides, e.g.[67]

$$2\,EtBr + Na_2Te \xrightarrow{\text{NH}_3} Et_2Te$$

80%
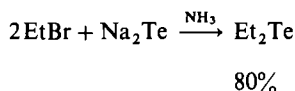
The recent exploitation of dipolar aprotic solvents such as DMF as a medium for the synthesis of sodium selenide is no less successful for the synthesis of sodium telluride from

the elements[12], e.g.

$$p\text{-}IC_6H_4I + Na_2Te \xrightarrow[110-120\,°C]{DMF} (\,C_6H_4Te\,)_n$$

(the product contains some residual iodine, the quantity suggesting a molecular weight of around 8000 for the poly-p-phenylenetelluride[14]).

Elemental tellurium will insert into some metal—carbon bonds. The most important examples involve Grignard and organolithium reagents. Recent examples of importance include the first synthesis of tetratellurafulvalene derivatives[68,69]. Although, in principle, those examples should be excluded by the constraints of the Introduction to this chapter, an exception will be made since the following 'one-pot' synthesis[69] elegantly illustrates the use of the RTeLi reagent:

The lithium reagent is also valuable for the synthesis of unsymmetrical tellurides, e.g.[70]

$$PhLi \xrightarrow{Te} PhTeLi \xrightarrow{RX} PhTeR + LiX$$

$$\downarrow CH_2I_2$$

$$PhTeCH_2TePh$$

also[71]

2. Organyl tellurides, RTe⁻

Clearly, the reactions of organolithium reagents given above proceed via the *in situ* synthesis of RTe⁻, hence Sections II.c.1 and II.c.2 overlap. A frequently used alternative synthesis of RTe⁻ is by the alkaline sodium borohydride reduction of diorganylditellurides, a route that is particularly attractive for aryl compounds. The following is a recent example of the use of the method to form a series of bis-tellurides[72,73]:

$$R_2Te_2 \xrightarrow[EtOH/C_6H_6]{NaBH_4/OH^-} NaTeR \xrightarrow{(CH_2)_nBr_2} RTe(CH_2)_nTeR$$

$$R = p\text{-}EtOC_6H_4 \qquad\qquad n = 1, 5, 6, 7, 9, 10$$

For $n = 1$, if the organic dihalide (CH_2Br_2 or CH_2I_2) is in excess, a charge-transfer complex is isolated, i.e. $(RTe)_2CH_2\cdot X_2CH_2$. When $n = 2$, the bis-telluride is unstable with respect to

elimination of ditelluride; however, this does provide a general reaction for the conversion of organic 1,2-dihalides to alkenes. When $n = 3$ or 4, internal quaternarization giving a telluronium salt is more rapid that nucleophilic attack by RTe^- on the second C—Br bond, e.g.

$$Br(CH_2)_4Br \xrightarrow{RTe^-} RTe(CH_2)_4Br \xrightarrow{fast}$$ Br^-
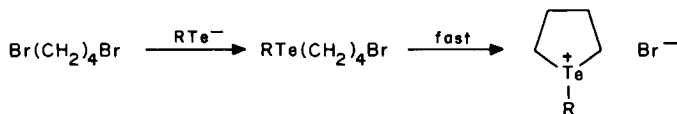
For the single case of $n = 5$, experimental conditions may be manipulated to prepare either the bis-telluride or the telluronium salt.

The reactions of RTe^- are not restricted to organic halogen substrates. Thus, for example, NaTeR (R = Ph, p-MeC$_6$H$_4$) will react with a range of carboxyl-substituted alkynes to give the expected products arising from nucleophilic attack at the β-carbon atom[74], e.g.

$$RTeNa + PhC{\equiv}CCOPh \xrightarrow{EtOH} RTeC(Ph) = CHCOPH$$

$$R = Ph, \text{p-MeC}_6H_4$$
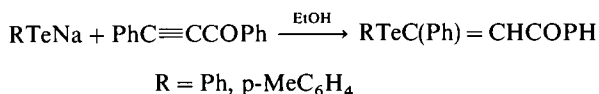
Although sodium borohydride is the commonly used reducing agent to prepare RTe^- from a diorganyl ditelluride, others such as lithium aluminium hydride may be used. An example is[75]

$$(RC_6H_4)_2Te_2 \xrightarrow[Et_2O, Ar]{LiAlH_4} LiTeC_6H_4R \xrightarrow[UV]{C_3F_7I} RC_6H_4TeC_3F_7$$

$$(R = H, \text{p-F}, \text{p-Br}, \text{m-F})$$
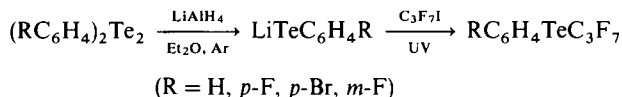
3. Tellurium(II) compounds

Following the reported synthesis of PhTeI[59], the compound has been used in conjunction with vinyl and alkynyl Grignard reagents to prepare unsymmetrical vinyl and alkynylaryl tellurides[76]:

$$CH_2 = CHMgCl + PhTeI \xrightarrow[-10\,°C]{THF} CH_2 = CHTePh$$

$$CH{\equiv}CMgBr + PhTeI \xrightarrow[r.t.]{THF} CH{\equiv}CTePh$$
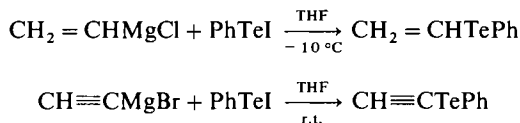
4. Tellurium(IV) compounds

Tellurium tetrachloride is the most common reagent. It may be prepared from the elements[77] or obtained commercially as such. It may be prepared in situ by reacting chlorine with a suspension of tellurium in refluxing tetrachloroethane[78]. The compound has electrophilic character and will react with aromatic compounds activated to electrophilic attack[79], e.g.

$$p\text{-EtOC}_6H_5 \xrightarrow[CHCl_3]{TeCl_4} (p\text{-EtOC}_6H_4)TeCl_3 \xrightarrow[neat]{p\text{-EtOC}_6H_5} (p\text{-EtOC}_6H_4)_2TeCl_2$$

$$\xrightarrow[\text{e.g. Na}_2S.9H_2O]{Reduce} (p\text{-EtOC}_6H_4)_2Te$$
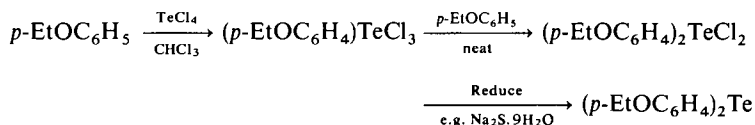
The reaction is more sluggish than in the selenium case and more forcing conditions must be used to obtain the diorganyl tellurium dihalide. However, the fact that the reaction may be stopped at the trihalide stage does mean that it has utility in the synthesis of unsymmetrical tellurides either by changing the organic substrate in the second stage or, alternatively, reacting another trihalide with an appropriately activated aromatic compound, in general:

$$RTeCl_3 + R^1H \longrightarrow RR^1TeCl_2 \xrightarrow{reduce} RR^1Te$$

where R^1 may be, for example, $p\text{-}EtOC_6H_4$

A wide range of reducing agents will convert diorganyltellurium dihalides to diorganyl tellurides. Very frequently used are $Na_2S \cdot 9H_2O$, $Na_2S_2O_5$ and hydrazine hydrate. Also used from time to time have been $LiAlH_4$, $SnCl_2$, Zn and $Na_2S_2O_3$.

In some cases condensation of $TeCl_4$ with aromatic compounds gives cyclic products. A well known example for which no mechanistic studies appear to have been made is[80]
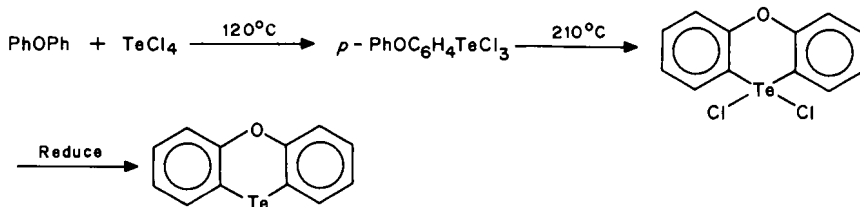
The generality of the reaction of $TeCl_4$ with aromatic compounds has been extended by using Lewis acid promoters such as aluminium trichloride[81]:

$$2C_6H_6 + TeCl_4 \xrightarrow{AlCl_3(3\ parts)} Ph_2TeCl_2 \xrightarrow{reduce} Ph_2Te$$
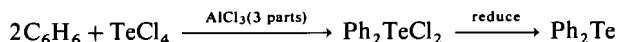
Methylene groups adjacent to carbonyl functions are also susceptible to direct attack, e.g.[82]

$$PyH^+PhTeCl_4^- + Me_2CO \longrightarrow Ph(MeCOCH_2)TeCl_2 + PyH^+Cl^- + HCl$$
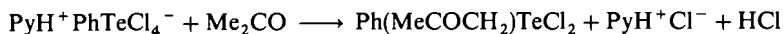
The dihalide may be reduced to an unsymmetrical telluride.

Transmetallation reactions with tellurium tetrachloride are commonly used. The classic examples involve the use of Grignard, organolithium or organomercury reagents. Tellurium tetrachloride will, for example, react with phenylmagnesium bromide as follows[83,84]:

$$TeCl_4 + 4PhMgBr \longrightarrow Ph_2Te + Ph_2 + 4MgBr$$
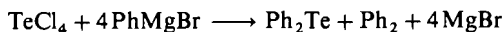
The reaction is convenient but is inefficient in terms of moles of reagent consumed. There has been speculation that it proceeds via a tetraorganyl tellurium compound. It is certainly known that methylmagnesium bromide will reduce diaryltellurium dichlorides to diaryl tellurides with the evolution of ethane, which presumably is formed by the decomposition of Ar_2TeMe_2[85].

Organylmercury(II) halides are valuable for the synthesis of unsymmetrical (usually aryl) tellurides; the following is typical[86]:

$$RTeCl_3 + R^1HgCl \xrightarrow[reflux]{dioxane} RR^1TeCl_2 \xrightarrow[90-95\ °C]{Na_2S \cdot 9H_2O} RR^1Te$$
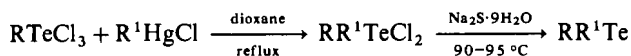
Organotin[18] and organolead[87] compounds may also be employed to transfer organic

groups to $TeCl_4$, in general

$$R_4M + TeCl_4 \longrightarrow R_2MCl_2 + R_2TeCl_2 \xrightarrow{\text{reduce}} R_2Te$$
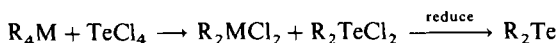
(M = Sn, Pb)

Other processes exist in which tellurium(IV) compounds occur as isolated intermediates, although the actual starting material is elemental tellurium. The method is valuable for the synthesis of cyclic tellurides[88]:
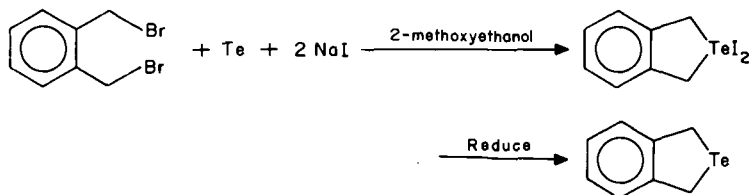
However, in some cases the method can succeed with monofunctional organic halides, for example with cetyl chloride $(C_{16}H_{33}Cl)$[89]:

$$2C_{16}H_{33}Cl + Te + 2NaI \longrightarrow (C_{16}H_{33})_2TeI_2 \xrightarrow{Na_2S \cdot 9H_2O} (C_{16}H_{33})_2Te$$
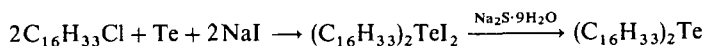
5. Miscellaneous

A very large number of reactions can yield tellurides. Those listed above are the most generally useful but in this section some examples are quoted of more recent reports using novel reagents or new conditions.

Aliphatic diazo compounds may be used both for initial synthesis and for the modification of an existing telluride. The following examples illustrate these points:

$$Ph_2Te_2 + CH_2N_2 \longrightarrow N_2 + (PhTe)_2CH_2 \qquad \text{(Ref. 70)}$$

(E = Se, Te)   (Ref. 90)
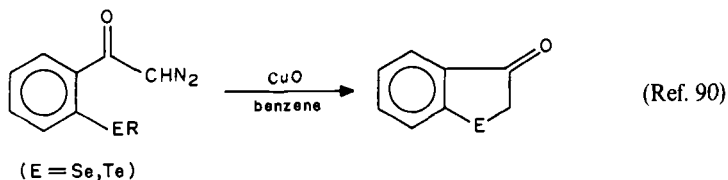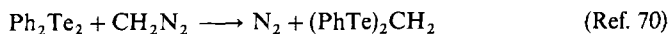
Diazonium salts are useful in the aryl series. For example, reaction of aryldiazonium tetrafluoroborates with ditellurides using 18-crown-6 as a phase-transfer catalyst provides a convenient route to aryl alkyl tellurides[91], e.g.

25%
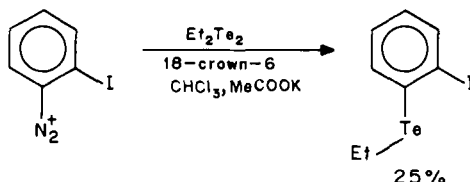
The same diazonium salts react with potassium tellurocyanate at room temperature to give symmetric tellurides[92].:
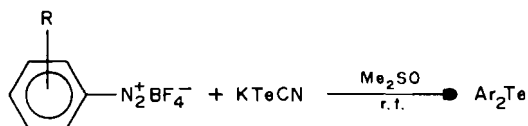
Organic tellurocyanates [which could also be seen as organyltellurium(II) cyanides, RTeCN] react with organolithium reagents as follows[93], e.g.:
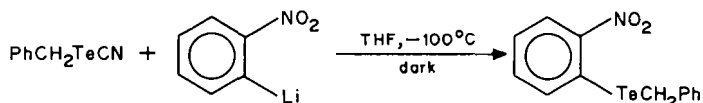
Many reactive species may be generated in radiofrequency plasmas and such systems are finding increasing use in synthetic chemistry. They are particularly attractive for the synthesis of perfluoro compounds such as $(CF_3)_2Te$[94], but the method is general for the synthesis of metal alkyls (including tellurium). The reactive radicals are co-condensed with metal vapour on a cold finger at $-196\,°C$[95]. The products often include ditellurides.

Tellurium dioxide has been little used as a source of tellurium in the synthesis of tellurides. Bergman and Engman[96] have used their valuable TeO_2–glacial acetic acid – lithium halide reagent to produce aryl alkyl tellurides by the following sequence of reactions:
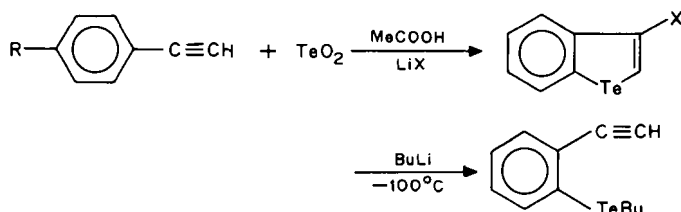
The same workers[97] have also developed a neat variation on the reduction of tellurium (the reaction will also work for selenium). Thus tetraalkylammonium borohydrides will react with tellurium in a toluene medium to give dialkyl tellurides:

$$2R_4N^+BH_4{}^- + Te \xrightarrow{\text{toluene}} R_2Te + H_2 + 2R_3NBH_3$$
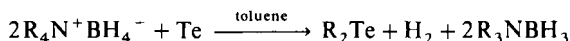
D. Diorganyl Ditellurides and Related Compounds

Like diselenides, the diorganylditellurides are strongly coloured, usually orange–red or deep red. To date no pure unsymmetrical ditelluride has been isolated although their existence in solution is now well documented (see Section V.A). The lower molecular weight dialkyl ditellurides (and for that matter the corresponding dialkyl tellurides) are foul-smelling materials, but in contrast the diaryl ditellurides are odourless crystalline solids.

1. Syntheses based on tellurium

Two major routes to symmetrical ditellurides are based on tellurium as starting material. In the first, prior reduction to the ditelluride anion, $Te_2{}^{2-}$, is required. This may

be achieved in aqueous alkaline medium by treating tellurium with rongalite[98] followed by an organic halide. Alternatively, the reaction could be carried out in liquid ammonia using sodium as reducing agent, e.g.[99]

$$2\,Te + 2\,Na + 2\,MeI \xrightarrow{\;NH_3(l)\;} Me_2Te_2$$

However, the recently developed method using solvents such as DMF is the preferred route, e.g.[44]
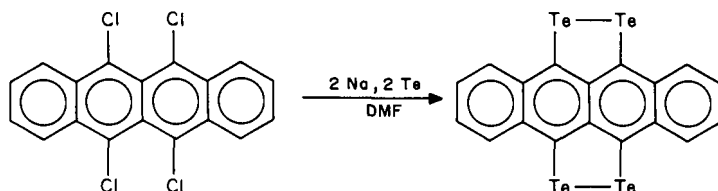
The other major route based on elemental tellurium involves insertion of a Te atom into a C—Mg or C—Li, followed by oxidation with dioxygen. In the case of the Grignard route, the method is applicable only in the aromatic series[100], e.g.

$$PhMgBr + Te \longrightarrow PhTeMgBr \xrightarrow{\;O_2\;} Ph_2Te_2 \quad (80\%)$$

The organolithium route is identical and a recent application offered a simple preparation of the sterically crowded di[2,4,6-tri(tert-butyl)phenyl] telluride[101]:
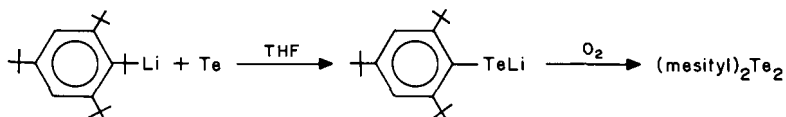
2. Syntheses based on tellurium(II) compounds

Although tellurium(II) compounds are almost certainly intermediates in the reduction of organyl tellurium(IV) trihalides (see Section II.D.3), they are of little practical importance for the synthesis of ditellurides. One of the few examples in the literature involves the preparation of di(2-naphthyl) ditelluride by the alkaline hydrolysis of 2-naphthyltellurium(II) iodide or alternatively by reacting the iodide with triethylamine or with triisopropyl phosphite[102].

3. Syntheses based on tellurium(IV) compounds

The reaction of an organyl tellurium(IV) trihalide with a wide variety of reducing agents will give good yields of ditelluride (e.g. $Na_2S\cdot9H_2O$, $Na_2S_2O_5$ and N_2H_4 are commonly used. With a suitable choice of organic groups, intermediate stages in the reduction may be identified, e.g. the reduction of (phenylazophenyl-C,N^1)tellurium(IV) trichloride[60,103]:

If sodium borohydride is selected rather than hydrazine as the reducing agent, the azo linkage is reduced and di(o-aminophenyl) ditelluride results[60], illustrating the possibility of modifying the organic group without destroying the Te—Te linkage.

The two variations on this route involve selection of reducing agent and choice of synthesis for the organyl tellurium(IV) trihalide. Organomercury halides react with tellurium tetrahalides to give the RTeX₃ compounds, a route favoured in at least one early classic paper on diorganyl ditelluride chemistry[104].

Morgan and Drew[105] reported the synthesis of CH_2Te_2 in poor yield. It was obtained by the potassium disulphite reduction of bis(trichlorotelluro)methane, $(Cl_3Te)_2CH_2$, which, in its turn, was a product of the reaction of acetic anhydride with tellurium tetrachloride. The reaction was recently reinvestigated[106] and it was argued that the following sequence of steps occurred:

$$Ac_2O + 2TeCl_4 \longrightarrow (Cl_3TeCH_2CO)_2O + 2HCl$$

$$(Cl_3TeCH_2CO)_2O + TeCl_4 \longrightarrow Cl_3TeCH_2COTeCl_3 + ClCOCH_2TeCl_3$$

$$\Big| -CO_2$$

$$Cl_3TeCH_2TeCl_3$$

Hence, by use of the stoichiometric ratio of $Ac_2O + 3TeCl_4$, a 50% yield of the bis(trichlorotelluro)methane was obtained that could be reduced to CH_2Te_2, which is a red powder when initially prepared but which converts to a grey solid.

4. Polytellurides

The tendency to form oligomeric E_n chains declines in the order S > Se ≫ Te. A salt containing the tritelluride anion, Te_3^{2-}, has been structurally characterized[107]. Thus the compound (4, 7, 13, 16, 21, 24-hexaoxa-1, 10-diazobicyclo[8.8.8]hexacosane)potassium tritelluride, ethylenediamine containing a cryptate complexed potassium ion and ethylenediamine of crystallization contains Te_3^{2-} anions with Te—Te 2.692 and 2.720 Å with TeT̂eTe = 113.1°, but no organyl tritellurides appear to have been reported in the literature. Very recently, in the author's laboratory[108], in the reduction of (phenyl-2-pyridyl-C, N¹)tellurium(IV) tribromide, a reaction in which some elemental tellurium was released, a product analysing as 2-pyC_6H_4TeTeTeC_6H_4py-2 was isolated. The material has been crystallographically characterized*.

Mixed selenium and tellurium trichalcogenides are known; a recent example of such a compound is[109]

III. STRUCTURE

A brief survey of relevant X-ray crystallographic investigations of diselenides, ditellurides, selenides, and tellurides is given in this section. In the case of some lower alkyl derivatives, techniques such as electron diffraction and microwave spectroscopy have been successfully applied to give structural data for the vapour phase.

*$[(Me_3Si)_3C]_2Te_3$ has now been reported[108a].

A. Selenides

Simple VSEPR[110] considerations for Se[II] (and Te[II]) predict non-linear structures for selenides (and tellurides) and, indeed, this is confirmed by the available structural data. Estimates of the Se—C single bond length vary slightly depending on the choice of covalent radii. Thus the commonly quoted Pauling values[111] suggest 1.93 Å, whereas estimates due to Van Vechten and Phillips[112] predict 1.999 Å for bonding to sp^3 carbon (strictly, the selenium radius is 'tetrahedral', but with two spare pairs this may not be an unreasonable estimate). Small differences (0.03 Å) may be expected between E—alkyl and E—aryl (E = Se, Te). Some representative data for selenides are given in Table 1. It is noted that Se—C varies from 1.916 to 1.97 Å (but phase differences are involved, so no great significance can be deduced from the differences). Bond angles, CŜeC, vary more and may be determined by repulsive forces [cf. 96.2° for Me$_2$Se and 104.4° for (CF$_3$)$_2$Se]. The observed angles are between the extremes expected for bonding involving pure selenium p orbitals (90°) and sp^3 hybridization with strongly directed lone pairs. It must be concluded that significant s character is included in the selenium bonding orbitals. When selenium is constrained in a ring structure, C$_3$H$_7$NSeBr (Table 1) for example, understandably the CŜeC angle is much reduced, to 86° in this case; yet in the complex of diiodine with selenacyclopentane the CŜeC angle is 94°, which is comparable to values in non-cyclic selenides.

B. Di- and Poly-selenides

Diselenides (and ditellurides), when the Se—Se linkage is not constrained within a ring structure, have the 'hydrogen peroxide' structure, the dihedral angle (θ, Figure 1) varying between 75° and 82°. Attempts have been made to calculate rotational barriers in Me$_2$Se$_2$[118]. It is generally accepted that torsional barriers are greater for the cis ($\theta = 0°$) configuration than for the trans ($\theta = 180°$) configuration, and indeed calculations indicated differences of the order of 28 kJ mol^{-1}.

Estimates of the Se—Se bond length based on Pauling covalent radii[111] suggest values around 2.32 Å, a figure in reasonable agreement with data in Table 2. It is possible that the Se—Se linkage is part of a ring structure. If the ring is sufficiently large and flexible, e.g. 13, 13-dimethyl-8, 13-dihydro-5H-dibenzo[d,g]-1, 2-diselena-6-silonine (3)[119], this

TABLE 1. Some structural data for selenides, R$_2$Se

Compound	Se—C (Å)	CŜeC (°)	Phase	Ref.
Me$_2$Se	1.943	96.2	g	113
(CF$_3$)$_2$Se	1.96	104.4	g	114
p-Tol$_2$Se	1.92, 1.93	106.2	s	115
C$_3$H$_7$N$_2$SeBr:	1.88, 1.99	86	s	116
	1.916	100.9	s	117
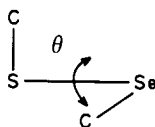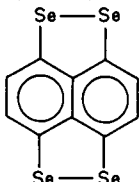
makes little difference to the geometry around selenium. However, if the system is much more constrained, e.g. 1,8:4,5-bis(diseleno)naphthalene[43], θ in Figure 1 is effectively zero and the observed Se—Se bond length is marginally longer at 2.364 Å than the sum of the Pauling covalent radii.
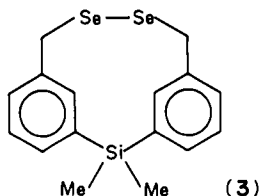
The structures of some tri- and tetra-selenides have been determined[56]. Thus pure tetraselenium dipiperidide and tri- and tetra-selenium dimorpholide have been structurally characterized. N—Se—Se—Se—Se—N and N—Se—Se—Se—N chains occur in extended helix rotational–isomeric forms; variations of Se—Se bond lengths occur along the chains. In triselenium dimorpholide an intermolecular contact of 3.404 Å occurs. Some data for di- and poly-selenides are given in Table 2.

TABLE 2. Some structural data for di- and poly-selenides, R_2Se_n

Compound	Se—C (Å)	Se—Se (Å)	$C\hat{S}eC$(°)	θ (°)[a]	Ref.
$(PhCH_2)_2Se_2$	1.97	2.285	100.1	82	120
Ph_2Se_2	1.93	2.29	105	82	121
$(p\text{-}ClC_6H_4)_2Se_2$	1.9	2.33	100	74.5	122
$(CF_3)_2Se_2$	1.93	2.34	103.5	—	114
3 (see text)	2.01	2.288	104.4	73.7	119
(naphthalene structure)	$\begin{cases}1.905\\1.915\end{cases}$	2.364	$\begin{cases}91.8\\91.3\end{cases}$	0	43
$(C_5H_{10}N)_2Se_4$ (dipiperidide)	1.832	2.328 2.346	107.2	88.6 76.3	56
$(C_4H_8ON)_2Se_4$ (dimorpholide)	1.836[b]	2.336 2.356	106.8	90.2 75	56
$(C_4H_8ON)_2Se_3$ (dimorpholide)	1.845[b]	2.346	109.0	94.6	56
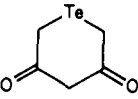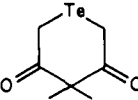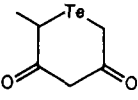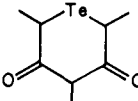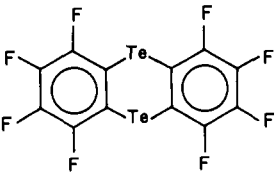
[a] θ, Dihedral angle (see Figure 1).
[b] Se—N.

C. Tellurides

Tellurides closely resemble selenides in the structural sense and some relevant information is given in Table 3. The sum of the Pauling[111] covalent radii for Te and C is 2.12 Å and most observed bond lengths are close to this estimate. Both inter- and intra-molecular interactions can be important, e.g. for 3,4-quinoxalino-1-telluracyclopentane (4)[123], Te···Te contacts of 3.998 Å are less than the sum of the Pauling estimates of Van der Waals radii (4.40 Å[111]); in contrast, the Te···N distances of 4.087 and 4.090 Å are too long to suggest any interaction.

(4)
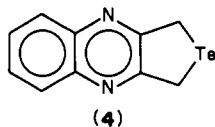
TABLE 3. Structural data for tellurides, R_2Te

Compound	Te—C(Å)	CT̂eC(°)	Ref.
p-Tol$_2$Te	2.05	101	126
	2.16	89.5	127, 128
	2.168	86.4	129
	2.202 2.157 (Te···Te = 4.042 Å)	88.4	130
	2.184 (Te···Te = 4.068 Å)	89.7	131
4 (see text)	2.145 2.123 (Te···Te = 3.998 Å)	80.7	123
5 (see text)	2.05	94	124
6 (see text)	2.08		125
	2.117 2.111	92.9	132

For 5^{124}, the unit cell contains two independent molecules with Te$\cdots$O contacts of 2.577 and 2.574 Å (Van der Waals distance 3.6 Å), giving a distorted three-fold coordination about tellurium. This situation is also observed in 6^{125}, with Te$\cdots$N contacts of 2.773 Å, well within the Van der Waals distance of 3.7 Å[111]. The tellurium atom in 5 and 6 therefore shows weak Lewis acidity.

(5)   (6)
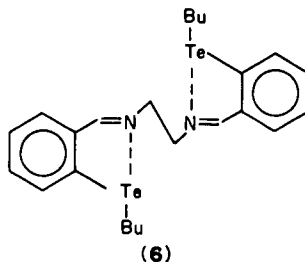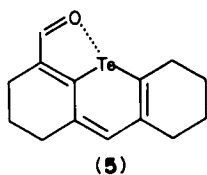
Another way in which tellurium in a telluride may extend its coordination number is by acting as a Lewis base. This is dealt with in another Section IV.E.

D. Ditellurides

Similar general comments apply to ditellurides as to diselenides. Thus a 'hydrogen peroxide' structure is the expected configuration unless the ditelluride linkage is constrained in a small ring. Dihedral angles often approach 90°, although a dipole moment study[133] suggests that significant variation of the angle may occur. Thus between 25 and 45 °C free rotation about the Te—Te bond in $(p\text{-BrC}_6\text{H}_4)_2\text{Te}_2$ and $(p\text{-CH}_3\text{C}_6\text{H}_4)_2\text{Te}_2$ may occur, but for Ph_2Te_2, $(p\text{-FC}_6\text{H}_4)_2\text{Te}_2$ and $(m\text{-FC}_6\text{H}_4)_2\text{Te}_2$ rigid dihedral angles of 89.7, 47.7 and 89.7°, respectively are calculated.

Intermolecular Te$\cdots$Te contacts are more important and frequent for ditellurides than for diselenides and sometimes they can be remarkably short. Thus contacts of 3.701 Å are seen for tetratelluratetracene[134] and for one of the polymorphs of bis(2-naphthyl)ditelluride, namely the 'cisoid' form, a Te$\cdots$Te contact of 3.707 Å is observed. In contrast, the other polymorph ('transoid') has no Te$\cdots$Te intermolecular contract less than 4.128 Å; the transoid structure is currently unique amongst the ditellurides.

Some representative structural data are given in Table 4.
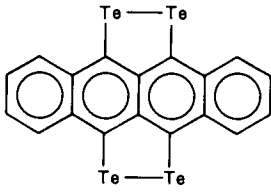
IV. REACTIONS

The general reactions of the heavier diorganyl chalcogenides and dichalcogenides have been very adequately summarized in previous reviews[4−6] and books[1−3]; there seems little point in duplicating that material in this chapter. Consequently, attention will be devoted to updating the surveys already available by concentrating on more recent contributions. This section is arranged to reflect areas of major current effort; thus much reaction chemistry of selenides and tellurides relates to their use in organic synthesis. Also, there are an increasing number of papers reporting on the photochemistry of the compounds; a further area of rapid growth is the ligand chemistry of the materials.

A. Diorganyl Selenides and Tellurides

This sub-section (and the following one) gathers together some recent work which is not readily classifiable under the major growth areas mentioned above.

TABLE 4. Structural data for ditellurides, R_2Te_2

Compound	Te—C(Å)	Te—Te(Å)	$\hat{\text{C}}$TeC(°)	θ(°)	Ref.
Ph_2Te_2	2.15	2.712	97.4	88	135
	2.08		100.3		
$(p\text{-}ClC_6H_4)_2Te_2$	2.16	2.702			122
$p\text{-}Tol_2Te_2$	2.13	2.697		85.7	136
$p\text{-}An_2Te_2$	2.14	2.72	$\begin{cases} 99.8 \\ 100.7 \end{cases}$	81.2	137
	2.114	2.673	87.5	0	134, 138
	2.111				

One theme detectable in recent publications is a growing interest in the mechanisms of the reactions of selenides and tellurides. Systematic kinetic studies remain scarce but will surely increase in number in the near future. Russian workers[139] have investigated the thermal decomposition of Me_2Te at 350 °C under static conditions. The products are CH_4, C and Te. It is considered that $(CH_2Te)_n$ is an intermediate which arises from the intramolecular disproportionation of methyl groups. At 500 °C, radical intermediates become more prominent. Tributyltin radicals will react with $(alkyl)_2E(E = Se, Te)$ via an S_H2 reaction[140].

The acid-catalysed hydrolysis of vinyl selenides has been investigated by two groups. The rate-determining step for the hydrolysis of $RSeCH=CH_2$ (R = aryl) is the protonation of the double bond to give a selenium stabilized carbonium ion. When R = Ph, the order of reactivity is RO > RS > RSe (relative rates 42:7:1)[141]. For the specific case of the following reaction[142]:

$$\text{Me(CH}_2)_9\text{CH}=\text{C} \underset{\text{Me}}{\overset{\text{SePh}}{<}} \xrightarrow{(\text{H}^+)} \text{Me(CH}_2)_{10}\text{COMe}$$

(7)
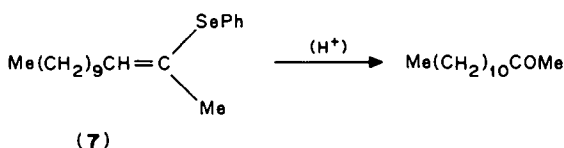
a kinetic solvent deuterium isotope effect is observed, suggesting that the protonation is partially reversible. Also, hydrolysis of a mixture of the E and Z isomers of (7) in the presence of D_2O gave 25% incorporation of D into the unreacted vinyl selenides.

Oxidation of selenides and tellurides is a commonly observed reaction. In some cases this might be achieved electrochemically, e.g. 1, 3-dihydro-2-telluraindene may be oxidized in MeCN solution in the presence of tetraalkylammonium salts to C_8H_8TeX (X = ClO_4, PF_6)[143]. More conventional means of oxidation have also been employed, e.g. $(CF_3)_2Te$ will react with Cl_2, Br_2, O_2 and $ClONO_2$ to give $(CF_3)_2TeX_2$ (X = Cl, Br, NO_3) and $CF_3)_2TeO$. Ozone and $(CF_3)_2Te$ are reported to give an unstable compound[144]. A further variation on this theme involves the oxidative addition of interhalogens to unsymmetrical diaryl tellurides; no disproportionation to symmetrical compounds was observed[145].

The well known reaction of an alkyl halide with a telluride has been the subject of further investigation[146]. Experiments in the presence of a spin trap [PhCH = N(O)Bu^t] have

detected radical intermediates and when the organic radical enjoys some resonance stabilization, e.g. allyl, the tellurium product is often R_2TeX_2 (X = halogen) rather than the telluronium salt; thus,

$$Ph_2Te \; + \; RX \; \rightleftharpoons \; \underset{(8)}{Ph_2Te\cdots XR} \; \longrightarrow \; Ph_2TeX \; R \; \xrightarrow[\text{more}]{RK} \; \underset{\text{stable } R^\bullet}{Ph_2TeX_2}$$

$$\downarrow \text{less stable } R^\bullet$$

$$Ph_2TeR^+ \; + \; X^- \; \rightleftharpoons \; Ph_2Te(R)X$$
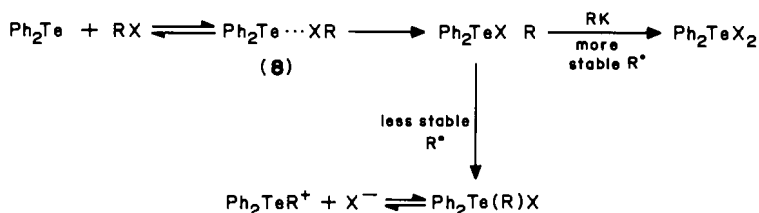
The initial step is considered to be the formation of a charge-transfer complex (**8**), a view that gained recent support from the isolation of such materials in the preparation of *p*-AnTe(CH$_2$)TeAn-*p* from ArTe$^-$ and CH_2X_2 (X = Br, I) when stable complexes ArTe(CH$_2$)TeAr·CH$_2$X$_2$ were isolated. The significantly reduced value of the ^{125}Te Mössbauer quadrupole splitting (7.58 mm s^{-1} for the CH_2Br_2 complex), compared with values of ca. 10 mm s^{-1} expected for a telluride, indicates a relatively strong interaction between donor and acceptor[72].

B. Diorganyl Diselenides and Ditellurides

In contrast to selenium chemistry where solid RSeSeR[1] compounds are known (Section II.B.2), no unsymmetrical ditellurides have been isolated as solids, but they are well known in solution where they are conveniently identified by ^{125}Te NMR spectroscopy[147] (Section V.A). In organic solvents such as chloroform a slow exchange reaction occurs:

$$R_2Te_2 + R_2^1Te_2 \rightleftharpoons 2RTeTeR^1$$
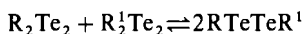
with an equilibrium constant close to 4 and independent of temperature, implying that the process is under entropy control. It is speculated[148] that the exchange occurs via a non-radical mechanism and involves a square $R_2Te_2 \cdot R_2^1Te_2$ intermediate which affords RTeTeR[1] in a concerted process. In the presence of dioxygen evidence for radical species is found, but this has been shown to be due to a photochemically promoted reaction between the ditelluride and dioxygen[149]:

$$R_2Te_2 \xrightarrow{h\nu} R_2Te_2^* \xrightarrow{O_2} R_2Te_2O_2 \longrightarrow \text{radical intermediates}$$
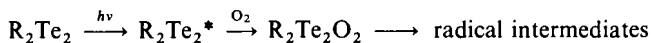
This reaction may also involve a square intermediate and is strongly catalysed by ethanol.

When diselenides and ditellurides react with aqueous alkali under phase transfer conditions (PTC) some oxidized products are observed[150]:

$$2ArSeSeAr + 4KOH \longrightarrow 3ArSeK + ArSeO_2K + 2H_2O$$

$$2\,ArTeTeAr \xrightarrow[\text{PTC}]{NaOH, 40\%} 3\,ArTeNa + ArTeO_2Na \xrightarrow{(H^+)} (ArTeO)_2O$$
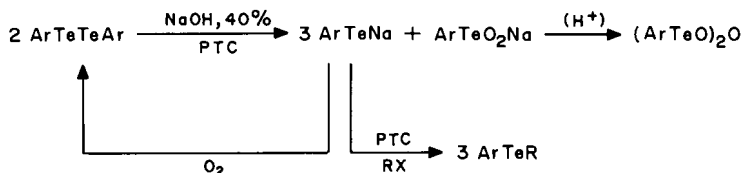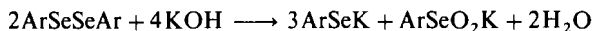
The oxidation of ditellurides by halogen is a well documented means of synthesizing $RTeX_3$ (X = halogen)[2]. Recently the mechanism of the reaction between $(p\text{-}EtOC_6H_4)_2Te_2$ and diiodine was investigated[151] and kinetic data were consistent with the following mechanism:

$$R_2Te_2 + I_2 \xrightarrow{k_1} 2\,RTeI \qquad (k_1 = 56 \pm 2\,dm^3\,mol^{-1}\,s^{-1} \text{ at } 7\,°C)$$

$$RTeI + I_2 \overset{k_2}{\rightleftharpoons} RTe^{II}(I_3) \qquad (k_2 = 1570\,dm^3\,mol^{-1} \text{ at } 25\,°C)$$

$$RTe^{II}(I_3) \xrightarrow{k_3} RTe^{IV(I)}{}_3 \qquad (k_3 = 6.2 \times 10^{-4}\,s^{-1} \text{ at } 25\,°C)$$
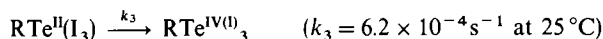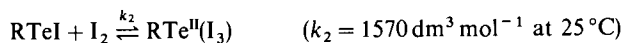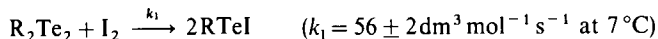
Again, a square intermediate is suggested to produce RTeI via a concerted mechanism. RTeI then forms a 1:1 complex with a molecule of I_2, which is probably the aryltellurenyl triiodide which can undergo unimolecular rearrangement to the aryltellurium(IV) triiodide. Ditellurides may also react with organyltellurium(IV) trihalides, e.g.[152]

$$2R_2Te_2 + 2RTeX_3 \longrightarrow 6\,RTeX \longrightarrow 3\,Te + 3\,R_2TeX_2$$

The stability of the organyltellurenyl halide is for R Ph > 4-$MeOC_6H_4$ ≈ 3, 4-$(MeO)_2C_6H_3$ and for X I > Br > Cl.

A reaction of a triselenide with diiodine was recently reported. Thus $Se_3[C(Se)R]_2$ (R = morpholino) reacted with excess of I_2 in CH_2Cl_2 to give a stable 1:1 charge-transfer complex which reacted further in solution with a rate constant of $10.1 \times 10^{-6}\,s^{-1}$ at 25 °C to give $[RC(Se)_2]SeI$[153]. The oxidation of $(C_2F_5)_2Se_2$ by SbF_5 or by O_2^+ produces evidence of cationic species such as $(C_2F_5)_3Se^+$ and $\{[Se(C_2F_5)]_{4n}\}^{2n+}$. The value of n is likely to be 1, hence again a square intermediate may be involved, the oxidation of which gives the tetraselena cation[154].

Thus it would seem that, contrary to earlier belief[104], ditellurides (and diselenides) do not readily give rise to radical species. However, two recent reports[155,156] define conditions under which relatively stable radicals may be produced. If $(p\text{-}XC_6H_4)_2Se_2$ (X = H, F, Cl, Br) is reacted in solvents degassed at 77 K and under an argon atmosphere with $AlBr_3$, ESR evidence is obtained for species such as $(p\text{-}XC_6H_4Se^{\bullet})AlBr_3$ and $(p\text{-}XC_6H_4SeSe^{\bullet})AlBr_3$, which are said to be stable for several months in the absence of dioxygen and moisture. Gallium halides are also effective.

Another reaction which has attracted attention is the insertion of an atom or group into the Se—Se or Te—Te bond. Depending on the group, this may result in the formal oxidation or reduction of the chalcogen. The reaction with diazomethane[70] has already been mentioned (Section II.C.5) and a variation on the reaction was recently reported[157].

$$N_2CHCO_2Et + Ph_2Se_2 \xrightarrow[\text{xylene, 100 °C, 5 h}]{\text{Cu bronze}} (PhSe)_2CHCO_2Et$$
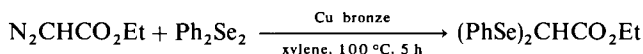
<div align="center">45%</div>

The products of such reactions are formally Se^{II} compounds. However, when, say, a ditelluride reacts with a low-valent transition metal complex such as $Pd(PPh_3)_4$, complexes $(Ph_3P)Pd(TeR)_2$(R = $p\text{-}EtOC_6H_4$ or 2-C_4H_3S) which are probably dimeric are formed[158] and the formal oxidation state of tellurium is now -1. The reaction of $(p\text{-}EtOC_6H_4)_2Te_2$ with Vaska's compound. $Ir(PPh_3)_2(CO)Cl$, has been the subject of a detailed mechanistic study[159]. It is considered that the first step is an addition to Ir^I followed by homolytic fission of the Te—Te bond to give radical intermediates which

ultimately combine to give *trans*-[IrCl(TeR)$_2$(CO)(PPh$_3$)$_2$]:

$$[IrCl(CO)(PPh_3)_2] + R_2Te_2 \overset{k_1}{\rightleftharpoons} [IrCl(CO)(PPh_3)_2] \cdot R_2Te_2$$

$$[IrCl(CO)(PPh_3)_2] \cdot R_2Te_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [IrCl(CO)(TeR)(PPh_3)_2] + RTe^{\cdot}$$

$$[IrCl(CO)(RTe)(PPh_3)_2] + RTe^{\cdot} \overset{k_3}{\longrightarrow} \textit{trans}\text{-}[IrCl(CO)(RTe)_2(PPh_3)_2]$$
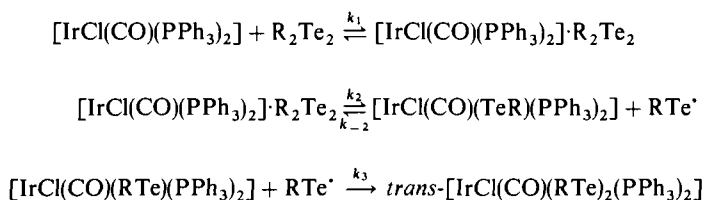
If the radical RTe· is confined to a solvent cage and the first equilibrium lies in favour of the reagents, then second-order kinetics are expected, and observed. The scheme is also in accord with spectroscopic and preparative data, although ^{125}Te NMR data do suggest that under some conditions the reverse reductive elimination of ditelluride might occur.

C. Applications in Organic Synthesis

A major growth area in selenium (and to a lesser extent, tellurium) chemistry is the development of synthetic methodologies based on organoselenium compounds. Many of the reagents are of the type RSeX and therefore not strictly within the scope of this chapter. However, tellurides or selenides are often intermediates and some new chemistry has been developed to convert these intermediates through to the final product. This section gives examples of such reactions as well as selecting other procedures which do not require RSeX as the starting reagent. It is worth pointing out that several workers who have made distinguished contributions in this field are also authors of recent review articles, e.g. Clive[3,5], Reich[23,160], Krief *et al.*[161] and Liotta[25,162].

1. .Coupling reactions

Degassed Raney nickel is a powerful reagent for the coupling of aryl groups in compounds such as Ar$_2$TeCl$_2$[163]. The coupling probably involves Ar$_2$Te as an intermediate. If RR^{1}TeCl$_2$ (RR^1 = aryl) is used, Raney nickel produces non-specific coupling giving relatively high yields of the symmetric products RR and R^{1}R^1; however, if a stoichiometric reaction of RR^{1}TeCl$_2$ and Pd(PPh$_3$)$_4$ is carried out, excellent (ca. 90%) yields of the unsymmetric coupling product are obtained[164], e.g.
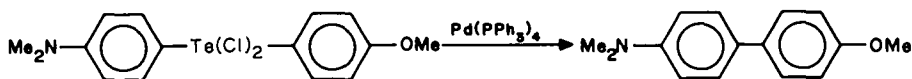
Bergman[164] attributes the difference to the differing interactions of RR^{1}Te with the polyatomic nickel surface and the monomeric Pd(0) complex, i.e.
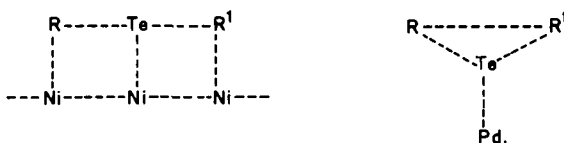
Benzylic and allylic couplings occur readily via tellurides which can be prepared by nucleophilic attack of Te^{2-} on an appropriate organic halide[165], e.g.
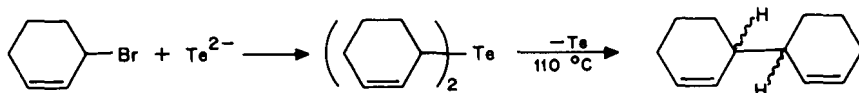
However, in contrast, the corresponding di(2-cyclohexenyl) selenide is stable at 110 °C, showing only 2% decomposition over 3h. Although many of these coupling reactions may be promoted thermally, some may be induced photochemically, e.g.
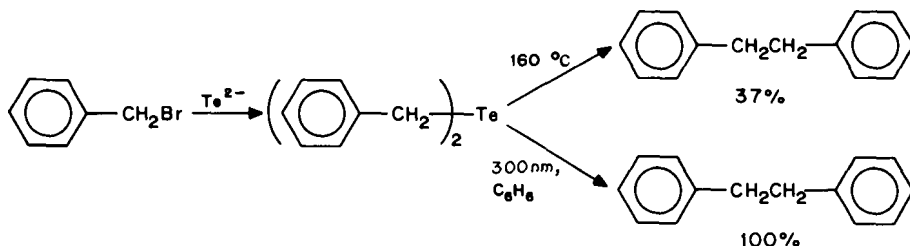
Allylic couplings may also be induced from ditellurides formed by nucleophilic attack of Te_2^{2-} on an allylic halide. These results have been the subject of an excellent review[164].

2. Lithium reagents

The α-protons of selenides are mildly acidic and this fact has been exploited for synthetic purposes via lithiation of the α-carbon atom; for example, it opens up a new route to alkenes[166]:
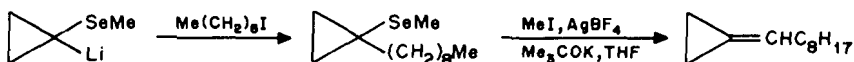
A variation on the theme is the addition of RLi to a vinylic selenide[167]:

$$PhSeCH = CH_2 \xrightarrow{RLi} PhSeCHLiCH_2R \xrightarrow[(R)']{\text{electrophile}}$$

$$PhSeCHR'CH_2R \xrightarrow{-PhSeH} RCH = CHR'$$
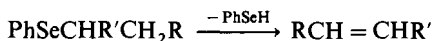
An earlier work describes a route to allylic alcohols[168], e.g.
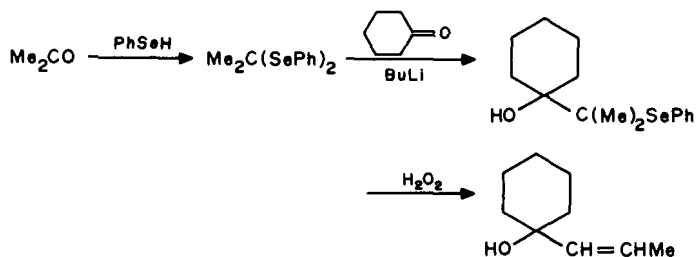
Reich and coworkers[23,169,170] point out that the α-protons of selenoxides are more acidic than those of selenides, hence there is some advantage in oxidizing the selenide; an example of the methodology is[169]
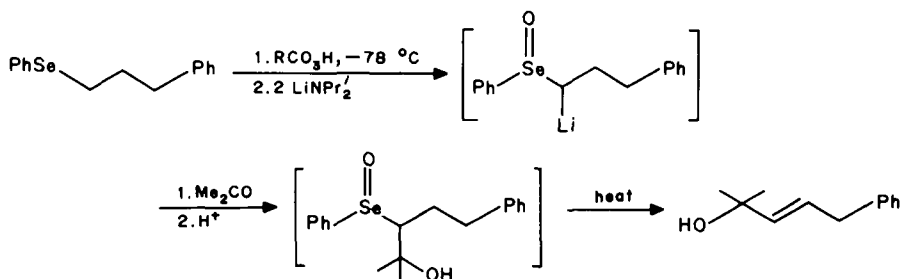
3. Removal of—ER (E = Se, Te)

As explained earlier, often an organyl selenide or telluride is an intermediate produced by reaction of RSeX with an organic substrate. The removal of the RSe (or RTe) group is then required to give the final product. In the examples immediately above both thermolysis and oxidation have been effective. A variety of other methods are available, however. For example, Clive et al.[171] have used triphenyltin hydride to cleave R—SePh bonds:

$$RSePh \xrightarrow[120\,°C]{Ph_3SnH} RH + Ph_3SnSePh$$
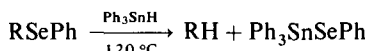
The reaction with RTePh goes under even milder conditions (ca. 80 °C). The products, Ph_3SnEPh (E = Se, Te), have been the subject of a Mössbauer investigation[148]. Other reagents, e.g. KIO_4, may serve as alternative oxidants[172]:

$$PhCOCH(Me)SePh \xrightarrow{KIO_4} PhCOCH = CH_2$$
$$(9)$$
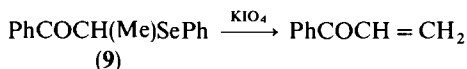
In the above example, the selenide is formed by reaction of the carbonyl compound with strong base ($LiNR_2$) which traps the enol form:

$$PhCOEt \xrightarrow[-78\,°C]{LiNR_2} Ph\overset{\displaystyle OLi}{C} = CHMe \xrightarrow{PhSeBr} 9$$
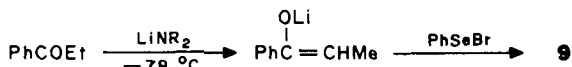
This reaction was dicovered simultaneously and independently by Reich et al.[173] and Sharpless et al.[174,175].

A further example of alkene synthesis involves the intermediate formation of a bistelluride via a vic-dibromide. Recent examples include the reaction of 5α, 6β-dibromocholestan-3β-ol with $NaBH_4$–dithienyl ditelluride [i.e. $NaTe(C_4H_3S)$], which in ethanol gave a 90% yield of cholesterol[176]. Similarly, $NaTe(C_6H_4OEt$-$p)$ reacts with a range of 1, 2-dibromo compounds to give alkene via concerted eliminauon of ditelluride[72]. Similar effects may be obtained with the corresponding selenium reagents. Thus vic-dichlorides undergo a syn reductive elimination with NaSeMe or NaSePh and other vic-dihalides undergo anti elimination[177a].

It was recently reported that the 2-pyridylseleno group is a better leaving group than PhSe[177b] in selenoxide elimination to enones. An example is

$$RCH_2C(O)R' + 2\text{-}PyrSeBr \longrightarrow R'C(O)CH(R)SePyr\text{-}2 \xrightarrow{[O]} R'C(O)CH = CHR^2$$

$$R^2CH = R$$
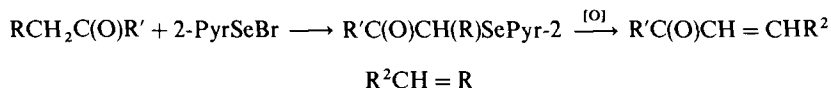
Also, treatment of alkyl phenyl selenides and tellurides with *m*-chloroperbenzoic acid in alcoholic media leads to substitution of PhSe or PhTe by alkoxide, e.g.

$$Me(CH_2)_9SePh \xrightarrow[\text{MeOH, 1 h}]{3\,m\text{-}ClC_6H_4C(O)OOH} Me(CH_2)_9OMe$$
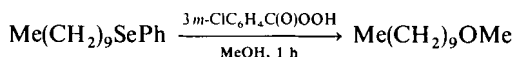
The reaction appears to proceed via the selenone or tellurone[177c].

4. Carbon to oxygen bond formation

The reaction between PhSe⁻ and a carbonyl compound, RCOR′, gives a bis-selenide, RR′C(SePh)$_2$, which may then react with butyllithium to give RR′C(Li)SePh[178]. This reagent may be exploited to afford a new route to epoxides[179,180], e.g.

$$RCHO + 2\,HSePh \longrightarrow RCH(SePh)_2 \xrightarrow{\text{Li}} LiRCHSePh$$

$$\xrightarrow{R^1R^2CO} PhSeCHRCR^1R^2OH \xrightarrow[\text{base}]{\text{MeX}} R \underset{O}{\overset{R^2}{\diagdown \diagup}} R^1$$
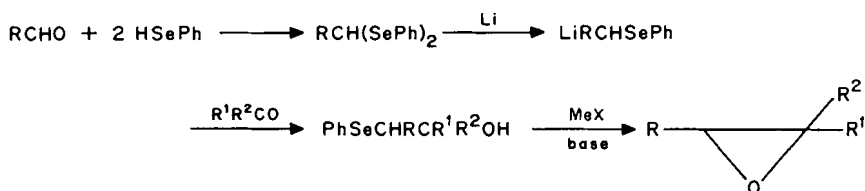
Uemura *et al.*[181] recently demonstrated a new ether synthesis by reaction of *m*-chloroperbenzoic acid with alkyl phenyl selenides, e.g.

$$Me(CH_2)_{11}CH(Me)SePh \xrightarrow[\text{MeOH, r.t.}]{m\text{-}ClC_6H_4C(O)OOH} Me(CH_2)_{11}CH(Me)OMe$$

$$100\%$$
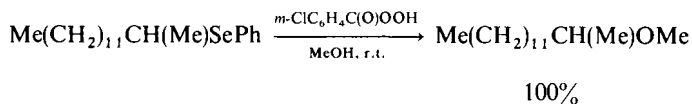
It now seems clear that both organoselenium and organotellurium reagents are well established within the synthetic armament of the organic chemist. Those readers requiring more detailed information and more comprehensive coverage of the subject are advised to consult the review literature referenced here.

D. Photochemical Reactions

Clive *et al.*[171] have warned that tellurides of satisfactory purity may only be obtained under red light (photographic dark-room conditions). This does not seem to reflect general experience in this field; however, it is the present writer's experience that tellurides of the (alkyl)(aryl)Te class tend to be less photolytically stable than (alkyl)$_2$Te or (aryl)$_2$Te, and it is generally true that many tellurides encountered in organic synthesis are indeed of the (alkyl)(aryl)Te type. Hence Clive *et al.*'s warning should be heeded when such materials are studied.

Despite clear evidence that organyl selenium and tellurium compounds may be photosensitive, the number of papers devoted to studies of their photochemistry is not extensive. The topic was reviewed in 1980 by Martens and Praefcke[182].

1. Selenides and tellurides

The choice of solvent can have a profound influence on the products and/or product ratios when an organyl selenium (or tellurium) compound is photolysed, e.g.[183]

$(NCCH_2CH_2)_2Se \xrightarrow{h\upsilon}$

$\xrightarrow[40 \text{ h}]{MeOH}$ Se + trace of other products

63%

(no organic products isolated)

$\xrightarrow[96 \text{ h}]{THF}$ Se + $(NCCH_2CH_2)_2$ Se$_2$ + traces of other products

23%   66%

$\left(\text{e.g.} \quad \text{[tetrahydrofuran ring]} - SeCH_2CH_2CN \right)$

6%
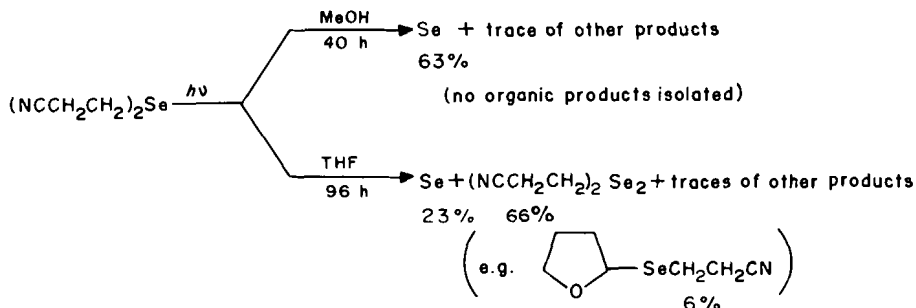
In some cases selenium will be more cleanly eliminated, e.g. diindolyl selenide gives almost 100% selenium when subjected to photolysis in benzene[184]:

$\left(\text{[indolyl]} \right)_2 Se \xrightarrow[C_6H_6, 48 \text{ h}]{h\upsilon}$ [indole] + $\left(\text{[indolyl]} \right)_2$ + Se

69%
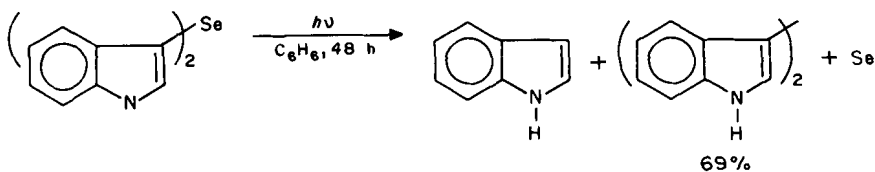
It is not generally true that irradiation of selenides and tellurides will produce elemental selenium and tellurium. For example, the following interesting cyclization reaction was observed[185]:

MeCOCH(SePh)COMe $\xrightarrow[\substack{benzene-p-toluenesulphonic \\ ocid}]{h\upsilon}$ [benzoselenophene derivative with Me, COMe, Se, H]
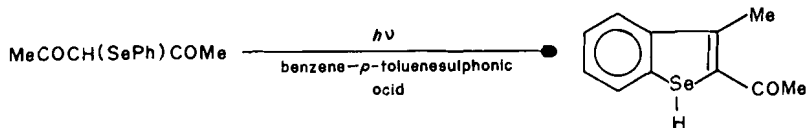
The cyclization is considered to go via an enol to a selenocarbonyl ylid which rearranges to 10, which in turn undergoes acid-catalysed dehydration to the product.

[structure with OH, Me, COMe, Se]

(10)
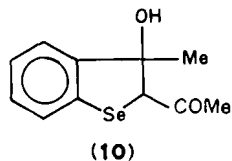
Another example involves aryl alkyl selenides, e.g. PhSeCH$_2$Ph:

PhSeCH$_2$Ph $\xrightarrow{h\upsilon}$ $\left(\text{[benzene ring]}-CH_2Ph, Se \right)_2$ $\xrightarrow[MeX]{NaBH_4}$ [benzene ring]$-CH_2Ph$, SeMe
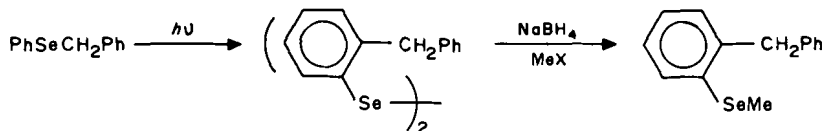
This reaction is general for PhSeR and has been exploited to form selenium-substituted C-nucleosides[186].

Azides may eliminate dinitrogen and rearrange. As shown in the following reaction[187] very different product ratios are obtained on thermolysis and photolysis:

$$190\ ^\circ C$$

(11)   (12)

40   :   60

$$h\nu, C_6H_6$$

11 + 12
90 : 10
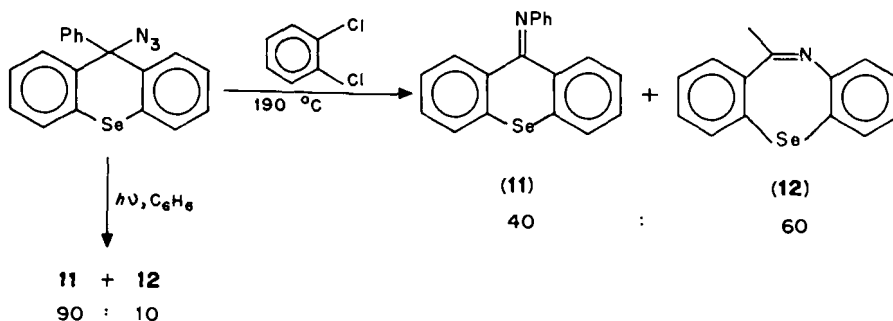
Tellurides also undergo interesting reactions, for example the telluride (13) forms a thioxanthone via a cyclization reaction[188]:

$$h\nu$$

(13)
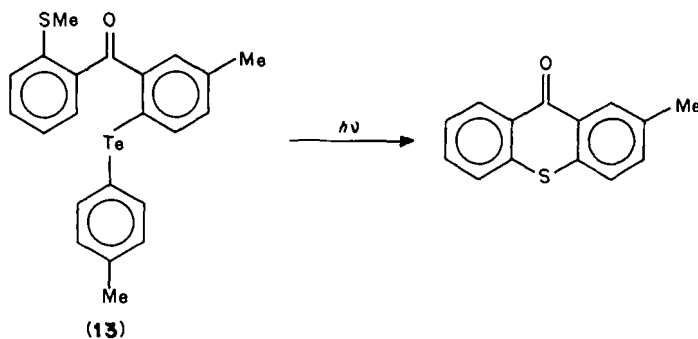
Photo-oxidation reactions may occur. For example, a new route to selenoxides is provided by the following reaction[189]:

$$RSeR' \xrightarrow[h\nu]{O_2} RR'SeO$$

28–95%

$$R = Ph;\ R' = Me,\ CH_2Ph,\ CHPrCH(OH)Pr$$
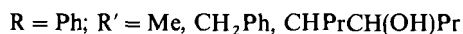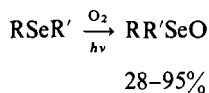
Although not strictly organyl tellurium compounds, it is of interest that the following reaction was recently observed[190]:

$$Te(S_2CNR_2)_n \xrightarrow[h\nu]{O_2} TeO_2 + \frac{n}{2}R_2NC(S)SS(S)CNR_2$$

$$(n = 2\ or\ 4)$$
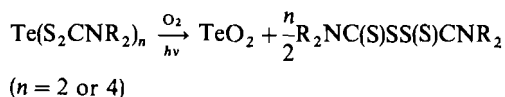
2. Diselenides and ditellurides

The photolysis pathway for diselenides and ditellurides is very dependent on the presence or absence of dioxygen in the reaction system. In the absence of dioxygen,

photolysis of dibenzyl diselenide proceeds as follows[191]:

$$(PhCH_2)_2Se_2 \xrightarrow[\text{MeCN, 2h}]{h\nu(\lambda > 280\,nm)} Se + (PhCH_2)_2Se$$
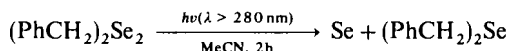
The reaction is considered to proceed via the following mechanism:

$$R_2Se_2 \xrightarrow{h\nu} R^{\cdot} + {}^- \cdot SeSeR$$

$$RSeSe^{\cdot} \longrightarrow RSe^{\cdot} + Se$$

$$R^{\cdot} + R_2Se_2 \longrightarrow R_2Se + RSe^{\cdot}$$

$$R^{\cdot} + RSe^{\cdot} \longrightarrow R_2Se$$

$$RSe^{\cdot} + RSe^{\cdot} \longrightarrow R_2Se_2$$
$$R = PhCH_2$$
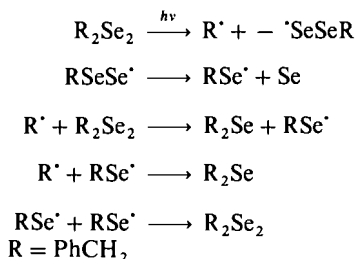
The quantum yield for disappearance of the diselenide is 0.16. Although ESR evidence has been obtained for the formation of $PhSe^{\cdot}$ radicals on UV irradiation of Ph_2Se_2[192], it is believed that C—Se bond scission is the main mechanistic pathway in the above case.

In contrast, in the presence of dioxygen, photolysis of $(PhCH_2)_2Se_2$ leads to a variety of products. Thus, if the material is in chloroform solution the products identified included $PhCHO$ (47%), $PhCH_2OH$ (24%), $PhMe$ (4%), $Ph(CH_2)_2Ph$ (5%) and Se (53%)[193]. Very similar results are obtained for $(PhCH_2)_2Te_2$[193], where the same range of products is obtained in the presence of dioxygen. Thermolysis of $(PhCH_2)_2Te_2$ gives a clean decomposition to $(PhCH_2)_2Te$ and Te. A further interesting variation has been observed. Thus, when dioxygen is passed into a toluene solution containing $(p\text{-}EtOC_6H_4)_2Te_2$ and $[Pd(PPh_3)_4]$ irradiated with visible light, good yields of $PhCOOH$ are obtained via $PhCHO$[194]. Almost certainly the reaction mentioned in Section IV.B[149] is involved, but the presence of the Pd(0) complex is essential, possibly to catalyse the formation of radicals such as $RTeO^{\cdot}$. There is much chemistry in this area which is in need of exploitation.

Cross and coworkers[195,196] have observed that elimination of selenium on photolysis of diselenides under oxygen-free conditions may be suppressed in the presence of triorganyl-phosphines. Thus:

$$R_3P + R'_2Se_2 \xrightarrow[\text{350 nm, MeCN}]{h\nu} R_3PSe + R'_2Se$$
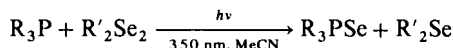
The rates of the reactions decreased in the orders: $R_3 = Me_2Ph > MePh_2 > Ph_3$ and $R' = CH_2Ph > Et > Me > Ph$. A mechanism involving photocleavage of the Se—Se bond was favoured. Presumably this is readily reversible, but the intermediate $RSe^{\cdot}$ radicals may be captured by R_3P:

$$R'_2Se \xrightarrow{h\nu} R'Se^{\cdot} + \cdot SeR'$$

$$R'Se^{\cdot} + PR_3 \longrightarrow R'' + R_3PSe$$

$$R'' + R'_2Se_2 \longrightarrow R'Se^{\cdot} + R'_2Se$$

$$2R'' \longrightarrow R'R'$$
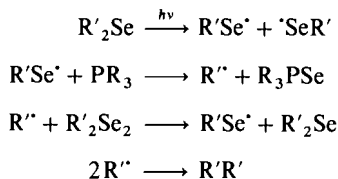
Similar observations have been made by others[197] who estimate the quantum yield for the disappearance of $(PhCH_2)_2Se_2$ to be 1. Identical observations are again made for ditellurides, but in this case the triorganyl phosphine tellurides, R_3PTe, deposit tellurium

after irradiation has ceased[198]. In the presence of dioxygen, elemental selenium and R_3PO are products in the diselenide reactions.

Another group exploiting the photolysis of diselenides and ditellurides in the presence of triphenylphosphine observed CIDNP effects[199].

UV irradiation of $(CF_3)_2Se_2$ gave $(CF_3)Se^{\cdot}$ radicals, which were trapped by metal carbonyls, e.g. $[Mn_2(CO)_{10}]$ to give $[Mn(CO)_4(SeCF_3)]_2{}^{200}$. $RTe^{\cdot}$ radicals have been produced in pulse radiolysis experiments[201].

Although not strictly photochemistry of ditellurides, the following reaction is of interest:

$$Ph_2Te_2 \xrightarrow[NH_3(l)]{Na} PhTe^- \xrightarrow[h\nu]{RX} PhTeR$$

$$R = Ph, \text{ 1-Naph}$$
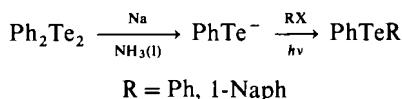
A photo-$S_{RN}1$ mechanism has been proposed[202].

E. Lewis Base Reactions

Both diorganyl chalcogenides and diorganyl dichalcogenides have lone pairs of electrons which should confer the property of Lewis basicity. This is indeed the case and a considerable growth in the ligand chemistry of selenium and tellurium is detectable in the current literature. The topic has been most comprehensively reviewed by Gysling[203,204], who is also a contributor to this series, hence the topic will receive only brief treatment here.

Selenides and, even more particularly, tellurides show very pronounced class B[205] or 'soft'[206] character as ligands. Thus the majority of complexes reported are either with metals of strong class B character, e.g. Hg^{II}, with metals in low oxidation states or with those such as Pd^{II}, Pt^{II} and Rh^{III} which may be considered borderline A/B in their behaviour. Tellurium ligands, for example, show no affinity for copper(II) but readily form complexes with copper(I). It is generally advisable to carry out complex-forming reactions under dinitrogen since, in some cases, there is evidence that ions such as copper(II) may catalyse the oxidation of tellurides, e.g.[73]

$$RTeCH_2TeR \xrightarrow[but\ O_2-Cu^{II},\ 15\,min]{O_2,\ 16\,h} RTe(O)CH_2Te(O)R$$

$$R = p\text{-}EtOC_6H_4$$
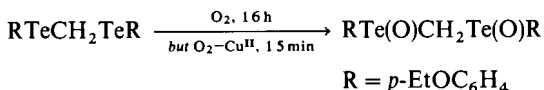
The telluroxide is isolated as a copper(II) complex.

1. Selenides and tellurides as ligands

Typical examples of the type of complex formed are presented here. Complexes with metals in low oxidation states are, for example, $[Mo(CO)_3(Phen)(SePh_2)]^{207}$ and trans-$[RhCl(CO)(EEt_2)_2]$ (E = Se, Te)[208] and $[RhCl(TePh_2)_3]^{209}$. trans-$[PdCl_2(SeEt_2)]$ has been the subject of a crystallographic study[210]. Fac and mer isomers of $[RhCl_3(TePh_2)_3]$ have been prepared[211], as have similar iridium(III) complexes and compounds of the type $[RhCl_3(bipy)(TePh_2)]^{211}$. A complex of $Pd(SCN)_2$ with $Te[(CH_2)_3SiMe_3]_2$ (= L) has been shown by X-ray crystallography to be a thiocyanato complex, trans-$[Pd(SCN)_2L_2]^{212}$.

As more crystallographic studies become available, it is notable that the telluride ligands often bridge metal ions. For example, $[CuCl(TeEt_2)]$ has a structure based on layers of CuCl bridged by $TeEt_2$ with $Cu \rightarrow Te$ bond lengths of 2.625 and 2.535 Å[213]. A further example is produced by the complex $[IAg(\mu\text{-}TePh_2)AgI]^{214}$.

In solution, fluxional behaviour is often shown by the chalcogen ligand. Thus, ^{77}Se NMR studies on [PtMe$_3$X(MeSe(CH$_2$)$_n$SeMe)] ($n = 2$ or 3; X = Cl, Br, or I) clearly show the presence of invertomers[215]. For the case of $n = 1$ (dimeric complexes) metallotropic 1,3-shifts are observed[216,217].

2. Diselenides and ditellurides as ligands

Very frequently the diorganyl dichalcogenides undergo oxidative addition to a metal centre, resulting in complexes of RE$^-$ (E = Se, Te) which are not relevant to this chapter. However, Mehdi and Miller[159] express the view that simple coordination of ditelluride may be a precursor step to rupture of the Te—Te bond. There are some examples in the literature in which the Se—Se or Te—Te bond of R$_2$E$_2$ (E = Se, Te) remains intact on coordination. Thus, for example, the rhenium complexes [(OC)$_3$Re(μ-Br)$_2$(μ-E$_2$Ph$_2$)Re(CO)$_3$] (E = Se[218] or Te[219]) have been crystallographically characterized. Variable-temperature NMR studies of [M(CO)$_5$(Me$_3$SiCH$_2$SeSeCH$_2$SiMe$_3$)] have established that not only does the coordinated selenium atom undergo pyramidal inversion but also, above ambient temperature, a novel 1,2-shift between adjacent selenium atoms occurs[220]. Copper(I) complexes [CuCl·R$_2$Te$_2$] (R = p-EtOC$_6$H$_4$) have been reported and are probably polymeric[221]. It has also been suggested that Lewis acids such as copper(I) may trap unsymmetrical ditellurides[222].

3. Bi- and poly-dentate ligands

MeSe(CH$_2$)$_2$SeMe has been mentioned in another context[215] (Section 1 IV.E.1) and the syntheses of some Pt^{II}[223] and Pt^{IV}[224] complexes have been described. Compound 14 is a further example of a bidentate selenium ligand used to complex Pt^{IV}[224]. In this instance the carbon backbone is rigid. Compound 15 is related to 14 and is of interest in that it has been shown to form well defined complexes with nickel(II), e.g. [Ni(15)X]ClO$_4$ (X = Cl, Br, I, NCS), which are trigonal bipyramidal complexes. The bis-complex [Ni(15)$_2$](ClO$_4$)$_2$ contains octahedral nickel(II)[225]. A tetradentate selenoether, MeSe(CH$_2$)$_2$Se(CH$_2$)$_3$Se(CH$_2$)$_2$SeMe, has been reported, which gives binuclear complexes with [PdCl$_4$]$^{2-}$ in which the ligand is bidentate to each palladium atom[226]. Bis(2-pyridylethyl) selenide forms 1:1 complexes with copper(II) halides, nitrate and perchlorate[227]. It is often the case that the presence of a nitrogen donor atom will increase the affinity of the ligands for 'harder' acids.

(14)   (15)
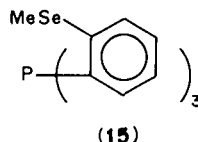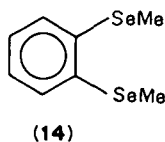
Very few bi- or poly-dentate tellurium ligands are known but Ph$_2$P(o-C$_6$H$_4$TePh)(= L) is an exception, and the complex [PtL$_2$][Pt(SCN)$_4$]·2DMF has been the subject of an X-ray study[228]. The author's group has recently attempted to add more tellurium ligands to this list. Thus 6 (Section III.C) readily forms complexes with Pd^{II}, Pt^{II} and Rh^{I}. Of particular interest is the monomeric complex [HgCl$_2$(6)], in which the two tellurium atoms, but not the nitrogen atoms, are coordinated to mercury thus forming a 13-membered chelate ring. In fact the nitrogen–tellurium interaction seen in uncoordinated 6 is retained in the complex; thus tellurium is simultaneously a Lewis acid and a Lewis base[108]. The ligands RTe(CH$_2$)$_n$TeR (R = p-EtOC$_6$H$_4$; $n = 7,9$ or 10) give soluble macrocyclic complexes with PdCl$_2$ and PtCl$_2$. In the solid state the palladium complexes

appear to be *trans* and the platinium complexes *cis*, but in solution ^{125}Te NMR data reveal a *cis*$\rightleftharpoons$*trans* equilibrium[229].

4. Scales of Lewis acidity

Quantitative scales of Lewis acidity and basicity are very attractive concepts which, if realized, would greatly enhance the accuracy of chemical predictions. Great problems arise because the acid–base pair can rarely be considered free of their environment in practice, so lattice or solvation factors could become dominant. Drago[230] has given an interesting treatment of the problems involved. ^{125}Te Mössbauer parameters are rarely sensitive to effects more than one atom away from tellurium. When a telluride, R_2Te, coordinates to a Lewis acid, p electron density will be removed from tellurium, thus reducing the imbalance of occupancy of the tellurium p orbital set. Hence it is expected that the quadrupole splitting should decrease on coordination and, further, that this decrease will be independent of lattice effects and may be related directly to the coordinate bond strength. It was suggested that a scale of Lewis acidity might be set up relative to (*p*-EtOC$_6$H$_4$)$_2$Te, selected for its ease of preparation, handling and purification. The quadrupole splitting did indeed decrease in the order Cu^I > Pd^{II} $\approx$ Pt^{II} > Hg^{II} [231]. However, as more crystallographic data become available it is clear that the model in its present form is too simplistic. Thus, tellurides often bridge metal centres (e.g. Cu^I [213]), bond angles about coordinated tellurium often depart significantly from 90°, bringing into question the initial assumption of p orbital bonding, and sometimes the metal may be in more than one coordination environment in the same complex, e.g. [HgI$_2$(TePh$_2$)]$_4$[232]. The original postulate is not without merit, but it requires refinement in a well designed Mössbauer/crystallographic study.

5. Conclusion

This brief, and to some extent superficial, survey of ligand chemistry claims no more than to place the topic in context in this chapter. It is safe to predict, however, that this will prove to be a growth area in organyl selenium and tellurium chemistry, not only because the new ligands will be of interest to coordination chemists but also because of the possibilities that some of the new complexes may possess interesting electrical or catalytic properties.

F. Charge-Transfer Complexes

In Section IV.A reference was made to charge-transfer complexes of tellurides with organic halides[72,146]. Even simple selenides when reacted with iodine do not undergo the oxidative addition reaction but form a complex $R_2Se\cdots I_2$[233]; indeed, the following may be general:

$$AE^{II}B + XY \rightleftharpoons (AB)E^{II}\cdots XY \rightleftharpoons (AB)E^{IV}(XY)$$
$$E = Se, Te$$
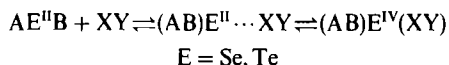
where the position of the equilibrium depends on the identity of groups A, B, X and Y and also on E.

It is to be expected that organylchalcogens will form charge-transfer (CT) complexes with acceptors such as TCNQ (7, 7, 8, 8-tetracyano-*p*-quinodimethane), but studies with simple organyl selenium or tellurium compounds are scarce. However, Heller *et al.*[234] have made 1:1 complexes of **16** (X = Se, Te) with the related tetracyanoethene. The same group more recently reported complexes of the same donors with TCNQ[235]. The

interactions were considered to be of a π–π type.
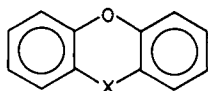
(16)

The range of TCNQ complexes of simple organyltellurium compounds was recently extended[236] to include donors such as diphenyltelluride (1:1), 1,3-dihydro-2-telluraindene (1:1), R_2Te_2 (1:2) (R = Ph or p-EtOC$_6$H$_4$) and dibenzotellurophene (1:1). The crystal structure of the last complex[236] showed interesting differences from that of the dibenzothiophene complex[237] in that significant Te$\cdots$N interactions occur between the mixed stacks. It was suggested that ^{125}Te Mössbauer spectroscopy will prove a useful tool to determine the degree of charge transfer in tellurium complexes. Certainly the difference in quadrupole splitting for the 1,3-dihydro-2-telluraindene complexes of TCNQ ($8.72 \, \text{mm s}^{-1}$) and chloranil ($10.24 \, \text{mm s}^{-1}$) is significant. The former complex is considered to have an ionic ground state[236].

A major impetus for the study of CT complexes is the hope that some may exhibit enhanced solid-state conductivities. Much of the synthetic work involves heterocyclic compounds which are beyond the scope of this chapter, but some of the work does involve diselenides and ditellurides. For example, tetraselenatetracene (TSeT) forms a metallic compound $(TSeT)_2{}^+Cl^-$, but the PF_6^- and AsF_6^- salts are only semiconducting, a fact attributed to the greater volume expansion induced by the larger anions which is likely to weaken the essential Se$\cdots$Se contacts[238,239]. Tetratelluratetracene (TTeT) will form CT complexes with reagents such as TCNQ, $CuCl_2$, $CuBr_2$ and I_2. The materials have compacted disc conductivities in the range 0.1–$1 \, \Omega^{-1} \, \text{cm}^{-1}$[240].

Poly(p-phenylene selenide), a yellow powder which may have some diselenide linkages, gives a black solid on exposure to AsF_5 vapour and undergoes a 40% increase in weight. The compacted disc conductivity of the black material was 10^{-2}–$10^{-3} \, \Omega^{-1} \, \text{cm}^{-1}$[238]. The polymeric diselenides mentioned in Section II.B.1[44] seem to undergo only surface reaction with reagents such as AsF_5. Poly(methylene ditelluride) undergoes a semiconductor–metal transition at 280 K[106].

V. SPECTROSCOPY

Other chapters in both Volumes I and II of this book cover, in some detail, aspects of NMR and ESR spectroscopy, UV and vibrational spectroscopy, photoelectron spectroscopy and ^{125}Te Mössbauer spectroscopy. All that will be attempted here is to place these techniques in the context of this chapter. Since it is probable that NMR spectroscopy is likely to be the most important of these techniques in the future, it is given more prominence than the others.

A. Nuclear Magnetic Resonance Spectroscopy

In addition to the obvious possibility of studying organylselenium and tellurium compounds by ^{1}H and ^{13}C NMR spectroscopy, both elements contain isotopes which permit selenium and tellurium NMR spectra to be recorded directly. Details of the magnetic isotopes are given in Table 5.

The advent of FT NMR spectrometers with multinuclear facilities has greatly eased the experimental difficulties in determining selenium and tellurium NMR spectra, with the result that there is now a minor explosion of new data appearing in the literature, although

TABLE 5. Properties of NMR nuclei of selenium and tellurium

Species	Spin	Natural abundance(%)	Receptivity ($^{13}C = 1$)
^{77}Se	$\frac{1}{2}$	7.50	. 2.9
^{125}Te	$\frac{1}{2}$	6.99	12.5
^{123}Te	$\frac{1}{2}$	0.87	0.88

the data for ^{77}Se remain more numerous. The chemical shift range for ^{77}Se is about 2700 ppm and for ^{125}Te 4700 ppm. ^{125}Te chemical shifts show a marked temperature fluctuation during long accumulation times[241]. The nuclear Overhauser effect is rarely observed for ^{125}Te NMR, and when it is observed it leads to a reduction in signal intensity. Spin–lattice relaxation times are, in general, 4–6 times shorter for ^{125}Te than for ^{77}Se[242], which together with the greater receptivity of the tellurium nucleus does make it the more attractive to study. Three excellent reviews are available which relate particularly to organyl selenium[243] and organyl tellurium[244,245] compounds.

The relative electronegativities of selenium and the bonded group seem to be the major influence on selenium shielding in organylselenium compounds, high shielding being characteristic of negative selenium[250]. Data for dialkyl selenides show some surprises; thus the alkyl shielding effect is the inverse of expectation if it depended entirely on inductive effects, e.g. Me_2Se, $\delta = 0$ ppm; Me(Et)Se, $\delta = 108$ ppm[246]. On the other hand, replacement of Me by CF_3 produces an additive effect on the chemical shift: $Me(CF_3)Se$, $\delta = 370$ ppm; $(CF_3)_2Se$, $\delta = 737$ ppm[247]. The selenium chemical shift in alkyl aryl selenides is dependent on the alkyl group for constant aryl and is also sensitive to substituents in the aryl group for constant alkyl. Symmetrical diaryl selenides also show sensitivity to the substituent on the aryl group. The general trend is, as expected, that electron-with drawing groups are deshielding and electron-releasing groups are shielding, e.g. for p-XC_6H_4SeMe: X = OMe, $\delta = 189$ ppm; X = H, $\delta = 202$ ppm; X = NO_2, $\delta = 233$ ppm[248].

The selenium chemical shifts for diselenides are sensitive to the organic group and also show substituent effects when aryl groups are present. It is interesting to consider the spectra of unsymmetrical diselenides, e.g. Ph_2Se_2, $\delta = 460$ ppm; PhSeSeMe, $\delta = 445$, 294 ppm; Me_2Se_2, $\delta = 275$ ppm. Not only is the presence of the unsymmetrical species readily detected by ^{77}Se NMR, but the data indicate that the effect of alkyl/aryl substitution is almost entirely on the shielding at the selenium atom bonded to the new group[243].

It appears that for heavier atoms such as ^{77}Se and ^{125}Te the paramagnetic contribution (σ_p) to the shielding is dominant[249]. Similar trends are observed in ^{125}Te data to those discussed above for ^{77}Se data. Thus, in particular, the shielding is dependent on the relative electronegativities and for diaryl tellurides the same influence of substituents is seen, e.g. Ph_2Te, $\delta = 688$ ppm; $(p$-$MeOC_6H_4)PhTe$, $\delta = 668$ ppm; $(p$-$BrC_6H_4)PhTe$, $\delta = 1079.6$ ppm[249] [N.B. All shift data are relative to Me_2Se (^{77}Se) or Me_2Te (^{125}Te).]

Although no unsymmetrical ditellurides have been isolated, their existence in solution is readily demonstrated by ^{125}Te NMR spectroscopy[147,245]. An exchange reaction, slow on the NMR time scale, occurs when two symmetrical ditellurides are mixed:

$$R_2Te_2 + R'_2Te_2 \cdots 2RTeTeR'$$
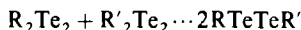
The reaction is under entropy control since the equilibrium constant is independent of temperature and approaches a value of 4[147,148]. In the presence of dioxygen anomalous

chemical shifts are observed and in some spectra CIDNP effects are seen; the radicals causing these effects result from a competing reaction of dioxygen with the ditellurides[149], which was discussed in Section IV.B. For the unsymmetrical species $^{125}Te-^{125}Te$ coupling constants of the order of 200 Hz are observed. As for the diselenides, the major effect of changing an organic group in a ditelluride is on the shielding at the tellurium atom to which the group is bonded. Thus, for the following equilibrium, chemical shifts are as indicated[147]:

$$(p\text{-ClC}_6\text{H}_4)_2\text{Te}_2 + (p\text{-EtOC}_6\text{H}_4)_2\text{Te}_2 \rightleftharpoons 2(p\text{-ClC}_6\text{H}_4)\text{Te}-\text{Te}(\text{C}_6\text{H}_4\text{OEt-}p)$$

$$\quad\quad 448.5 \quad\quad\quad\quad 457.9 \quad\quad\quad\quad\quad\quad 438.5 \quad\quad\quad\quad\quad 469.6\,\text{ppm}$$
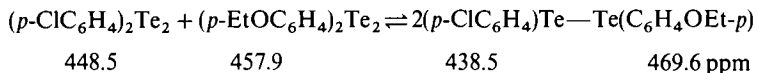
Other workers[245] have noted a much larger influence on the shielding of the second tellurium atom in alkyl aryl ditellurides, e.g. Pr_2Te_2, $\delta = 115\,\text{ppm}$; $PrTeTePh$, $\delta = 223$, 305 ppm; Ph_2Te_2, $\delta = 420\,\text{ppm}$. It is now certain that, for ditellurides, reliable chemical shift data can only be obtained in the absence of dioxygen. It has been suggested that tellurium–proton coupling patterns can be a valuable aid to spectral assignment in ^{125}Te NMR studies[250].

One area in which ^{77}Se and ^{125}Te NMR spectroscopy is likely to find increasing application is in the ligand chemistry of the elements. For example, in complexes of metals such as Pd^{II} and Pt^{II} differences in shielding are experienced by the ^{77}Se nucleus in cis and trans isomers of the complexes $[MCl_2(Me_2Se)_2]$[246]. The same is true for ^{125}Te NMR, which was used to demonstrate a solution equilibrium of the cis and trans isomers of $[\{(PhCH_2CH_2)_2Te\}_2PtCl_2]$[251]; similarly, ^{125}Te data for $[MCl_2RTe(CH_2)_nTeR]$ (M = Pd, Pt; n = 7, 9 or 10; R = $p\text{-EtOC}_6\text{H}_4$) show a solution equilibrium of the cis and trans isomers[252].

A number of ^{13}C NMR studies of organylselenium and tellurium compounds have been reported. Thus, for example, Chadha and Miller[253] have surveyed a range of organotellurium compounds which included a few tellurides and one ditelluride. For aryl compounds, the resonance of the carbon atom bond to tellurium can be assigned via the low intensity of the resonance or, better, by measurement of the spin–lattice relaxation time, T_1, since carbons bearing no hydrogen atoms generally relax on order of magnitude more slowly than those bonded to hydrogen. In this way the ^{13}C chemical shift of carbon bonded to chalcogen in the series Ph_2S_2 (137 ppm), Ph_2Se_2 (130.9 ppm) and Ph_2Te_2 (108 ppm) were assigned (all vs. TMS)[254]. Relative to benzene (128.8 ppm), there is a downfield shift for Ph_2S_2 and Ph_2Se_2, but an upfield shift for Ph_2Te_2. When related phosphorus and tellurium compounds are compared, e.g. $Ph_2P(CH_2)_nPPh_2$ and $RTe(CH_2)_nTeR$ (R = $p\text{-EtOC}_6\text{H}_4$), the resonance of the aliphatic carbon bonded to tellurium is ca. 14 ppm upfield compared with the similar resonance in the phosphorus compound. Interestingly, when the tellurium compound coordinates to a metal, the carbon resonance undergoes a large downfield shift[73]. A very interesting development will be the application of solid-state high-resolution ^{13}C NMR spectroscopy to organyl chalcogen compounds. In their study of dithiocarbamate and xanthate complexes of tellurium(IV) and tellurium(II), Zumbulyadis and Gysling illustrated the potential of the technique for probing crystal as opposed to molecular symmetry[255].

Other applications of NMR spectroscopy in this field are conventional. For example 2,11-diselena[3.3]metacyclophane (17) undergoes conformational flipping between syn and anti conformers at $-110\,°C$ and the energy barrier was calculated to be 33 kJ mol^{-1}[256]. In the same way the dynamic stereochemistry of the related bis-diselenide 18 is illustrated by the fact that the methylene group shows an AB spectrum at low temperature and a singlet at high temperature. The coalescence temperature was 208 K and the free energy of activation is 46.5 kJ mol^{-1}. The data were interpreted in terms of the interconversion of syn conformers[257]. Russian workers[258] have demonstrated barriers to

rotation around aromatic ring Se of the order of $42\,kJ\,mol^{-1}$.

(17)   (18)
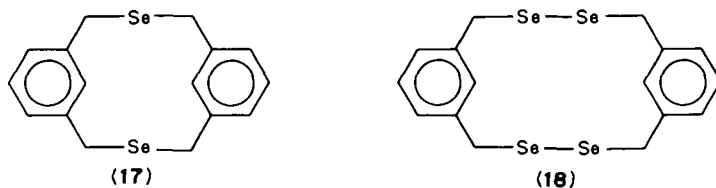
B. Vibrational Spectra

Only a few observations will be made. Carbon–selenium stretching modes in dialkyl selenides usually appear between 500 and $700\,mol^{-1}$. They are intense in the Raman spectrum[259]. In Me_2Te $\nu_s(TeC)$ and $\nu_{as}(TeC)$ are accidently coincident at $528\,cm^{-1}$[260], but they are seen as distinct vibrations when Me_2Te is coordinated to Pd^{II} or Pt^{II}[261]. For diaryl chalcogenides assignment of $\nu(EC)$ $(E = Se, Te)$ is more difficult, although isotopic studies on diphenyltellurium(IV) dihalides suggest that $\nu(TeC)$ occurs at ca. $300\,cm^{-1}$ (ν_{as}) and ca. $240\,cm^{-1}$ (ν_s)[262]. Rotational isomers of C_1 and C_3 symmetry for $Pr^i(Me)Se$ have been shown to co-exist in the liquid state, whereas for $(Pr^i)_2Se$ three (C_2, C_3, C_1) have been shown to co-exist in the liquid phase[263].

A remarkable claim by Hamada and Morishita[264] that vibrational data for R_2E $(E = O, S, Se, Te)$ suggested the molecules to be linear in structure has been shown to be based on a misinterpretation of the data[265].

C. ^{125}Te Mössbauer Spectra

This topic is covered comprehensively in this volume in Chapter 2 by Berry. The chemical isomer shift data for tellurides and ditellurides are relatively insensitive to the organic group. The shifts for ditellurides are, on average, slightly more positive (ca. 0.28–$0.37\,mm\,s^{-1}$) than for tellurides (ca. 0.06–$0.18\,mm\,s^{-1}$) (both with respect to I/Cu). Since the more positive the chemical isomer shift the greater is the s electron density at the nucleus, it follows that in both tellurides and ditellurides there are relatively small s electron densities at the tellurium nucleus[266,267].

Both tellurides and ditellurides have large (and similar) quadrupole splittings of the order of 10–$11\,mm\,s^{-1}$, which correspond to a large imbalance in the 5p orbital population on tellurium; this must, in turn, imply that the Te—C and Te—Te bonds have considerable covalent character. If the chemical isomer shift data, quadrupole splitting data and structural data (Section III) are considered together, the conclusion is that the tellurium must be using bonding orbitals which are between p^3 and sp^3 in character in tellurides and ditellurides[268].

The influence of coordination or charge-transfer interactions on, particularly, the quadrupole splitting of tellurides and ditellurides has been covered in Section IV. For the future, combined ^{125}Te NMR and ^{125}Te Mössbauer studies will be of considerable interest. One caveat in comparing Mössbauer data with other data is that, owing to the low recoil free fraction for organyltellurium compounds, it is necessary to record the spectra at 4 K. In some cases this might represent a different regime of stability for a particular material.

VI. CONCLUSION

This chapter has attempted to occupy the middle ground between coverage of selenium and tellurium analogues of ethers and peroxides that may be appropriate to a general text

on organometallic chemistry and the comprehensive coverage that would be expected in a specialist monograph on the subject. Overlap with other chapters in the series is inevitable but hopefully has been kept to a reasonable minimum. If this chapter proves a useful starting point for those wishing to know more of these compounds, it will have achieved its objective.

VII. REFERENCES

1. R. A. Zingaro and W. C. Cooper (Eds.), *Selenium*, Van Nostrand Reinhold, New York, 1975, Chapt. 8, pp. 408–545.
2. K. J. Irgolic, *The Organic Chemistry of Tellurium*, Gordon and Breach, New York, 1974.
3. D. L. J. Clive, *Modern Organoselenium Chemistry*, Pergamon Press, Oxford, 1979.
4. P. D. Magnus, in *Comprehensive Organic Chemistry* (Ed. D. N. Jones), Vol. 3, Pergamon Press, Oxford, pp. 491–538.
5. D. L. J. Clive, *Tetrahedron*, **34**, 1049 (1978).
6. K. J. Irgolic, *J. Organomet. Chem.*, **103**, 91 (1975); **130**, 411 (1977); **158**, 235 (1978); **189**, 65 (1980); **203**, 367 (1980).
7. *Proceedings of the Second International Symposium on Organic Selenium and Tellurium Chemistry, Including Biochemistry, Chem. Scr.*, **8A**, 1–117 (1975).
8. D. Cagniant and G. Kirsch (Eds.), *Proceedings of the Third International Symposium on Organic Selenium and Tellurium Compounds*, Université de Metz, Metz, 1979, pp. 1–413.
9. F. J. Berry and W. R. McWhinnie (Eds.), *Proceedings of the Fourth International Conference on the Organic Chemistry of Selenium and Tellurium*, University of Aston in Birmingham, Birmingham, 1983, pp. 1–678.
10. J. P. Mila and J. F. Labarre, *C. R. Acad. Sci., Ser. C*, **263**, 1481 (1966).
11. R. Paetzold, U. Lindner, G. Bochmann and P. Reich, *Z. Anorg. Allg. Chem.*, **352**, 295 (1967).
12. D. J. Sandman, J. C. Stark and B. M. Foxman, *Organometallics*, **1**, 739 (1982).
13. D. J. Sandman, M. Rubner and L. A. Samuelson, *J. Chem. Soc., Chem. Commun.*, 1133 (1982).
14. L. A. Acampora, D. L. Dugger, T. Emma, J. Mohammed, M. Rubner, L. A. Samuelson, D. J. Sandman and S. Tripathy, in *Polymers in Electronics* (Ed. T. Davidson), American Chemical Society, Washington, DC, 1983, p. 461.
15. S. C. Cohen, M. L. N. Reddy and A. G. Massey, *J. Organometal. Chem.*, **11**, 563 (1968).
16. H. Reinboldt, in *Methoden der Organischen Chemie, Vol. IX, Schwefel–, Selen– und Tellurverbindungen* (Eds. E. Muller, O. Bayer, H. Meerwein and K. Ziegler), 4th ed., Georg Thieme, Stuttgart, 1955; see F. Tabourg, *C. R. Acad. Sci.*, **138**, 982 (1904).
17. G. B. Deacon and J. C. Parrott, *J. Organomet. Chem.*, **22**, 287 (1970).
18. R. C. Paul, K. K. Bhasin, and R. K. Chadra, *J. Inorg. Nucl. Chem.*, **37**, 2337 (1975).
19. H. M. Leicester, *J. Am.. Chem. Soc.*, **60**, 619 (1938).
20. A. Arase and Y. Masuda, *Chem. Lett.*, 419 (1975).
21. F. N. Alquist and R. E. Nelson, *J. Am. Chem. Soc.*, **53**, 4033 (1931).
22. R. F. Riley, J. Flats and D. Bengels, *J. Org. Chem.*, **27**, 2651 (1962).
23. H. J. Reich, in Ref. 9, pp. 258–272.
24. G. A. Krauss and M. J. Taschner, *J. Org. Chem.*, **45**, 1175 (1980).
25. G. Zima and D. Liotta, *Synth. Commun.*, **9**, 697 (1979); see also D. Liotta, *Acc. Chem. Res.*, **17**, 28 (1984).
26. A. E. Feiring, *J. Org. Chem.*, **45**, 1962 (1980).
27. S. Raucher, *J. Org. Chem.*, **42**, 2950 (1977).
28. N. Miyoshi, H. Ishii, S. Murai and N. Sonoda, *Chem. Lett.*, 873 (1979).
29. A. Osuka, N. Ohmassa and H. Suzuki, *Synthesis*, 857 (1982).
30. P. A. Grieco, S. Gilman and M. Nishizawa, *J. Org. Chem.*, **41**, 1485 (1976).
31. E. G. Kataev, T. G. Mannafov, A. B. Remizov and O. A. Komarouskaya, *Zh. Org. Khim.*, **11**, 2322 (1975).
32. E. G. Kataev, T. G. Mannafov and Yu. Yu. Samitov, *Zh. Org. Khim.*, **11**, 2324 (1975).
33. B. Lindgren, *Tetrahedron Lett.*, 4347 (1974).
34. S. -I. Murahashi and T. Yano, *J. Am. Chem. Soc.*, **102**, 2456 (1980).
35. H. Hauptmann and W. E. Walter, *J. Am. Chem. Soc.*, **77**, 4929 (1955).

36. Y. Okamoto and T. Yano, *J. Organomet. Chem.*, **29**, 99 (1971).
37. R. H. Mitchell, *Can. J. Chem.*, **54**, 238 (1976).
38. R. Weber, L. Christiaens, Ph. Thibaut, M. Renson, A. Croisy and P. Jacquignon, *Tetrahedron.*, **30**, 3865 (1974).
39. N. Petragnani, J. V. Comasseto, R. Rodrigues and T. J. Bracksem, *J. Organomet. Chem.*, **124**. 1 (1974).
40. E. Weissflog, *Phosphorus Sulfur*, **8**, 87 (1980).
41. R. Paetzold, H. D. Schumann and A. Simon, *Z. Anorg. Allg. Chem.*, **305**, 88 (1960).
42. Ref. 16, p. 1337.
43. J. C. Stark, R. Reed, L. A. Acampora, D. J. Sandman, S. Jansen, M. T. Jones and B. M. Foxman, *Organometallics*, **3**, 732 (1984); see also A. Yamahira, T. Nogami and H. Mikawa, *J. Chem. Soc., Chem. Commun.*, 904 (1983).
44. D. J. Sandman, J. C. Stark, M. Rubner, G. P. Hamill, L. A. Acampora, L. A. Samuelson, M. A. McGrath and G. W. Allen, *Proc. Sixth ICCOSS, Freiburg, Germany, 4–8 Oct., 1982.*
45. A. Runet and M. Renson, *Bull. Soc. Chim. Belg.*, **75**, 157 (1966).
46. W. Ried and G. Sell, *Synthesis*, 447 (1976).
47. W. H. H. Gunther and J. Y. C. Chu, *J. Org. Chem.*, **43**, 2672 (1978).
48. E. Rebane, *Ark. Kemi*, **20**, 205 (1962).
49. T. Naito, S. Ina, S. Inove, H. Hanai and S. Katagiri, *Nagoya Shiritsu Daigaku Yakagakubu Kiyo*, **5**, 43 (1957); *Chem. Abstr.*, **52**, 6248e (1958).
50. K. Y. Jen and M. P. Cava, *J. Org. Chem.*, **48**, 1449 (1983).
51. B. Kh. Strelets, M. Gel'mont, Yu. I. Akulin and L. S. Efros, *Khim. Geterotsikil. Soedin.*, 1205 (1979).
52. M. Nakazaki, *J. Chem. Soc. Jpn. Pure Chem. Sect.*, **75**, 338 (1954).
53. J. Meinwald, D. Dauphaise, F. Wudl and J. J. Hauser, *J. Am. Chem. Soc.*, **99**, 255 (1977).
54. K. A. Lestrup and D. O. Cowan, *J. Phys. (Paris), Colloq.*, 1247 (1983).
55. H. Reinboldt and E. Giesbrecht, *Chem. Ber.*, **88**, 1 (1955).
56. O. Foss and V. Janickis, *J. Chem. Soc., Dalton Trans.*, 628 (1980).
57. R. P. Shibaeva, V. F. Kaminskii, E. E. Kostynchenko and E. B. Yagubskii, *J. Organomet. Chem.*, **260**, 293 (1984).
58. R. E. Hollands, A. G. Osborne and I. Townsend, *Inorg. Chim. Acta.*, **37**, L541 (1979).
59. W. L. Dorn, A. Knoechel, P. Schulz and G. Klar, *Z. Naturforsch., Teil B*, **31**, 1043 (1976).
60. R. E. Cobbledick, F. W. B. Einstein, W. R. McWhinnie and F. H. Musa, *J. Chem. Res. (S)*, 145 (1979); (*M*) 1901 (1979).
61. F. Wohler, *Justus Liebigs Ann. Chem.*, **35**, 111 (1840).
62. G. Natta, *Giorn. Chim. Ind. Appl.*, **8**, 367 (1926).
63. L. Chugaev and W. Chlopin, *Chem. Ber.*, **47**, 1269 (1914).
64. B. A. Trofimov, N. K. Gurasova, A. A. Tatarinova, S. V. Amosova, L. M. Sinegovskaya, V. V. Keiko and V. A. Potapov, *Zh. Org. Khim.*, **20**, 1802 (1984).
65. B. A. Trofimov, S. V. Amosova, N. K. Gurasova, V. A. Potapov and A. A. Tatarinova, *Sulfur Lett.*, **1**, 151 (1983).
66. N. K. Gurasova, V. A. Potapov, S. V. Amosova and B. A. Trofimov, *Zh. Org. Khim.*, **19**, 2477 (1983).
67. L. Brandsma and H. E. Wijers, *Recl. Trav. Chim. Pays-Bas*, **82**, 68 (1963).
68. K. Lestrup, D. Talham, A. Bloch, T. Poeler and D. Cowan, *J. Chem. Soc., Chem. Commun.*, 336 (1982).
69. F. Wudl and E. Ahron-Shalom, *J. Am. Chem. Soc.*, **104**, 1154 (1982).
70. D. Seebach and A. K. Beck, *Chem. Ber.*, **108**, 314 (1975).
71. N. Dereu and J. L. Piette, *Bull. Soc. Chim. Fr.*, 623 (1979).
72. K. G. K. De Silva, Z. Monsef-Mirzai and W. R. McWhinnie, *J. Chem. Soc., Dalton Trans.*, 2143 (1983).
73. H. M. K. K. Pathirana and W. R. McWhinnie, *J. Chem. Soc., Dalton Trans.*, 2003 (1986).
74. S. R. Buzilova, I. D. Sadekov, T. V. Lipovich, T. M. Flippora and L. I. Vereshchagin, *Zh. Obshch. Khim.*, **47**, 1999 (1977).
75. N. V. Kondratenko, V. I. Popov, A. A. Kolomeitsev, I. D. Sadekov, V. I. Minkin and L. M. Yagupol'skii, *Zh. Org. Khim.*, **15**, 1561 (1979).
76. T. Kauffmann and H. Ahlers, *Chem. Ber.*, **116**, 1001 (1983).
77. J. F. Suttle and C. R. F. Smith, *Inorg. Synth.*, **3**, 140 (1950).

78. C. Elgy and W. R. McWhinnie, unpublished observation.
79. G. T. Morgan and F. H. Burstall, *J. Chem. Soc.*, 2599 (1930).
80. H. D. K. Drew, *J. Chem. Soc.*, 223 (1926).
81. W. H. H. Gunther, J. Nepywoda and J. Y. C. Chu, *J. Organomet. Chem.*, **74**, 79 (1974).
82. P. Thavornyntikarn and W. R. McWhinnie, *J. Organomet. Chem.*, **50**, 135 (1973).
83. H. Reinboldt and N. Petragnani, *Chem. Ber.*, **89**, 1270 (1956).
84. W. R. McWhinnie and M. G. Patel, *J. Chem. Soc., Dalton Trans.*, 199 (1972).
85. K. Lederer, *Chem. Ber.*, **49**, 2663 (1916).
86. H. Reinboldt and G. Vicentini, *Chem. Ber.*, **89**, 624 (1956).
87. B. C. Pant, *J. Organomet. Chem.*, **54**, 19 (1973).
88. R. F. Ziolo and W. H. H. Gunther, *J. Organomet. Chem.*, **146**, 245 (1978).
89. S. S. Abed-Ali and W. R. McWhinnie, *J. Organomet. Chem.*, **277**, 365 (1984).
90. W. Lohner and K. Praefcke, *J. Organomet. Chem.*, **194**, 173 (1980).
91. A. Luxen and L. Christiaens, *Tetrahedron Lett.*, **23**, 3905 (1982).
92. L. Engman, *J. Org. Chem.*, **48**, 2920 (1983).
93. P. Wiriyachitra, S. J. Falcone and M. P. Cava, *J. Org. Chem.*, **44**, 3957 (1979).
94. R. J. Lagow, L. L. Gerchman, R. A. Jacob and J. A. Morrison, *J. Am. Chem. Soc.*, **97**, 518 (1975).
95. T. J. Juhlke, R. W. Braun, T. R. Bierscheuk and R. J. Lagow, *J. Am. Chem. Soc.*, **101**, 3229 (1979).
96. J. Bergman and L. Engman, *Tetrahedron Lett.*, 1509 (1979).
97. J. Bergman and L. Engman, *Synthesis*, 569 (1980).
98. G. Bergson, *Acta Chem. Scand.*, **11**, 571 (1957).
99. M. T. Chen and J. W. George, *J. Organomet. Chem.*, **12**, 401 (1968).
100. W. S. Haller and K. J. Irgolic, *J. Organomet. Chem.*, **38**, 97 (1972).
101. L. Lange and W. W. Du Mont, *J. Organomet. Chem.*, **286**, C1 (1985).
102. N. Petragnani and M. de Moura Compos, *Tetrahedron*, **21**, 13 (1965).
103. M. A. K. Ahmed, W. R. McWhinnie and T. A. Hamor, *J. Organomet. Chem.*, **281**, 205 (1985).
104. W. V. Farrar, *Research*, **4**, 177 (1951).
105. G. T. Morgan and H. D. K. Drew, *J. Chem. Soc.*, 531 (1925).
106. C. W. Dirk, D. Nalewajeh, G. B. Blauchet, H. Sfchaffer, F. Moraes, R. M. Boysel and Wudl, *J. Am. Chem. Soc.*, **107**, 675 (1985).
107. A. Cisar and J. D. Corbett, *Inorg. Chem.*, **16**, 632 (1977).
108. W. R. McWhinnie and N. I. Al-Salim, (In Press).
109. N. Dereu and M. Renson, *J. Organomet. Chem.*, **258**, 163 (1983).
110. R. J. Gillespie and R. S. Nyholm, *Q. Rev. Chem. Soc.*, **11**, 339 (1957).
111. L. Pauling, *The Nature of the Chemical Bond*, 3rd ed., Cornell University Press, Ithaca, NY, 1960.
112. J. A. Van Vechten and J. C. Phillips, *Phys. Rev. B*, **2**, 2160 (1970).
113. J. F. Beecher, *J. Mol. Spectrosc.*, **21**, 414 (1966).
114. H. J. M. Bowen, *Trans. Faraday Soc.*, **50**, 452 (1954).
115. W. R. Blackmore and S. C. Abrahams, *Acta Crystallogr.*, **8**, 323 (1955).
116. L. Karle, *Angew. Chem., Int. Ed. Engl.*, 7, 811 (1968).
117. R. Kirekas and T. Laitalaineu, *Acta Chem. Scand., Ser. B*, **37**, 61 (1983).
118. V. Ramgopalakrishnan and R. Walter, *J. Am. Chem. Soc.*, **106**, 3413 (1984).
119. Yu. E. Ovchinnikov, V. E. Shklover, Yu. T. Struchkov, V. A. Palyulin, V. I. Rokitskaya, M. Yu. Aismont and V. F. Traren, *J. Organomet. Chem.*, **290**, 25 (1985).
120. H. T. Palmer and R. A. Palmer, *Acta Crystallogr.*, **258**, 1090 (1969).
121. R. E. Marsh, *Acta Crystallogr.*, **5**, 458 (1952).
122. F. H. Kruse, R. E. Marsh and J. D. McCullough, *Acta Crystallogr.*, **10**, 201 (1957).
123. A. E. McCarthy and H. B. Singh, *J. Organomet. Chem.*, **275**, 57 (1984).
124. J. Lamotte, H. Campsteyn, L. Dupont and M. Vermeire, *Cryst. Struct. Commun.*, **6**, 749 (1977).
125. N. Al-Salim, T. A. Hamor and W. R. McWhinnie, *J. Chem. Soc., Chem. Commun.*, 453 (1986).
126. W. R. Blackmore and S. C. Abrahams, *Acta Crystallogr.*, **8**, 317 (1955).
127. C. L. Ralston, R. J. Secomb and A. H. White, *J. Chem. Soc., Dalton Trans.*, 2307 (1976).
128. J. C. Dewan and J. Silver, *Acta Crystallogr., Sect. B*, **33**, 1469 (1977).
129. J. C. Dewan and J. Silver, *J. Chem. Soc., Dalton Trans.*, 644 (1977).
130. J. C. Dewan and J. Silver, *J. Organomet. Chem.*, **125**, 125 (1977).
131. J. C. Dewan and J. Silver, *Aust. J. Chem.*, **30**, 487 (1977).

132. D. P. Rainville, R. A. Zingaro and E. A. Meyers, *J. Fluorine Chem.*, **16**, 245 (1980).
133. G. C. Pappalardo, S. Gruttadauria and K. J. Irgolic, *J. Organomet. Chem.*, **97**, 173 (1975).
134. D. J. Sandman, J. C. Stark, G. P. Hamill, W. A. Burke and B. M. Foxman, *Mol. Cryst. Liq. Cryst.*, **86**, 79 (1982).
135. G. Llabres, O. Dideberg and L. Dupont, *Acta Crystallogr., Sect. B*, **28**, 2438 (1972).
136. M. R. Spirlet, G. Van den Bossche, O. Dideberg and L. Dupont, *Acta Crystallogr., Sect. B*, **35**, 1727 (1979).
137. A. E. McCarthy and S. Ludlow, *J. Organomet. Chem.*, **219**, 169 (1981).
138. D. J. Sandman, J. C. Stark and B. M. Foxman, *Organometallics*, **1**, 739 (1982).
139. R. F. Galiallira, E. A. Pavlenko, O. N. Pruzhkov and T. K. Postnikova, *Tr. Khim. Tekhnol. Fak. Donetsk. Ind. Inst.*, 82 (1975).
140. J. C. Scaiano, P. Schmid and K. U. Ingold, *J. Organomet. Chem.*, **121**, C4 (1976).
141. R. A. McClelland and M. Leung, *J. Org. Chem.*, **45**, 187 (1980).
142. J. L. Piquard and L. Hevessi, *Tetrahedron Lett.*, **21**, 1901 (1980).
143. H. B. Singh and W. R. McWhinnie, *J. Organomet. Chem.*, **264**, 305 (1984).
144. S. Herberg and D. Naumaun, *Z. Anorg. Allg. Chem.*, **494**, 151 (1982).
145. T. N. Srivastava, R. C. Srivastava and V. K. Srivastava, *Indian J. Chem., Sect. A*, **22**, 503 (1983).
146. N. S. Dance, W. R. McWhinnie, J. Mallaki and Z. Monsef-Mirzai, *J. Organomet. Chem.*, **198**, 131 (1980).
147. P. Granger, S. Chapelle, W. R. McWhinnie and A. Z. Al Rubaie, *J. Organomet. Chem.*, **220**, 149 (1981).
148. N. S. Dance, W. R. McWhinnie and C. H. W. Jones, *J. Organomet. Chem.*, **125**, 291 (1977).
149. R. T. Mehdi, *PhD Thesis*, University of Aston in Birmingham, 1981.
150. J. V. Comasseto, J. T. B. Ferreira and J. A. Foutanillas Val, *J. Organomet. Chem.*, **277**, 261 (1984).
151. R. T. Mehdi and J. D. Miller, *J. Chem. Soc., Dalton Trans.*, 1071 (1983).
152. W. L. Dorn, A. Knoechel, P. Schulz and G. Klar, *Z. Naturforsch., Teil B*, **31**, 1043 (1976).
153. F. Bigoli, E. Leporati, M. A. Pellinghelli, G. Crisponi, P. Delplano and E. F. Trogu, *J. Chem. Soc., Dalton Trans.*, 1763 (1983).
154. J. Passmore, E. K. Richardson and P. Taylor, *J. Chem. Soc., Dalton Trans.*, 1006 (1979).
155. I. P. Romm, I. V. Oliferenko, E. N. Gur'yanova, V. V. Troitsky, V. A. Chernoplekova, L. M. Kataeva and E. G. Kataev, *Zh. Obshch. Khim.*, **53**, 477 (1983).
156. I. V. Oliferenko, I. P. Romm, E. N. Gur'yanova, V. V. Troitsky, L. M. Kataeva, V. A. Chernoplekova and E. G. Kataev, *J. Organomet. Chem.*, **265**, 27 (1984).
157. R. Pellicciari, M. Curini, P. Ceccherelli and R. Fringuelli, *J. Chem. Soc., Chem. Commun.*, 440 (1979).
158. L. Y. Chia and W. R. McWhinnie, *J. Organomet. Chem.*, **148**, 165 (1978).
159. R. T. Mehdi and J. D. Miller, *J. Chem. Soc., Dalton Trans.*, 1065 (1984).
160. H. J. Reich, *Acc. Chem. Res.*, **12**, 22 (1979).
161. A. Krief, W. Dumont, A. Cravador, J. N. Dennis, S. Halozy, L. Hevesi, D. Labor, J. Lucchetti and J. Remion, *Bull. Soc. Chim. Fr.*, 519 (1980).
162. D. Liotta, in Ref. 9, pp. 278–296.
163. J. Bergman, *Tetrahedron*, **28**, 3323 (1972).
164. J. Bergman, in Ref. 9, pp. 215–241.
165. D. L. J. Clive, P. C. Anderson, N. Moss and A. Singh, *J. Org. Chem.*, **47**, 1641 (1982).
166. S. Halazy and A. Krief, *Tetrahedron Lett.*, 4233 (1979).
167. S. Rancher and G. A. Koolpe, *J. Org. Chem.*, **43**, 4252 (1978).
168. W. Dumont, P. Bayet and A. Krief, *Angew. Chem.*, **86**, 857 (1974).
169. H. J. Reich, S. K. Shah and F. Chow, *J. Am. Chem. Soc.*, **101**, 6648 (1979).
170. H. J. Reich and S. K. Shah, *J. Am. Chem. Soc.*, **97**, 3250 (1975).
171. D. L. J. Clive, G. J. Chittattu, V. Farina, W. A. Keil, S. M. Meuchen, C. G. Russell, A. Singh, Chi Kwong Wong and N. J. Curtis, *J. Am. Chem. Soc.*, **102**, 4438 (1980).
172. H. J. Reich, J. M. Renga and I. L. Reich, *J. Am. Chem. Soc.*, **97**, 5434 (1975).
173. H. J. Reich, I. L. Reich and J. M. Renga, *J. Am. Chem. Soc.*, **95**, 5813 (1973).
174. K. B. Sharpless, R. F. Laver and A. Y. Teranishi, *J. Am. Chem. Soc.*, **95**, 6137 (1973).
175. K. B. Sharpless, in Ref. 7, pp. 9–13.
176. L. Engman, *Tetrahedron Lett.*, **23**, 3601 (1982).

177. (a) M. Sevrin, J. N. Davis and A. Krief, *Tetrahedron Lett.*, **21**, 1877 (1980); (b) A. Toshimitsu, H. Owada, K. Terao and S. Uemura, *J. Org. Chem.*, **49**, 3796 (1984); (c) S. Uemura and S. I. Fukuzawa, *J. Chem. Soc., Perkin Trans. 1*, 471 (1985).
178. D. Seebach and A. K. Beck, *Angew. Chem.*, **86**, 859 (1974).
179. W. Dumont and A. Krief, *Angew. Chem.*, **87**, 347 (1975).
180. D. Van Erde and A. Krief, *Tetrahedron Lett.*, 457 (1976).
181. S. Uemura, S. Fukuzawa and A. Toshimitsu, *J. Chem. Soc., Chem. Commun.*, 1501 (1983).
182. J. Martens and K. Praefcke, *J. Organomet. Chem.*, **198**, 321 (1980).
183. G. Ahlgren, B. Åkermark and M. Nils, *J. Organomet. Chem.*, **30**, 303 (1971).
184. J. Bergman, *Acta Chem. Scand.*, **22**, 1883 (1968).
185. A. G. Schultz, *J. Org. Chem.*, **40**, 3466 (1975).
186. J. L. Fourrey, G. Henry and P. Jovin, *Tetrahedron Lett.*, 455 (1980).
187. J. P. Le Roux, P. L. Desbene and M. Seguin, *Tetrahedron Lett.*, 3141 (1976).
188. W. Lohner, J. Martens, K. Praefcke and H. Simon, *J. Organomet. Chem.*, **154**, 263 (1978).
189. L. Hevesi and A. Krief, *Angew. Chem.*, **88**, 413 (1976).
190. M. A. K. Ahmed, P. Granger and W. R. McWhinnie, *Polyhedron*, **5**, 859 (1986).
191. J. Y. C. Chu, D. G. Marsh and W. H. H. Gunther, *J. Am. Chem. Soc.*, **97**, 4905 (1975).
192. U. Schmidt, A. Muller and K. Markau, *Chem. Ber.*, **97**, 405 (1964).
193. K. H. Spencer and M. P. Cava, *J. Org. Chem.*, **42**, 2937 (1977).
194. Z. Monsef-Mirzai, *PhD Thesis*, University of Aston in Birmingham, 1982.
195. R. J. Cross and D. Millington, *J. Chem. Soc., Chem. Commun.*, 455 (1975).
196. D. H. Brown, R. J. Cross and D. Millington, *J. Chem. Soc., Dalton Trans.*, 159 (1977).
197. J. Y. C. Chu and D. G. Marsh, *J. Org. Chem.*,**41**, 3204 (1976).
198. D. H. Brown, R. J. Cross and D. Millington, *J. Organomet. Chem.*, **125**, 219 (1977).
199. G. Vermeersch, N. Febray-Garot, S. Caplain, A. Couture and A. Lablanche-Combier, *Proc. IUPAC Symp. Photochem. 7th*, 347 (1978); *Chem. Abstr.*, **90**, 120645u (1979).
200. M. K. Chaudhuri, A. Haas and A. Wensky, *J. Organomet. Chem.*, **116**, 323 (1976).
201. J. Bergman, N. Eklund, T. E. Eriksen and J. Lind, *Acta Chem. Scand., Ser. A*, **32**, 455 (1978).
202. A. B. Pierini and R. A. Rossi, *J. Organomet. Chem.*, **168**, 163 (1978).
203. H. J. Gysling, *Coord. Chem. Rev.*, **42**, 133 (1982).
204. H. J. Gysling, in Ref. 9, pp. 32–82.
205. S. Ahrland, J. Chatt and N. R. Davies, *Q. Rev. Chem. Soc.*, **12**, 265 (1958).
206. R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).
207. L. W. Houk and G. R. Dobson, *Inorg. Chem.*, **5**, 2119 (1966).
208. F. Faraone, R. Pietropaolo and S. Sergi, *J. Organomet. Chem.*, **24**, 797 (1970).
209. S. A. Gardner, *J. Organomet. Chem.*, **190**, 289 (1980).
210. P. E. Skakke and S. E. Rasmussen, *Acta Chem. Scand.*, **24**, 2634 (1970).
211. V. Rattanaphani, *PhD Thesis*, University of Aston in Birmingham, 1973.
212. H. J. Gysling, H. R. Luss and D. L. Smith, *Inorg. Chem.*, **18**, 2696 (1979).
213. R. K. Chadha and J. E. Drake, *J. Organomet. Chem.*, **286**, 121 (1985).
214. Y. Hayashi, T. Arahawa, T. Shiga, M. Ozaki, H. Kobayashi (Asahi Chem. Ind. Co. Ltd.), *Jpn. Kokai*, 78 65, 827 (1978); *Chem. Abstr.*, **89**, 146588 (1978).
215. E. W. Abel, K. G. Orrell and A. W. G. Platt, *J. Chem. Soc., Dalton Trans.*, 2435 (1983).
216. E. W. Abel, A. R. Khan, Kite, K. G. Orrell and V. Šik, *J. Chem. Soc., Dalton Trans.*, 2208 (1980).
217. E. W. Abel, K. Kite, K. G. Orrell, V. Šik and B. L. Williams, *J. Chem. Soc., Dalton Trans.*, 2439 (1981).
218. J. Korp, I. Bernal, J. L. Atwood, F. Calderazzo and D. Vitali, *J. Chem. Soc., Dalton Trans.*, 1492 (1979).
219. F. Calderazzo, D. Vitali, R. Poli, J. L. Atwood, R. D. Rodgers, J. M. Cummings and I. Bernal, *J. Chem. Soc., Dalton Trans.*, 1004 (1981).
220. E. W. Abel, S. K. Bhargava, P. K. Mittal, K. G. Orrell and V. Šik, *J. Chem. Soc., Dalton Trans.*, 1561 (1985).
221. I. Davies and W. R. McWhinnie, *Inorg. Nucl. Chem. Lett.*, **12**, 763 (1976).
222. A. Z. Al-Rubaie and W. R. McWhinnie, *J. Organomet. Chem.*, **235**, 59 (1982).
223. E. W. Abel, S. K. Bhargava, K. Kite, K. G. Orrell, V. Šik and B. L. Williams, *Polyhedron*, **1**, 289 (1982).
224. E. W. Abel, S. K. Bhargava, K. Kite, K. G. Orrell, V. Šik and B. L. Williams, *J. Chem. Soc., Dalton Trans.*, 583 (1982).

225. G. Dyer and D. W. Meek, *Inorg. Chem.*, **6**, 149 (1967).
226. W. Levason, C. A. McAuliffe and S. G. Murray, *J. Chem. Soc., Dalton Trans.*, 269 (1976).
227. E. Uhlig, B. Borek and H. Glänzer, *Z. Anorg. Allg. Chem.*, **348**, 189 (1966).
228. H. J. Gysling and H. R. Luss, *Organometallics*, **3**, 596 (1984).
229. H. M. K. K. Pathirana and W. R. McWhinnie, unpublished observations.
230. R. S. Drago, *J. Chem. Educ.*, **51**, 300 (1974).
231. I. Davies, W. R. McWhinnie, N. S. Dance and C. H. W. Jones, *Inorg. Chim. Acta*, **29**, L203 (1978).
232. F. W. B. Einstein, C. H. W. Jones, T. Jones and R. D. Sharma, *Inorg. Chem.*, **22**, 3925 (1983).
233. J. D. McCullough, G. Y. Chao and D. E. Zuccaro, *Acta Crystallogr.*, **12**, 815 (1959).
234. C. A. Heller, R. A. Zingaro and E. A. Meyers, *Can. J. Chem.*, **52**, 3814 (1974).
235. D. P. Rainville, R. A. Zingaro and J. P. Ferroris, *Can. J. Chem.*, **58**, 1133 (1980).
236. H. B. Singh, W. R. McWhinnie, R. F. Ziolo and C. H. W. Jones, *J. Chem. Soc., Dalton Trans.*, 1267 (184).
237. J. D. Wright and Z. A. Ahmad, *Acta Crystallogr., Sect. B*, **37**, 1848 (1981).
238. D. J. Sandaman, J. C. Stark, M. Rubner, G. P. Hamill, L. A. Acampora, L. A. Samuelson, M. A. McGrath and G. W. Allen, in Ref. 9, pp. 637–670.
239. A. V. Zvarykina, L. A. Kushch, V. N. Laukhin, O. L. Lependina, I. M. Yanovskaya and E. B. Yagubskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1625 (1983).
240. D. J. Sandman, J. C. Stark, M. Rubner, L. A. Acampora, L. A. Samuelson and B. M. Foxman, *Mol. Cryst. Liq. Cryst.*, **93**, 293 (1983).
241. P. Granger and S. Chapelle, *J. Magn. Reson.*, **39**, 329 (1980).
242. D. B. Denney, D. Z. Denney, P. J. Hammond and Y. F. Hsu, *J. Am. Chem. Soc.*, **103**, 2340 (1981).
243. M. Baiwir, in Ref. 9, pp. 406–467.
244. P. Granger, in Ref. 8, pp. 303–316.
245. D. H. O'Brien, K. J. Irgolic and C. K. Huang, in Ref. 9, pp. 468–491. *See also*: D. H. O'Brien, N. Dereu, R. A. Grigsby, K. J. Irgolic and F. F. Knapp, Jr., *Organometallics*, **1**, 513 (1982).
246. W. McFarlane and R. J. Wood, *J. Chem. Soc., Dalton Trans.*, 1397 (1972).
247. G. Llabres, M. Baiwir, L. Christiaens, J. Densel, L. Laitem and J. L. Piette, *Can. J. Chem.*, **56**, 2008 (1978).
248. G. A. Kalabin, D. F. Kushnarev, G. A. Chmutova and L. V. Kashurnikova, *Zh. Org. Khim.*, **15**, 24 (1979).
249. R. K. Chadha and J. M. Miller, *Can. J. Chem.*, **60**, 2256 (1982).
250. C. H. W. Jones and R. D. Sharma, *J. Organomet. Chem.*, **255**, 61 (1983).
251. H. J. Gysling, N. Zumbulyadis and J. A. Robertson, *J. Organomet. Chem.*, **209**, C41 (1981).
252. H. M. K. K. Pathirana, W. R. McWhinnie and P. Granger, unpublished observations.
253. R. K. Chadha and J. M. Miller, *J. Chem. Soc., Dalton Trans.*, 117 (1982).
254. A. Forchioni, V. Galasso, K. J. Irgolic and G. Pappalardo, *J. Organomet. Chem.*, **135**, 327 (1977).
255. N. Zumbulyadis and H. J. Gysling, *Inorg. Chem.*, **21**, 564 (1982).
256. R. H. Mitchell, *Tetrahedron Lett.*, 1363 (1975).
257. K. R. Dixon and R. H. Mitchell, *Can. J. Chem.*, **61**, 1598 (1983).
258. V. I. Naddaka, I. I. Logacheva and V. S. Yur'eva, *Zh. Org. Khim.*, **12**, 2606 (1976).
259. K. Ohno, T. Hirokawa, S. Aono and H. Murata, *Bull Chem. Soc. Jpn.*, **50**, 305 (1977).
260. J. R. Allkins and P. J. Hendra, *Spectrochim. Acta*, **22**, 2075 (1966).
261. J. R. Allkins and P. J. Hendra, *Spectrochim. Acta, Part A*, **24**, 1305 (1968).
262. N. S. Dance and W. R. McWhinnie, *J. Chem. Soc., Dalton Trans.*, 43 (1975).
263. K. Ohno, A. Mitsui and H. Murata, *Bull. Chem. Soc. Jpn.*, **52**, 2178 (1979).
264. K. Hamada and H. Morishita, *J. Mol. Struct.*, **44**, 119 (1975).
265. D. C. McKean and J. L. Duncan, *J. Mol. Struct.*, **51**, 149 (1979).
266. C. H. W. Jones, R. Schultz, W. R. McWhinnie and N. S. Dance, *Can. J. Chem.*, **54**, 3234 (1976).
267. F. J. Berry, E. H. Kustan and B. C. Smith, *J. Chem. Soc., Dalton Trans.*, 1323 (1975).
268. F. J. Berry, C. H. W. Jones and W. R. McWhinnie, in Ref. 9, pp. 492–506.

CHAPTER **14**

Organic selenocyanates and tellurocyanates and related compounds

AKIO TOSHIMITSU AND SAKAE UEMURA

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan

I. INTRODUCTION

The chemistry on selenocyanates and related compounds has been reviewed by Bulka[1], the literature coverage being up to 1973. Since then, this field has grown steadily and much progress has been achieved in the use of organic selenocyanates and in the chemistry of

organic tellurocyanates. This chapter deals with recent advances in this field after 1973, focusing mainly on the preparation, properties and reactions of organic selenocyanates (RSeCN), isoselenocyanates (RN=C=Se) and tellurocyanates (RTeCN), where R is any organyl group. The literature coverage is nearly complete up to the end of 1985.

II. ORGANIC SELENOCYANATES

A. Preparation

1. By exchange of halogen

The substitution of halogen by a selenocyanato group is known as a general route for the preparation of alkyl selenocyanates. The reaction has been utilized in the identification of alkyl iodide[2] produced by the ring opening of a selenetane as shown in equation 1. Potassium and sodium selenocyanates are normally used as a source of selenocyanate. They are conveniently prepared by the reaction of potassium and sodium cyanides with selenium in dimethylformamide[3] or N, N-dimethylacetamide[4].

The preparation and fungicidal effect of the furfuryl selenocyanate derivative 1 has been reported[5,6]. This reaction also proceeds when the alkyl halide bears a hydroxy[7] or isothiocyanato[8] group on the β-carbon atom. In the case of 1,3-dibromopropan-2-ol, however, only one bromine atom was substituted by an excess of selenocyanate to afford 1-bromo-3-selenocyanatopropan-2-ol (2) (equation 2)[9]. When the alkyl halide has an alkyl-[10] or aryl-seleno[11] substituent on the β-carbon atom, the selenocyanate ion attacks the selenium atom of an episelenonium ion intermediate (3) to afford an alkylselenenyl selenocyanate which decomposes to elemental selenium and 2-bromoethyl selenocyanate, and the latter reacts with potassium selenocyanate to produce bis(selenocyanato)ethane (equation 3). The substitution of halogen α to carbonyl has been utilized in the preparation of α-selenocyanatocarbonyl compounds[12-14]. A kinetic study of the substitution of bromine of 2-bromo-1-phenylethanone by selenocyanate in acetonitrile revealed that the reaction was almost 20 times faster than that of methyl iodide, owing to acceleration by the presence of the α-carbonyl group[15]. The rate and equilibrium constants of similar reactions were compared (equation 4), and the nucleophilicity order was found to be $NCSe^- \geqslant NCS^- > Cl^- \gg Br^-$ and the leaving group ability was $Br^- \gg Cl^- > NCSe^- > NCS^-$[16]. A similar reactivity order was also observed in the substitution reactions of benzyl halides by pseudohalide anions[17,18].

$$\text{Se} + \text{MeI} \longrightarrow \text{MeSeCH}_2\overset{\text{Me} \quad \text{Me}}{\underset{|}{\text{C}}}\text{CH}_2\text{I} \xrightarrow{\text{KSeCN}} \text{MeSeCH}_2\overset{\text{Me} \quad \text{Me}}{\underset{|}{\text{C}}}\text{CH}_2\text{SeCN}$$

(1)

$$O_2N \quad\diagdown\!\!\!\!\diagup O \diagdown\!\!\!\!\diagup \quad CH_2SeCN$$

(1)

$$\text{BrCH}_2\underset{|}{\text{C}}\text{HCH}_2\text{Br} + 2\,\text{KSeCN} \longrightarrow \text{BrCH}_2\underset{|}{\text{C}}\text{HCH}_2\text{SeCN}$$
$$\quad\quad\quad\text{OH} \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\text{OH}$$

(2)

(2)

$$BrCH_2CH_2SeCH_2CH_2Br \ + \ KSeCN \ \longrightarrow \left[\begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix} \diagdown \overset{+}{Se} - CH_2CH_2Br \right] \ Br^-$$

$$-SeCN^-$$

(3)

$$\longrightarrow \ [BrCH_2CH_2SeSeCN] \ + \ CH_2{=}CH_2 \ + \ KBr \tag{3}$$

$$Se \ +BrCH_2CH_2SeCN \ \xrightarrow{\ KSeCN\ } \ NCSeCH_2CH_2SeCN$$

$$PhCCH_2X \ + \ Y^- \ \underset{\xleftarrow{\hspace{2cm}}}{\overset{MeCN}{\xrightarrow{\hspace{2cm}}}} \ PhCCH_2Y \ + \ X^- \tag{4}$$
$$\underset{O}{\overset{\|}{}} \qquad\qquad\qquad \underset{O}{\overset{\|}{}}$$

$$X = Cl, Br$$
$$Y = SeCN, SCN$$
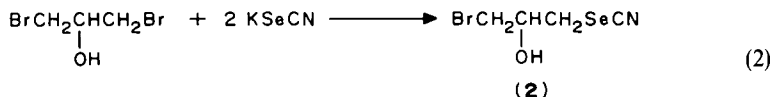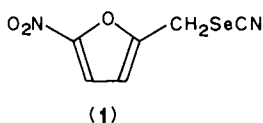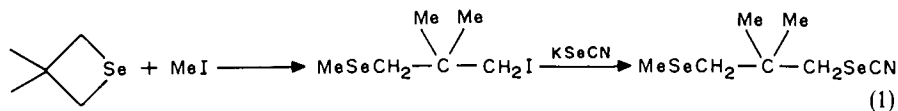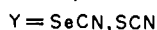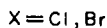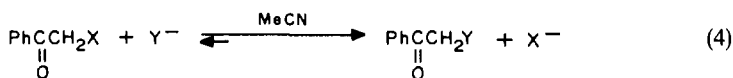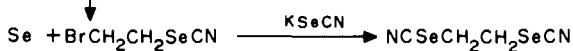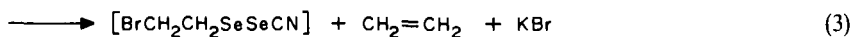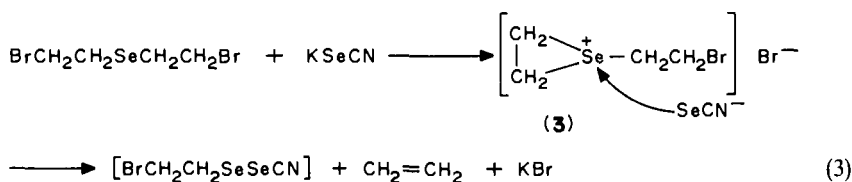
The reaction of iodonium ion with potassium selenocyanate has been utilized in the preparation of perfluoroalkyl selenocyanate[19], the leaving group being iodobenzene in this case (equation 5). The reaction of an epiiodonium ion with a selenocyanate ion has also been reported (equation 6)[20].

$$\overset{+}{PhI}C_3F_7 \ + \ KSeCN \ \xrightarrow{\ DMF\ } \ C_3F_7SeCN \ + \ PhI \ + \ KCl \tag{5}$$
$$Cl^-$$

$$\bigcirc \ + \ ISeCN \ \longrightarrow \ \left[\bigcirc \overset{+}{\hspace{2mm}} \ + \ I \ + \ SeCN^- \right]$$

$$\longrightarrow \quad \underset{49\%}{\text{(I, SeCN)}} \quad + \quad \underset{2\%}{\text{(SeCN, SeCN)}} \quad + \quad \underset{2\%}{\text{(I, NCSe)}} \tag{6}$$
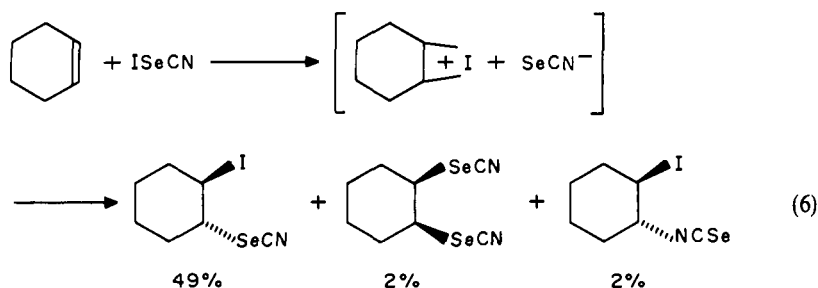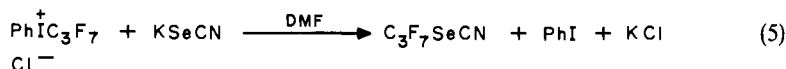
There are several examples of the substitution of an oxygen functional group by a selenocyanato group. Thus, the conversion of alcohols to alkyl selenocyanates by reaction with triphenylphosphine and selenocyanogen has been reported and the substitution of oxygen by SeCN was postulated as shown in equation (7)[21]. A tosyl group has also been utilized as a leaving group in the preparation of alkyl selenocyanates[22,23].

$$Ph_3P \ + \ (SeCN)_2 \ \longrightarrow \ Ph_3P(SeCN)_2$$

$$ROH \ + \ Ph_3P(SeCN)_2 \ \longrightarrow \ \left[\begin{matrix} Ph_3\overset{+}{P}{-}SeCN \\ | \\ O{-}R \end{matrix} \right] \ + \ HSeCN \tag{7}$$

$$RSeCN \ + \ Ph_3P{=}O$$
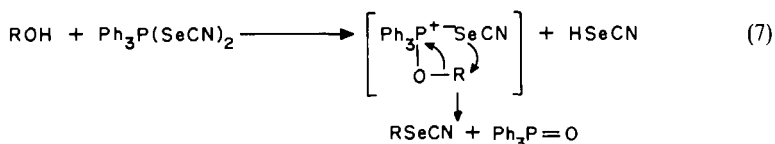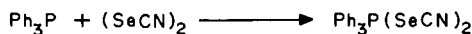
Displacement of chlorine of an acyl chloride has been carried out with sodium selenocyanate in the preparation of the fungicidal 2,4-disubstituted allophanoyl selenocyanate 4 (equation 8)[24].

$$\text{PhNHCNC} \overset{O}{\underset{\underset{O\,Me}{\|\,|}}{}} \text{Cl} \;+\; \text{NaSeCN} \longrightarrow \text{PhNHCNC} \overset{O}{\underset{\underset{O\,Me}{\|\,|}}{}} \text{SeCN} \;+\; \text{NaCl} \qquad (8)$$

(4)
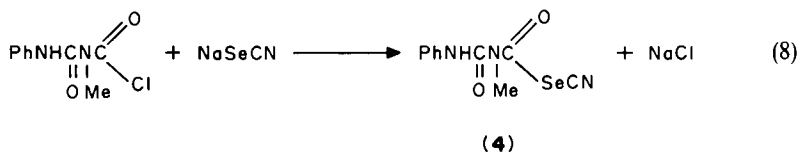
A bromine bound to the vinyl carbon of a cyclobutenedione derivative was substituted by a SeCN to afford the corresponding selenocyanate (5) (equation 9)[25].

(5)
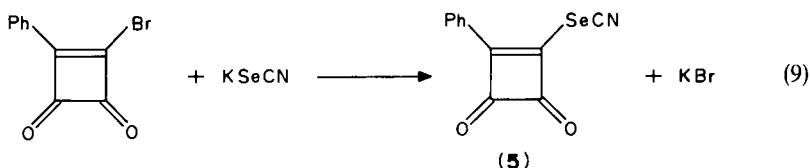
It is known that the halogen in an aromatic halide is substituted by a selenocyanate ion if the aromatic halide is activated by electron-withdrawing substituents. It was reported that halomethylsulphonyl groups enhanced the displacement of aromatic halogen (X), whereas the a halogen (X') of the halomethyl group itself resisted the displacement as shown in equation (10)[26]. The reaction of potassium selenocyanate with 2-nitro-3-bromo-thiophene or -selenophene has also been reported to afford the substitution products[27]. UV irradiation was found to be effective for the substitution of a halogen or sulphonyl group of aromatic compounds by a selenocyanate ion[28,29]. A characteristic feature of this photo-reaction is that aromatic selenocyanates bearing electron-donating substituents such as amino or alkoxy groups can be prepared by this procedure. Copper(I) iodide catalyses the reaction of non-activated aryl iodide with potassium selenocyanate and the reaction was utilized in the preparation of polyalkylated aromatic selenocyanates (equation 11)[30,31].

$$X = Cl, Br, I$$
$$X' = Cl, Br$$
$$R = NO_2, H$$

$$+ \; KSeCN \xrightarrow{\;CuI-HMPA\;} \qquad\qquad + \; KI \qquad (11)$$
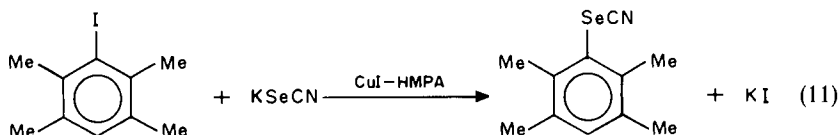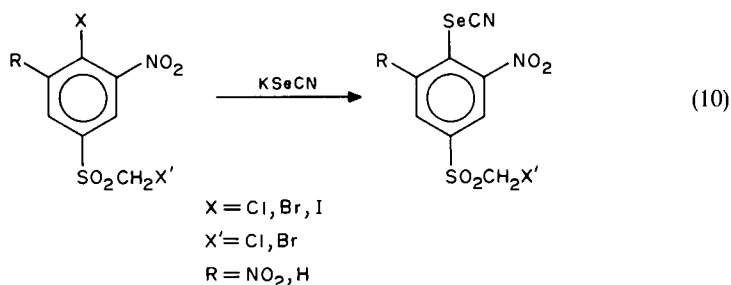
The substitution of a halogen of disubstituted azulenes by a selenocyanato group of $Cu(SeCN)_2$ was examined (equation 12)[32]. The reaction rates decreased in the order $R = MeO > Ph > COPh > SO_2Ph > NO_2$. This reaction was assumed to proceed through one-electron transfer to form a radical anion, which then reacted with $[Cu(SeCN)_2]^{+\cdot}$.

$$X = I, Br, Cl$$
$$R = OMe, Ph, COPh, SO_2Ph, NO_2$$

(12)
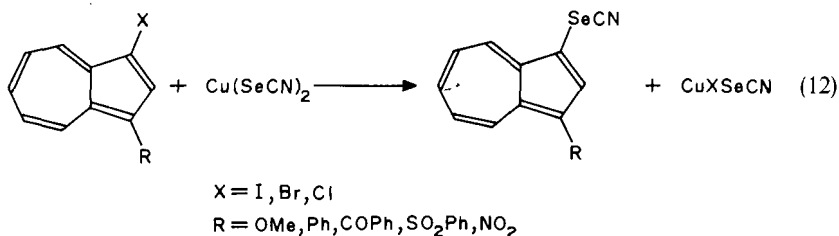
2. From diazonium salts

The reaction of diazonium salts with potassium (or sodium) selenocyanate is the most reliable procedure for the preparation of aromatic selenocyanates. Not only phenyl selenocyanate derivatives bearing various substituents[4,33–37] but also selenocyanato-thiophene and -selenophene derivatives[38] (equation 13) were prepared by this procedure. This reaction is feasible with diazotized poly(p-aminostyrene), providing a route to polymer-supported selenium reagents[39].

$$X = S, Se$$
$$R = CHO, COMe, NO_2$$

(13)
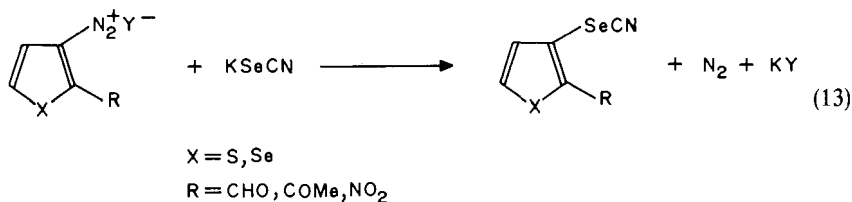
3. From organometallic compounds

The reaction of arylthallium(III) compounds (6) with a mixture of copper(II) sulphate and potassium selenocyanate affords aryl selenocyanates in good to excellent yields (equation 14)[40,41]. In the absence of a copper(II) salt, the yields of arylselenocyanates were poor. When arylmercury(II) compounds were used, the results were unsatisfactory owing to side reactions of aryl selenocyanate with the starting materials[42]. In the case of alkylthallium(III) compounds (7), a thallium(III) group was replaced by a selenocyanato group by treatment with only potassium selenocyanate. This reaction was utilized in a one-pot conversion of olefins to β-alkoxyalkyl selenocyanates (equation 15)[40,43].

$$p\text{-}RC_6H_4TlXY + Cu(SO_4)_2 + KSeCN \longrightarrow p\text{-}RC_6H_4SeCN$$

$$(6)$$

$$R = H, Me, MeO$$
$$X, Y = ClO_4, OAc$$
$$(CF_3COO)_2$$
$$(CCl_3COO)_2$$

(14)

$$\text{C}=\text{CH}_2 \; + \; \text{Tl(OAc)}_3 \xrightarrow{\text{ROH}} \left[\begin{array}{c} \text{RO} \\ \diagdown \\ \text{C}-\text{CH}_2\text{Tl(OAc)}_2 \\ \diagup \end{array} \right]$$

(7)

$$\xrightarrow{\text{KSeCN}} \begin{array}{c} \text{RO} \\ \diagdown \\ \text{C}-\text{CH}_2\text{SeCN} \\ \diagup \end{array}$$

(15)

Trialkylboranes react with potassium selenocyanate (2 equiv.) in the presence of Fe^{3+} ion (2 equiv.) in an aqueous solvent to afford alkyl selenocyanates (equation 16)[44]. When mixed trialkylboranes were used as starting materials, tertiary or secondary alkyl groups reacted prior to primary alkyl groups[45].

$$\text{R}_3\text{B} \; + \; 2\,\text{KSeCN} \; + \; \text{Fe}_2(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 24\,\text{H}_2\text{O} \xrightarrow{\text{H}_2\text{O}} \text{RSeCN}$$

(16)

4. By selenocyanation

Electrophilic substitution of 3-substituted thiophenes or selenophenes has been reported to produce 2-selenocyanato-thiophene or -selenophene derivatives (equation 17)[46,47]. Selenocyanogen bromide was prepared in situ by the reaction of potassium selenocyanate and bromine. Dicyanotriselenide was used in the selenocyanation of polystyrene, the selenium content in the product being estimated to be 1.6 mmol g^{-1} (equation 18)[48].

$$\begin{array}{c} \text{R} \end{array} + \text{BrSeCN} \xrightarrow{\text{MeOH}} \begin{array}{c} \text{R} \\ \text{SeCN} \end{array} + \text{HBr}$$

(17)

$$\text{X} = \text{S}, \text{Se}$$
$$\text{R} = \text{OMe}, \text{NH}_2, \text{NHCOMe}, \text{NHCHO}$$

$$\text{P} \text{—} \bigcirc \; + \; \text{Se(SeCN)}_2 \longrightarrow \text{P} \text{—} \bigcirc \diagdown_{\text{SeCN}}$$

(18)

Selenocyanogen was generated electrochemically by anodic oxidation and it reacted with electron-rich olefins to afford bis(selenocyanato) adducts (equation 19)[49], probably by electrophilic addition of an SeCN group. An electrophilic SeCN species was also generated by the reaction of potassium selenocyanate with copper(II) halides. It reacted with olefins to afford β-alkoxyalkyl selenocyanates (8) in alcoholic solvents and β-halogenoalkyl selenocyanates (9) in acetonitrile (equation 20)[50]. The conversion of (9) to (8) was catalysed by copper(I) or -(II) salts and proceeded with retention of configuration, suggesting the intermediacy of an episelenonium ion.

$$\text{SeCN}^- \; - \; \text{e}^- \longrightarrow (\text{SeCN})^{\bullet}$$

$$2\,(\text{SeCN})^{\bullet} \longrightarrow (\text{SeCN})_2$$

(19)

$$\text{ROCH}=\text{CH}_2 \; + \; (\text{SeCN})_2 \longrightarrow \underset{\underset{\text{SeCN}}{|}}{\text{ROCHCH}_2\text{SeCN}}$$

$$
\text{(20)}
$$

Nucleophilic addition to carbon—carbon triple bonds has been utilized in the preparation of vinyl selenocyanates. By the reaction of acetylene carboxylic acid with potassium selenocyanate, cis-β-selenocyanatoacrylic acid was produced through trans-addition of a selenocyanato group and a hydrogen (equation 21)[51]. The attack of selenocyanate on a propargyl bromide derivative was accompanied by loss of bromine to form allenyl selenocyanates (equation 22)[52].

$$
\text{CH} \equiv \text{CCOOH} + \text{KSeCN} \xrightarrow{\text{EtOH}} \quad (21)
$$

$$
\text{(22)}
$$
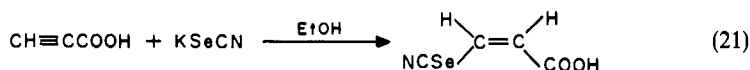
5. By formation of an Se—CN bond

The preparation of selenocyanates by the reaction of certain selenenyl compounds with potassium or silver cyanide is a well known procedure and is often used for the trapping of reactive intermediates or the identification of the products.

Chlorodifluoromethylselenenyl chloride ($F_2CCISeCl$), one of the products of chlorine cleavage of polymerized $Se=CF_2$, when treated with silver cyanide affords chlorodifluoromethyl selenocyanate ($F_2CCISeCN$)[53]. Dichlorofluoromethylselenenyl chloride ($FCCl_2SeCl$), prepared from carbon diselenide, fluorine chloride and chlorine, also reacts with silver cyanide to give $FCCl_2SeCN$[54].

The episelenonium ion 3, when treated with potassium cyanide, produces 2-bromoethyl selenocyanate as a final product[10,55].

UV irradiation or heating of a benzeneselenazole derivative (10) induced its rearrangement to a phenyl selenocyanate bearing the pyridine nucleus in the ortho position (11) (equation 23)[56]. The attack of a cyanide anion on selenium was proposed as the final step of this reaction, as silver cyanide was formed if the reaction was carried out in the presence of silver nitrate.

Both selenenyl bromide and sulphonate afforded the corresponding selenocyanates with potassium cyanide (equation 24)[57].

One of the most convenient procedures for the preparation of phenyl selenocyanate is the reaction of phenylselenenyl chloride with trimethylsilyl cyanide (equation 25)[58,59] at room temperature in dichloromethane or tetrahydrofuran. Essentially pure phenyl

(10)

(23)

(11)

(24)

$$X = Br, SO_2C_6H_4Me$$
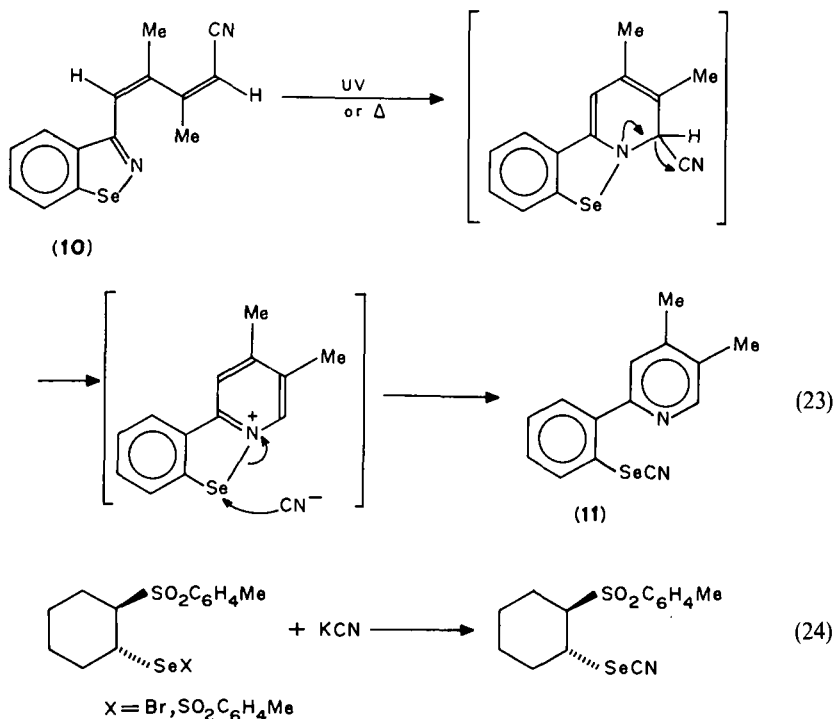
selenocyanate was obtained by evaporation of the solvent and the trimethylsilyl chloride produced.

$$PhSeCl \ + \ Me_3SiCN \ \longrightarrow \ PhSeCN \ + \ Me_3SiCl \tag{25}$$

An example in which selenium acts as a nucleophile in the Se—CN bond-forming reaction (equation 26)[60] is the reaction of aryl methyl selenide with lithium methyl selenide when nucleophilic substitution on methyl carbon gives dimethyl selenide and aryl lithium selenide. The latter was trapped by cyanogen iodide to afford aryl selenocyanate, the arylseleno group reacting as a nucleophile.

$$ArX \xrightarrow{\ MeSeLi\ } [ArSeMe] \xrightarrow{\ MeSeLi\ } [ArSeLi] + MeSeMe$$

$$\downarrow ICN$$

$$ArSeCN \tag{26}$$
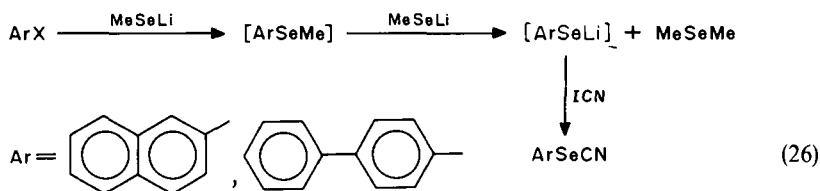
B. Physical Properties

The polarized IR spectra of 4-RC_6H_4SeCN (R = H, NO_2, NH_2) were recorded for a conformational study[61]. It was indicated that the CN group was in the plane of the aromatic ring. The NO_2 group was not coplanar with the ring; the protons of the NH_2

group were both above the ring plane. The IR spectra of $XC_6H_4SeCN(X = H, 4\text{-}F, 4\text{-}Cl,$ 4-Br, 3-F, 3-Cl, 3-Br) were recorded in the range 400–4000 cm^{-1}. The spectra were interpreted in terms of phenyl ring or SeCN group vibrations, with little interaction between the normal modes of the two frameworks[62]. IR and Raman spectra of benzyl selenocyanate was recorded and tentative assignments were proposed[63], based on force fields transferred from similar molecules such as ethyl selenocyanate[64] and ethyl thiocyanate after appropriate scalings.

The UV spectrum of phenyl selenocyanate was compared with those of the analogous cyanate and thiocyanate. All were found to agree well with the results of MO-LCAO calculations[65].

The He(I) photoelectron spectrum of CH_3SeCN was found to exhibit a series of five ionization bands below 15 eV, the first four being assigned to a sequence of n, π and σ orbitals of an SeCN group, based both on empirical correlations with simpler molecules and on semi-empirical and *ab initio* quantum mechanical calculations[66].

The structure of 4-nitrobenzyl selenocyanate and benzyl selenocyanate has been determined by X-ray crystallography[67]. They both exist in the *syn*-clinal (*gauche*) conformation in the solid state. More detailed results for the corresponding tellurocyanate are presented in Section IV.

Microwave spectral measurements were carried out using methyl and ethyl selenocyanates. For the main isotopic species of methyl selenocyanate (^{80}Se, ^{78}Se, ^{77}Se, ^{76}Se, ^{82}Se, ^{12}C and ^{13}C) a full centrifugal distortion analysis was reported[68]. Internal rotation splittings were analysed to give a barrier height to the methyl internal rotation of 1241 ± 50 and 1228 ± 50 cal mol^{-1} for the CH_3 and CD_3 species, respectively[69]. Stark measurements yielded dipole moments of $\mu = 4.42 \pm 0.05$ D for $CH_3{}^{80}SeCN$ and $\mu = 4.36 \pm 0.04$ D for $CD_3{}^{80}SeCN$[69]. Microwave spectroscopic studies of ethyl selenocyanate indicated that the preferred conformation of the linear SeCN group is *syn*-clinal[70].

A conformational study of *para*-substituted phenyl selenocyanates (RC_6H_4SeCN) was carried out by the determination of dipole moments and Kerr constants. The molecule is planar when R is an electron-donating group, while the coplanarity of the C_6H_4SeCN fragment is disputed when R is an electron-withdrawing group[71]. In solutions, *meta*-substituted selenocyanates (12) were a mixture of *syn* (12b) and *anti* (12a) forms; the proportion of the latter and the dihedral angle between the aromatic ring and the SeCN plane increased with increasing electron-withdrawing ability of R. *Ortho*-substituted phenyl selenocyanates (2-RC_6H_4SeCN; R = Me, Cl, Br, NO_2) existed as a planar or nearly planar *anti* conformers[72]. The coplanarity in the bis-selenocyanate $[p\text{-}(SeCN)_2C_6H_4]$ was lower than in the corresponding monosubstituted compound[73].

(12a)   (12b)

R = Me, Cl, Br, NO_2
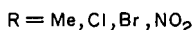
The mass spectrum of *m*-nitrophenyl selenocyanate was compared with that of the corresponding benzeneseleninic acid[74]. In the acid, a peak due to the diselenide was observed in addition to a very weak peak of a molecular ion. The selenocyanate showed an intense molecular ion peak and fragmentation peaks by loss of CN or NO_2, while the peak due to diselenide was of very low intensity. Mass spectral measurements on 2-(selenocyanatomethyl)-3-cyanobenzoselenophene were reported, together with the spectra of other 2,3-disubstituted benzoselenophenes[75].

Selenium-77 magnetic resonance is increasingly becoming a more popular spectroscopic technique. Technical developments of NMR spectroscopy, especially the use of Fourier transformation, have overcome the potential drawbacks such as the low natural abundance of the ^{77}Se isotope (7.58%) and an NMR sensitivity of 6.97×10^{-3} with respect to that of the proton at constant field. Hence ^{77}Se NMR spectra of a number of organoselenium compounds were determined, including organoselenocyanates[76-79]. A range of over 800 ppm was observed for the ^{77}Se chemical shift. The effect of the medium on the shielding of ^{77}Se chemical shifts was examined and it was found that the solvent exerted much less effect than the structure of the selenide[80]. It was reported that *ortho*-substitution by a carbonyl function had a highly deshielding effect on the ^{77}Se nucleus of aryl selenocyanates. In conjunction with the decrease in the carbonyl stretching frequencies in IR spectra, this was attributed to the intramolecular interaction between the carbonyl group and the selenium atom as depicted in 13[81].

R = H, Me, OMe

(13)
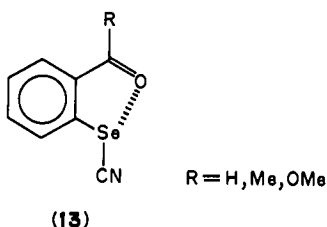
The coupling constants of ^{77}Se with α- and β-^{13}C atoms were determined in RC$_6$H$_4$SeCN (R = H, 2-MeO, 4-NH$_2$, 4-NO$_2$) and compared with those of selenides, diselenides and selenophene. The coupling constants were affected by the hybridization of the carbon atoms, the nature of the substituents and the orientation of the unshared electron pair of the selenium[82].

The ^{13}C NMR spectra of 2-RCOC$_6$H$_4$SeCN (R = H, Me, MeO, EtO) were measured and compared with those of RCOC$_6$H$_5$ and 2-RC$_6$H$_4$SeX. In all cases except one (R = EtO), the phenyl carbon attached to a selenocyanato group was deshielded relative to the *ortho* carbon of RCOC$_6$H$_5$. The variation in the chemical shifts of the phenyl carbon with various X revealed the transmission of the inductive effect of X through the selenium atom[83].

C. Reactions

1. Additions to the C≡N bond

Some cyclization reactions can be regarded as addition to a carbon—nitrogen triple bond. Other cyclization reactions involving the loss of a cyano group are classfied into substitution reactions on a selenium atom and are described in Section II.C.2.

The reaction of hydrazoyl halides with potassium selenocyanate afforded the substitution products 14, which cyclized spontaneously to 1,3,4-selenadiazole derivatives (15) (equation 27)[84]. Treatment of phenacyl selenocyanate with aryldiazonium salts afforded similar intermediates (14; R = PhCO) which underwent the same cyclization[85] as shown in equation 27. When this reaction was applied to the diazonium salts derived from anthranilic acid or its methyl ester, the 1,3,4-selenadiazole derivatives produced were susceptible to further cyclization to give 1,3,4-selenadiazolo[2,3-b]quinazoline derivatives (16) in good yields (equation 28)[86,87].

$$(27)$$

$$(28)$$
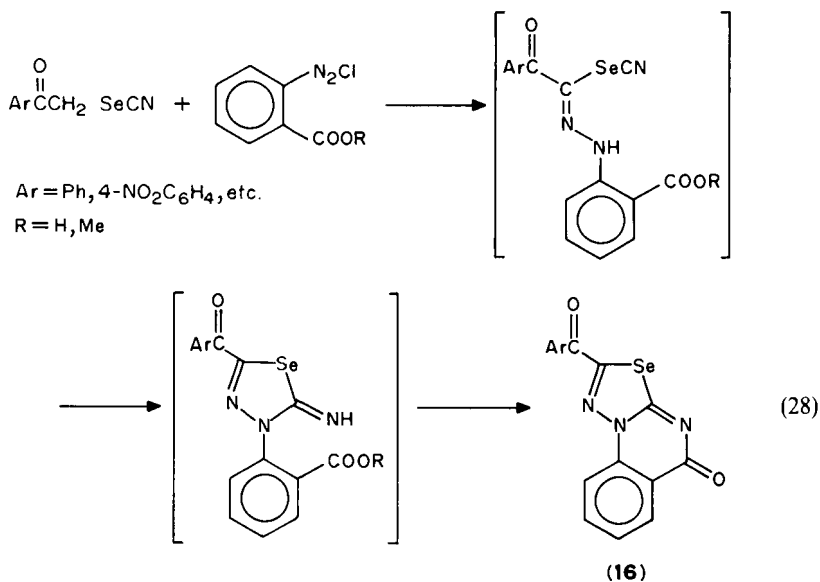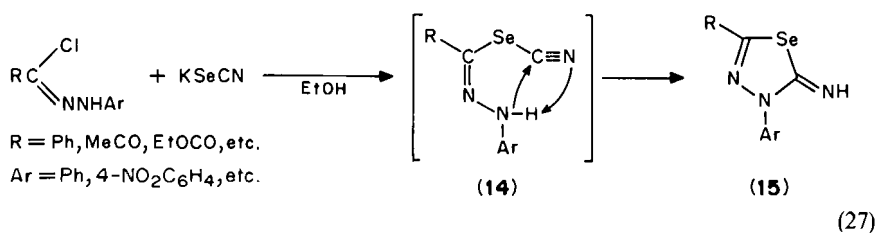
Intramolecular addition of an acyl carbon was also reported. The reaction of cis-β-selenocyanatoacrylic acid with phosphorus pentachloride produced the corresponding acid chloride, which cyclized to 2-chloro-1, 3-selenazin-4-one (equation 29)[51]. Cyclization of a thiazolidin-2-ylidene cyanoacetate derivative was also reported (equation 30)[88].

$$(29)$$

$$(30)$$

Ar = 4-An
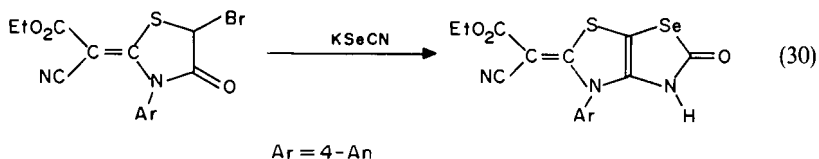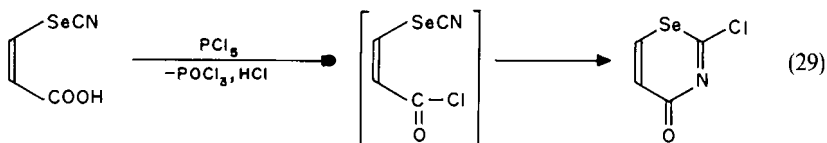
Potassium selenocyanate was used in the stereospecific conversion of epoxides to olefins[89]. The reaction was explained as proceeding through the intramolecular addition of an alkoxide ion to a cyano group to form the cyclic intermediate 17, which afforded the episelenide and then the olefin as shown in equation 31. The same reaction sequence may be included in the cis–trans interconversion of olefins by the use of β-hydroxyalkyl selenocyanates (equation 32)[7]. The preparation of cis-1-propenylphosphonic acid by the deoxygenation of the corresponding epoxide was also reported[90]. 2-N-Acetylimino-1,3-oxaselenoles, which have closely related structures to the postulated intermediate 17, were isolated by the reaction of gem-dicyano epoxides with potassium selenocyanate in acetic anhydride as solvent (equation 33)[91].

(17)

(31)

(32)

(33)
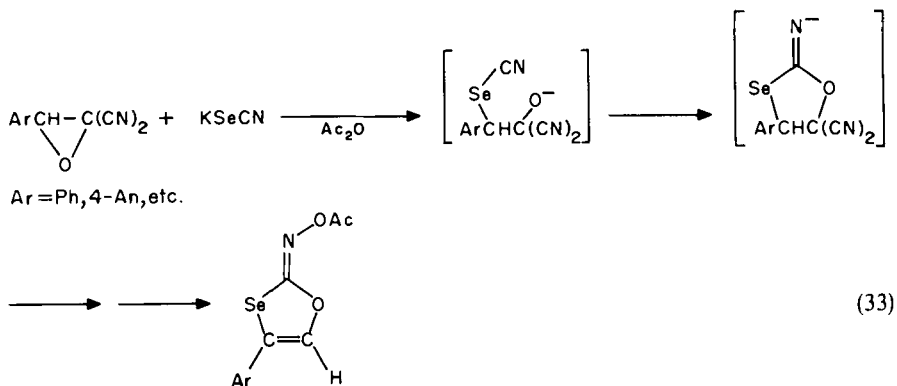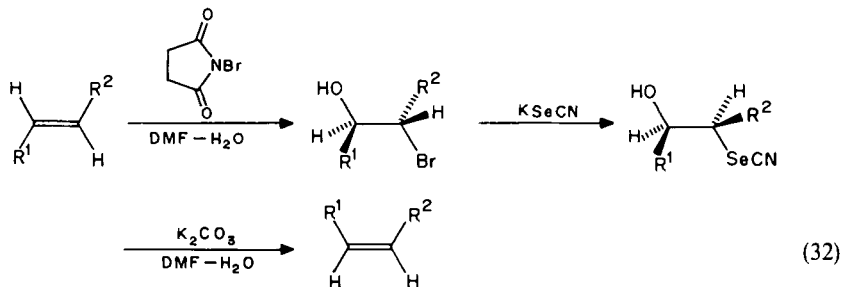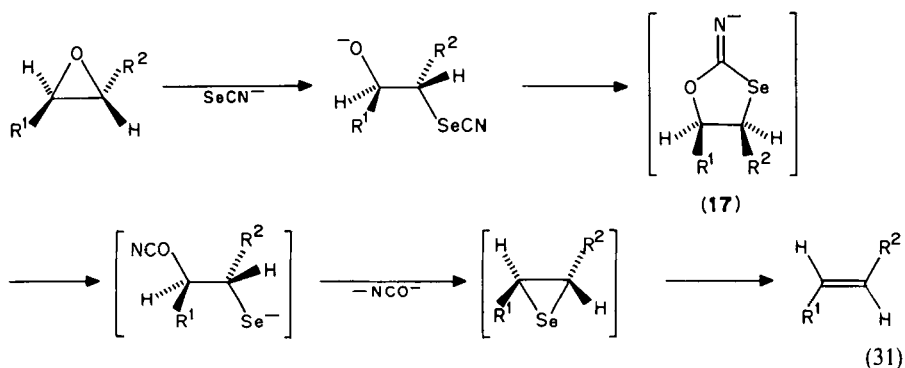
2. Substitution of the CN group

a. Substitution by heteroatoms. By the reaction of aryl selenocyanates with a halogen such as chlorine[37] or bromine[34,35], a cyano group was replaced by the halogen to afford arylselenenyl halides quantitatively, and the corresponding trihalides were formed when two equivalents of a halogen were employed (equation 34)[11].

$$ArSeCN \; + \; X_2 \longrightarrow ArSeX \; + \; XCN$$

$$ArSeCN \; + \; 2\,X_2 \longrightarrow ArSeX_3 \; + \; XCN \qquad (34)$$

$$X = Cl, Br$$
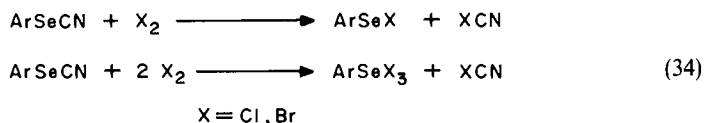
The substitution of a cyano group by a nitrogen atom was also observed. An unsaturated N, N-dimethyliminium salt was treated successively with sodium selenocyanate and an arylamine to afford a 1, 2-selenazolinium salt (equation 35)[92]. The final step was intramolecular substitution of a CN group by a nitrogen atom of the imine. A nitrogen atom of the oxime was also reported to replace the cyano group of aryl selenocyanate to afford cyclization to a benzoselenazole derivative (equation 36)[36].

$$Ar = Ph, 4\text{-}Tol, 4\text{-}An$$

(35)

(36)
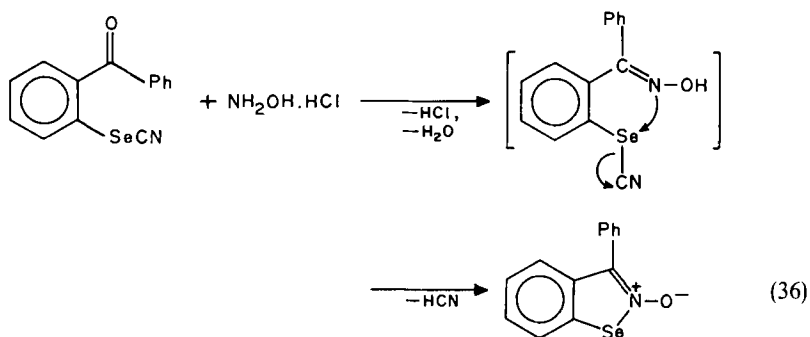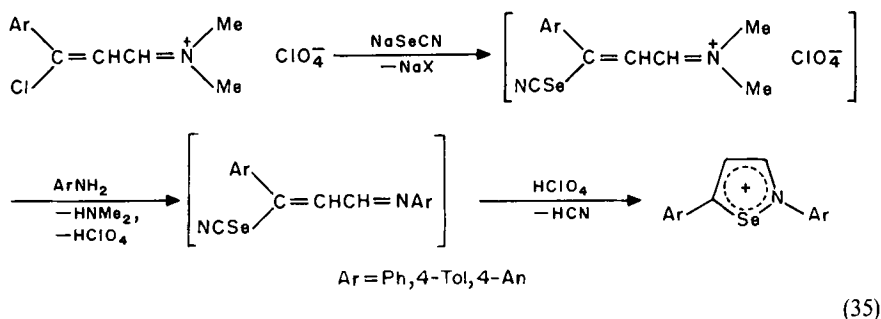
The reactions of o-nitrophenyl selenocyanate with arylthiols were investigated under anhydrous conditions in a nitrogen atmosphere[93]. The products were found to be selenide sulphides (equation 37). When p-nitrophenyl selenocyanate was used as the starting material, however, the product was diphenyl diselenide. The reason for this difference was not clarified.

$$\text{Ar} = 4\text{-Tol}, 4\text{-ClC}_6\text{H}_4, 4\text{-BrC}_6\text{H}_4, 2\text{-HOOCC}_6\text{H}_4 \tag{37}$$
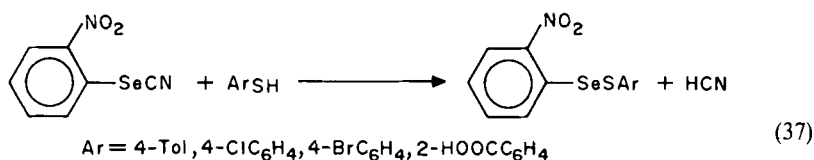
Selenocyanates are easily converted to diselenides in various procedures (equation 38). They include the reduction selenol and subsequent oxidation ($NaBH_4$–air[22], $Na_2S_2O_4$–H_2O_2[94], Na_2S–air[47]) and hydrolysis under acidic[56] or basic[3,21] conditions. Air oxidation might take part in the last reactions. This reaction was utilized in the preparation of diselenide polymers from 4,4'-bis(selenocyanato)azobenzene[95] or -benzene[33] for the study of photoreactions of the polymers. For the preparation of selenacyclophanes, hydrolysis of a selenocyanate shown in equation 39 was adopted, since the intermediate selenocyanates can easily be obtained and purified. The hydrolysis was carried out at high dilution to avoid the formation of linear polymeric diselenides[96].

$$\text{RSeCN} \longrightarrow \text{RSeSeR} \tag{38}$$
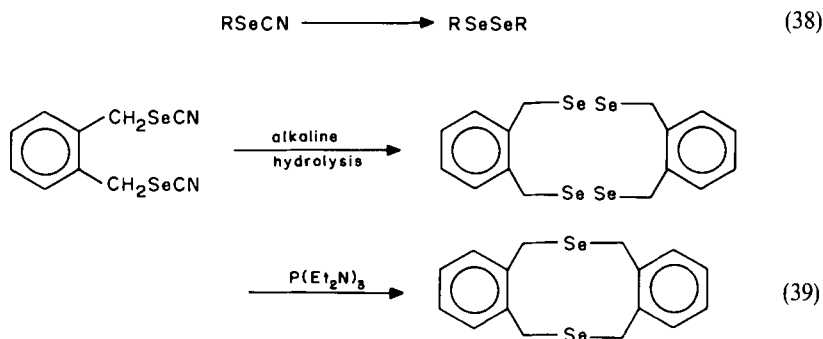
Synthesis of 1,1,4,4-tetramethyl-$1H$,$4H$-selenolo[3,4-c]selenophene was reported using allenyl selenocyanate as a starting material[52]. The first step of this reaction was the formation of diselenide. Subsequent two isomerization reactions afforded the product as shown in equation 40.
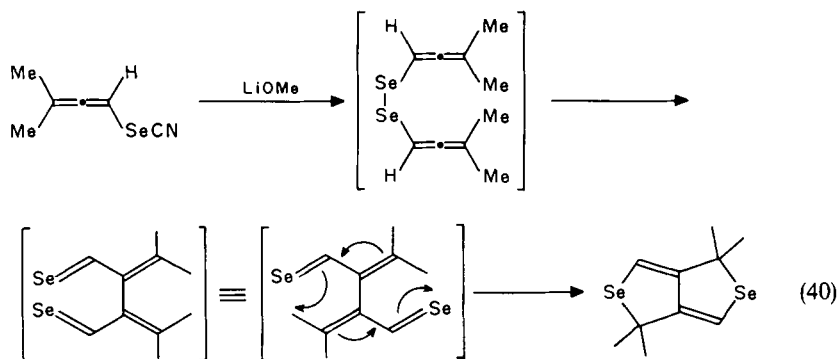
b. *Substitution by carbon atoms.*   The substitution of the cyano group of selenocyanates by a carbon atom was recently recognized as a very important reaction, because it results

in the introduction of an organoselenium group into the carbon atom. This reaction has usually been carried out through reduction of selenocyanates and subsequent reaction with alkyl halides or with their equivalents. Direct substitution by a nucleophilic carbon (a carbanion or its equivalents) is also possible. These reactions are summarized in this section. Two mechanistically different reactions are described in Sections II.C.2.c and d.

As an arylseleno group was usually used as a leaving group in selenoxide elimination reactions[97], many examples of the conversion of aryl selenocyanates to alkyl aryl selenides have been reported. By the reduction of aryl selenocyanates with sodium borohydride, sodium arylselenolates were formed. The subsequent reaction with alkyl halides[98-103] or epoxides[104] afforded alkyl aryl selenides in almost quantitative yields (equation 41). Polymer-bound phenyl selenocyanate was alkylated in a similar manner[39]. This reaction was utilized in the conversion of ethyl 2-bromobutyrate to ethyl crotonate by a combination with selenoxide elimination. After the elimination, the polymer-bound selenium reagent was easily removed by filtration. When benzoyl chloride was used instead of alkyl halide in reaction 41, aryl selenobenzoate was produced[105]. By the reaction of 4-methyl-2-nitrophenyl selenocyanate with sodium borohydride and then with propargyl bromide, aryl propargyl selenide was produced (equation 42)[106]. The difference between this result and that in equation (22) is interesting.

$$ \text{ArSeCN} \xrightarrow[\text{or Na}_2\text{S}]{\text{NaBH}_4} [\text{ArSeNa}] \xrightarrow{\text{RX}} \text{ArSeR} \qquad (41) $$

(42)
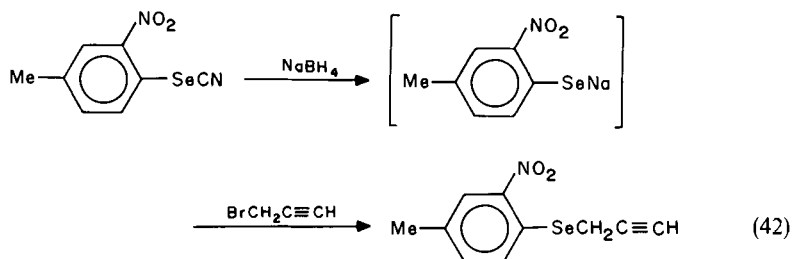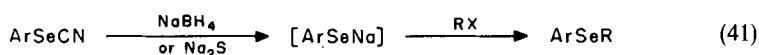
The order of reduction of selenocyanates and addition of halides can be altered. By the addition of a mixture of benzyl selenocyanate and benzyl halide to sodium borohydride in ethanol, dibenzyl selenide was produced almost quantitatively[107]. A similar reaction was carried out under high dilution with two doubly substituted reagents and diselena[3,3]cyclophanes were prepared[108] in yields more than ten times higher than those in the previous procedure[96] (equation 43).

(43)
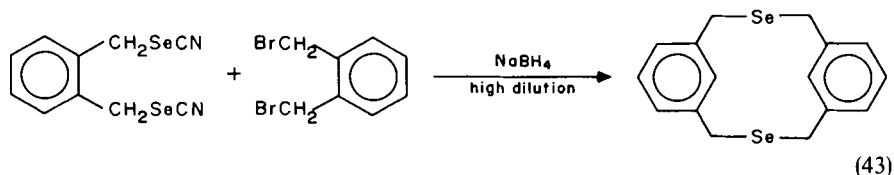
If necessary, it is possible to isolate the intermediate selenium species as a selenol. Thus, benzeneselenol and hexaneselenol were isolated by distillation under nitrogen after quenching by the addition of aqueous hydrogen chloride, the reaction mixture of the selenocyanates with sodium borohydride[109].

The use of reducing agents other than sodium borohydride was also reported.
2-Selenocyanatothiophene or selenophene derivatives (equation 17) were alkylated on the
selenium atom after reduction with sodium sulphide[46,47]. 1, 2-Diselenocyanatoethane was
reduced by hypophosphorous acid to 1,2-ethanediselenol, which was then treated with
thiocarbonyldiimidazole to afford 1, 3-diselenolane-2-thione (18) (equation 44)[3,110].

(18)

(44)
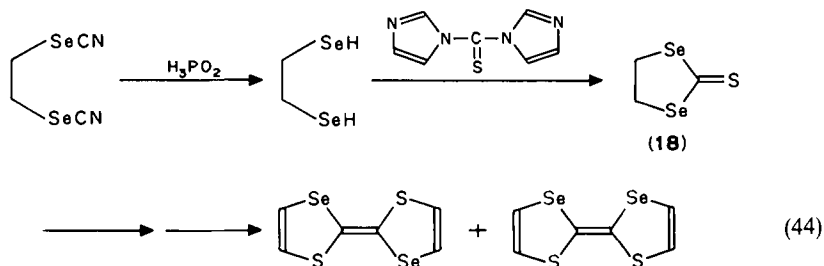
Compound 18 is an important precursor of sym-(E/Z)-diselenadithiafulvalene, the
conductivity of whose TCNQ complex was shown to be $700 \pm 300\,\Omega^{-1}$ at room
temperature.

Aryllithium or arylmagnesium compounds are known to react with aryl selenocyanates
to afford diaryl selenides[1]. This reaction was applied to the preparation of polymer-
bound diaryl selenide using 1% cross-linked polystyryllithium and p-methoxyphenyl
selenocyanate as starting materials (equation 45)[111].

(45)
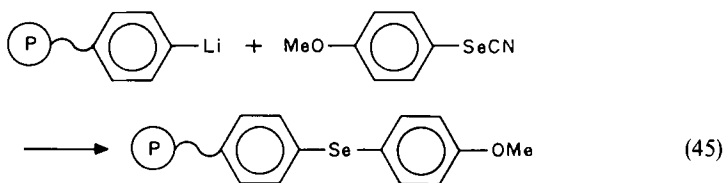
Trichloromethyl anion, generated from chloroform with 50% aqueous NaOH in the
presence of a phase-transfer catalyst, was shown to react with benzyl selenocyanate to give
the substitution product (equation 46)[112]. Benzyl trichloromethyl selenide is a good
precursor of selenium-stabilized carbenes and was used in the preparation of the
(5,10,15,20-tetraphenylporphinato)iron(II)–selenocarbonyl complex (equation 47)[112].
The substitution product was also obtained by the reaction of phenyl selenocyanate with
terminal acetylenes in the presence of triethylamine and copper(I) catalyst
(equation 48)[113]. The role of the copper(I) catalyst was explained to be the formation of
copper(I) acetylide, which then reacted with phenyl selenocyanate.

$$PhCH_2SeCN \;+\; CHCl_3 \xrightarrow[\substack{phase-transfer\\catalyst}]{50\% \text{ aq. NaOH}} PhCH_2SeCCl_3 \qquad (46)$$

$$Fe(TPP) \;+\; PhCH_2SeCCl_3 \xrightarrow[-Cl_2]{Na_2S_2O_4-H_2O} Fe(TPP)\,[C(Cl)SeCH_2Ph]$$

$$\xrightarrow[-PhCH_2Cl]{FeCl_2} Fe(TPP)\,(C{=}Se) \qquad (47)$$

$$PhSeCN + HC\equiv CR \xrightarrow[\text{CuBr cat.}]{\text{2 equiv.Et}_3\text{N}} PhC\equiv CR \qquad (48)$$
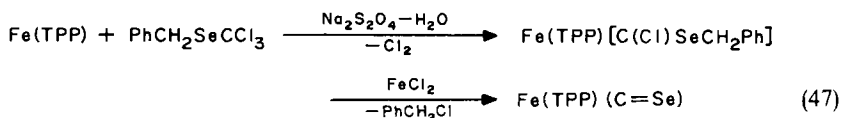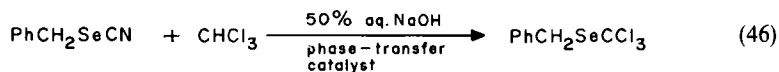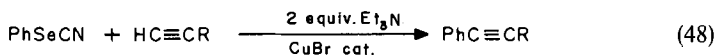
The substitution of a cyano group by an intramolecular carbon nucleophile has been reported. Treatment of 2-acetyl-3-selenocyanatothiophene with ammonia afforded a bicyclic compound (equation 49)[39]. The reaction of 2-acetylphenyl selenocyanate with phenylhydrazine produced benzoselenopheno[3,2-b]indole through the Fischer indole synthesis and cyclization by carbon—selenium bond formation (equation 50)[36].

$$X = S, Se$$

$$(50)$$
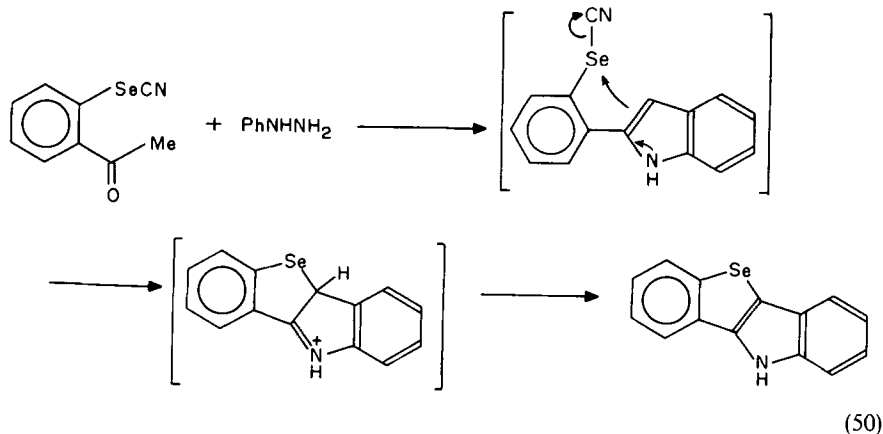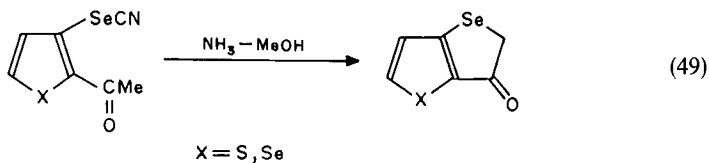
c. *Conversion of alcohol to selenide.* In 1976, Grieco et al.[114] reported the reaction of o-nitrophenyl selenocyanate with alcohols in the presence of tributylphosphine to afford the alkyl o-nitrophenyl selenides in almost quantitative yields (equation 51). Formally, this reaction involves the substitution of a cyano group by an alkyl carbon on the selenium atom, as already mentioned in the previous section. Actually, this reaction seems to proceed through the substitution by a phosphine atom as a first step as shown in Scheme 1, although the formation of Bu_3P^+ $CNArSe^-$ in the initial step cannot be ruled out.

$$R' = H, alkyl$$
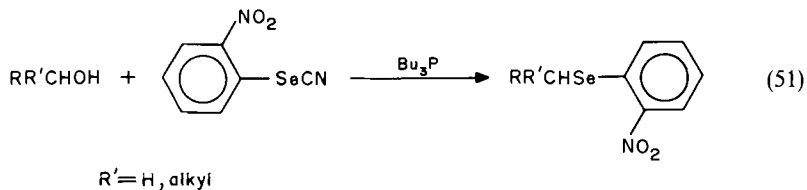
Later, the stereochemistry of this reaction was studied using secondary alcohols as substrates[115] (Scheme 2). This reaction proceeds with inversion of configuration on the

$$ArSeCN \ + \ Bu_3P \ \longrightarrow \ Ar\overset{+}{Se}PBu_3 \ CN^-$$

$$Ar\overset{+}{Se}PBu_3 \ CN^- \ + \ RCH_2OH \ \longrightarrow \ RCH_2O\overset{+}{P}Bu_3 \ + \ HCN \ + \ ArSe^-$$

$$RCH_2O\overset{+}{P}Bu_3 \ + \ ArSe^- \ \longrightarrow \ RCH_2SeAr \ + \ Bu_3P{=}O$$
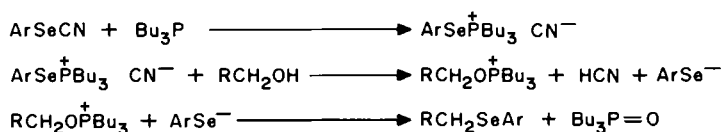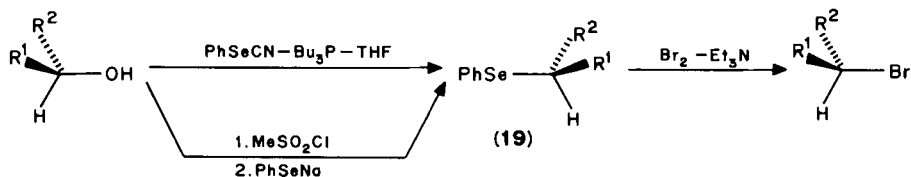
<p style="text-align:center">SCHEME 1</p>

<p style="text-align:center">SCHEME 2</p>

carbon atom, in good accord with the final step in Scheme 1. The stereochemistry of the
selenide **19** was confirmed by the preparation of an authentic sample and its conversion to
the bromide with the known stereochemistry (inversion in both steps). The reaction took
place with aryl selenocyanates (phenyl and *o*-nitrophenyl selenocyanate), but poor results
were obtained with diaryl diselenides or arylselenenyl chlorides[114]. It was reported that
N-phenylselenophthalimide (N-PSP) gave analogous results to those obtained with aryl
selenocyanates[116]. In the case of the secondary alcohol group in a steroid, however, it was
later reported that an arylseleno group could not be introduced into the steroid by the use
of N-PSP, whereas a satisfactory result was obtained by the use of aryl selenocyanate
(Scheme 3)[117]. Hence, the use of aryl selenocyanates is recommended in the reactions
described in this section.

When the reaction was applied to aldehydes, cyanoselenenylation products (**20**) were
obtained as shown in equation (52)[118]. This reaction was explained as proceeding through
the reaction of aldehydes with a cyano ion, which is the counter anion of the
selenophosphonium salt, to afford the cyanohydrin intermediate (**21**) (equation 53). When
ketones were used instead of aldehydes, cyanohydrins were isolated as products,
presumably owing to the steric hindrance in the nucleophilic substitution by selenium in
the final step of the reaction. Carboxylic acids also reacted with phenyl selenocyanate in
the presence of tributylphosphine to give the benzeneselenol esters (equation 54)[119].

$$(52)$$

$$(53)$$

$$(54)$$
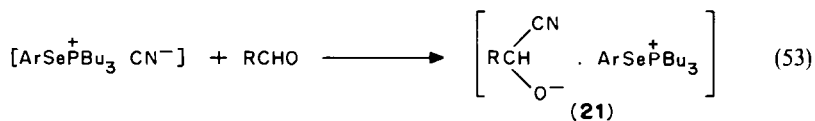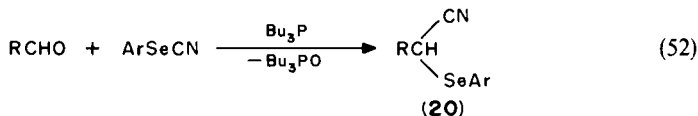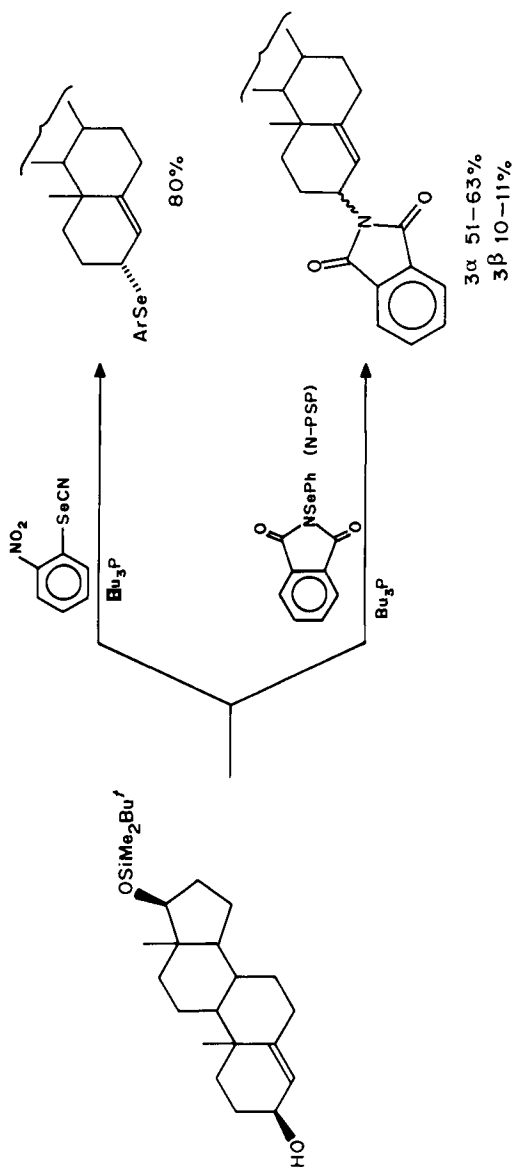
SCHEME 3

When the reaction 51 is combined with selenoxide elimination[97], these reactions constitute a very mild and elegant procedure for the introduction of a double bond into organic molecules. For faster rates and better yields e.g. of the terminal olefins o- or p-nitrophenyl selenocyanate was favourably used rather than phenyl selenocyanate. Considering the carbon atom, reaction 51 is the substitution of the hydroxy group by an arylseleno group. This direct substitution of the hydroxy group (without derivatization to a different leaving group) is of great merit as the hydroxy group is easily produced by the reduction of a carbonyl group, and the latter is commonly used in carbon—carbon bond formation reactions. The reaction is compatible with a wide range of functional groups, and was used in numerous syntheses of natural products and other compounds. The first example was the introduction of angular vinyl group in the synthesis of ($\pm$)-deoxy-vernolepin (equation 55)[120].

$$(55)$$
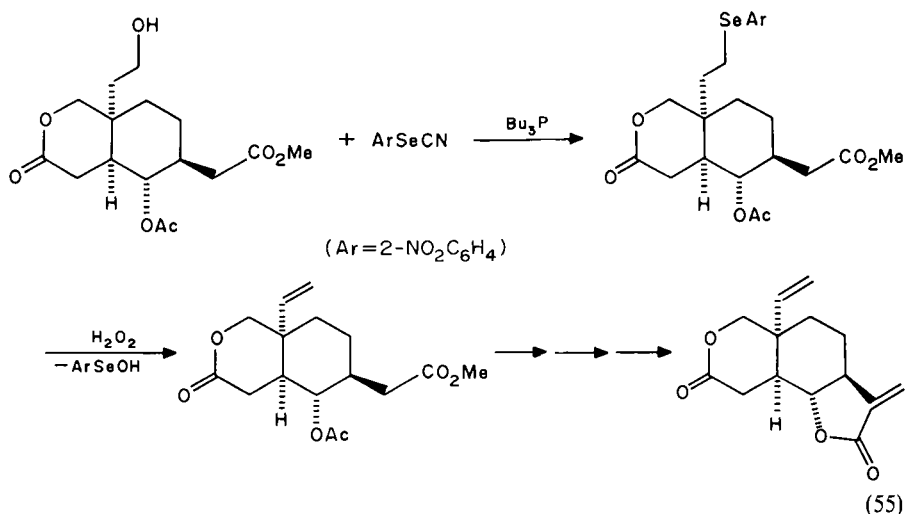
When both primary and secondary alcohols are present in the same molecule, it is possible to selenenylate the primary alcohol selectively. In the preparation of 8-deoxy-9β-hydroxyvernolepin, the primary alcohol group was converted to the selenide without the need to protect the secondary alcohol group (equation 56)[121].

$$\text{Ar} = 2\text{-NO}_2\text{C}_6\text{H}_4$$
$$\text{R} = \text{SiMe}_2\text{Bu}^t$$

$$(56)$$
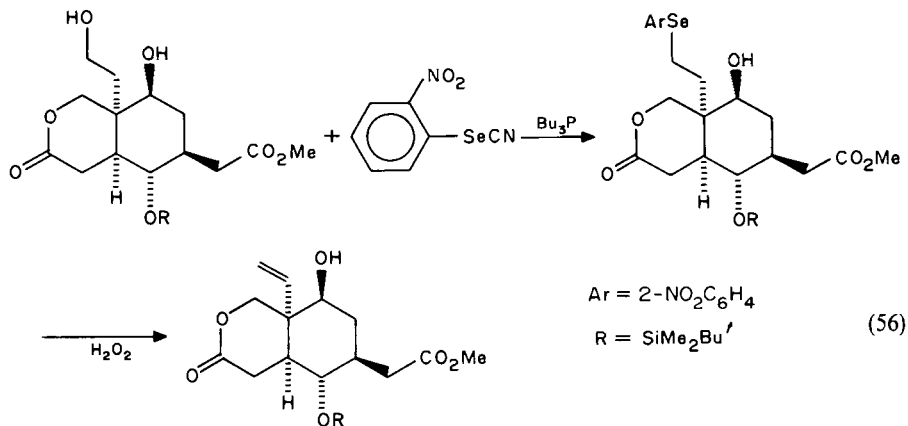
During the total synthesis of estrone, a diol (**22**) was treated with 1.5 equiv. of *o*-nitrophenyl selenocyanate to afford the selenide **23** selectively (equation 57)[122]. In diols, **24**[123], **25**[124] and **26**[125], again only the primary alcohol groups were converted to the selenides using the same procedure. In certain cases, discrimination between two primary alcohols is also possible, the more hindered alcohol being left intact. A good example was found in the synthesis of the alkaloid (±)-antirhine (equation 58)[126].

(57)

(58)
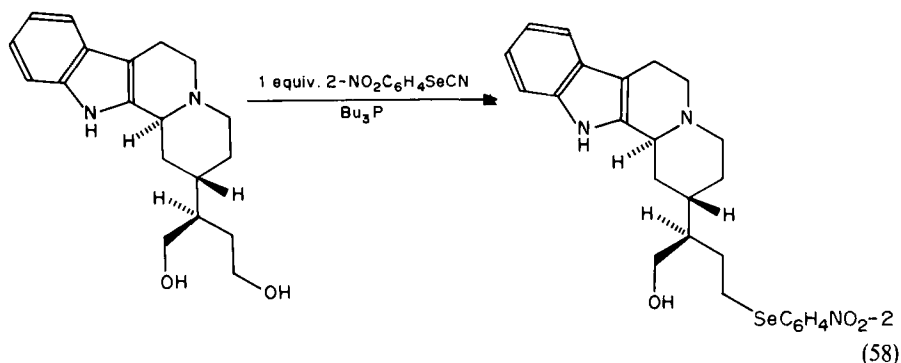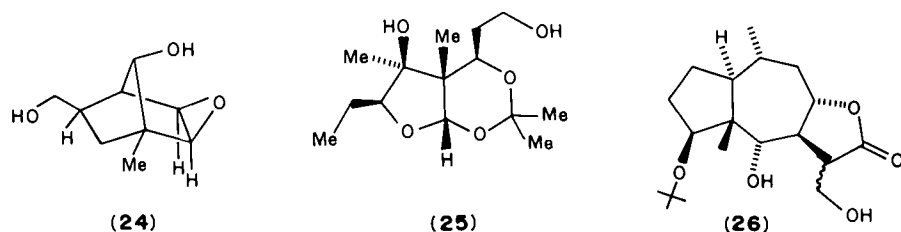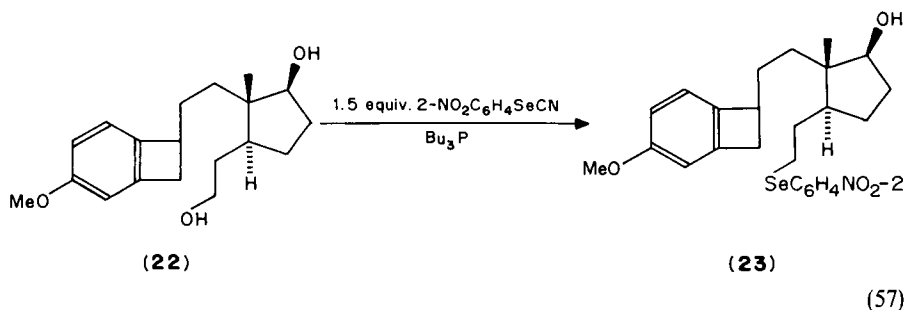
In the total synthesis of (+)-costunolide, it was reported that diselenenylation was not possible even by the use of excess of aryl selenocyanate. Although the difference was only in the relative position of a methyl substituent (β or γ), the hydroxy group with the methyl group in the γ-position was converted to the selenide selectively. Thus, the desired diene **27** was prepared by stepwise selenenylation and elimination (equation 59)[127]. A similar stepwise procedure was adopted in the conversion of the diol **28** to the diene in the total synthesis of temisin[128]. Later, a closely related diol (**29**) was treated with 4.8 equiv. of

o-nitrophenyl selenocyanate for a much longer time to afford a mixture of di- and mono-selenenylated products in 79% and 13% yields respectively (equation 60)[129]. A similar

$$Ar = 2\text{-}NO_2C_6H_4 \tag{59}$$

(27)

(28)

(29)

$$+ \quad 4.8 \text{ equiv.}$$

79%   13%   (60)
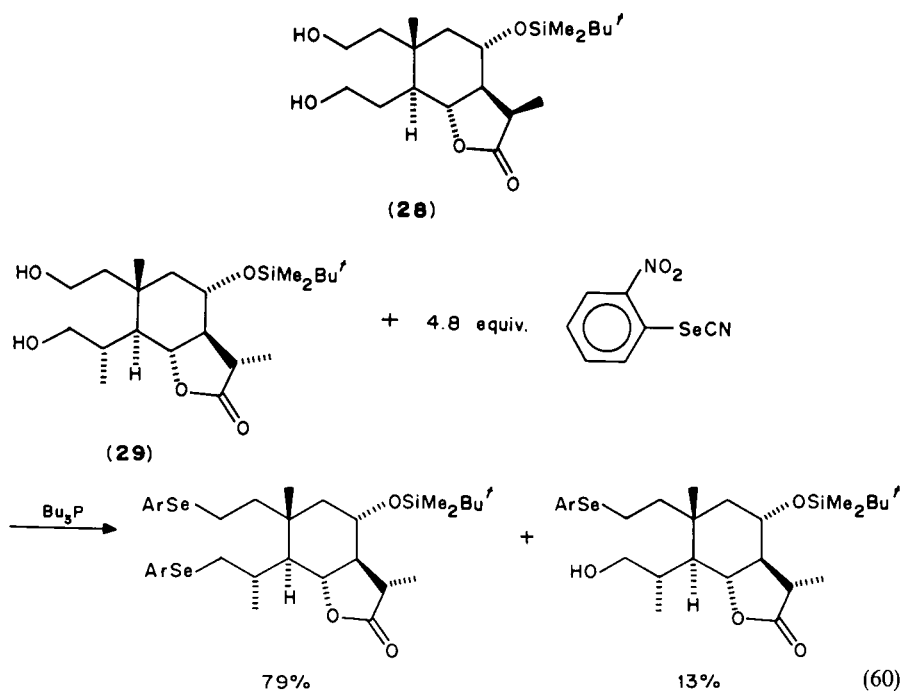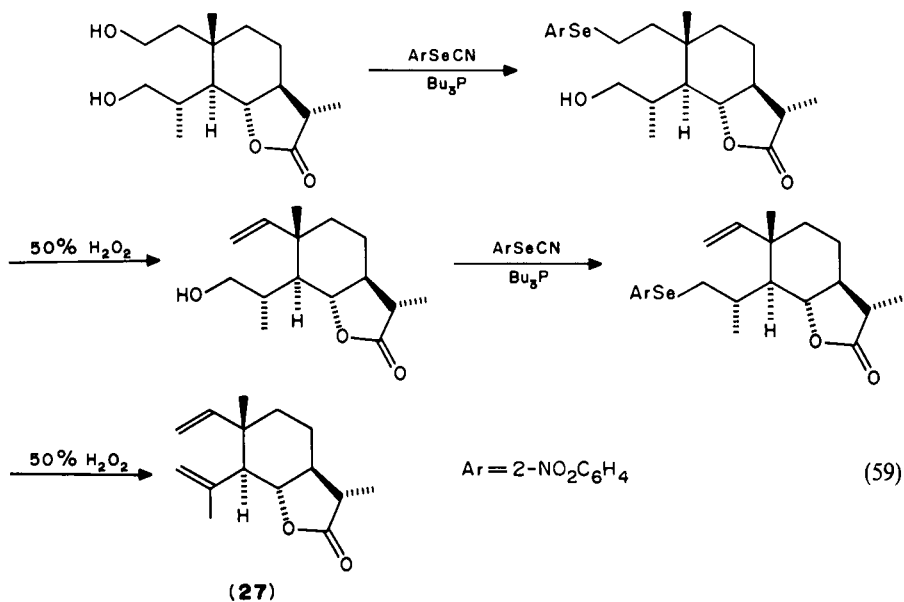
mixture was obtained from the diol **30** (R = Me)[130], but in the cases of simpler diols such as **30** (R = H)[130], **31**[131] and **32**[132], it was not difficult to displace both OH groups in a one-step reaction. As expected, the tertiary OH group in **32** was not converted to the selenide.

(**30**) R = H, Me

(**31**)

(**32**)
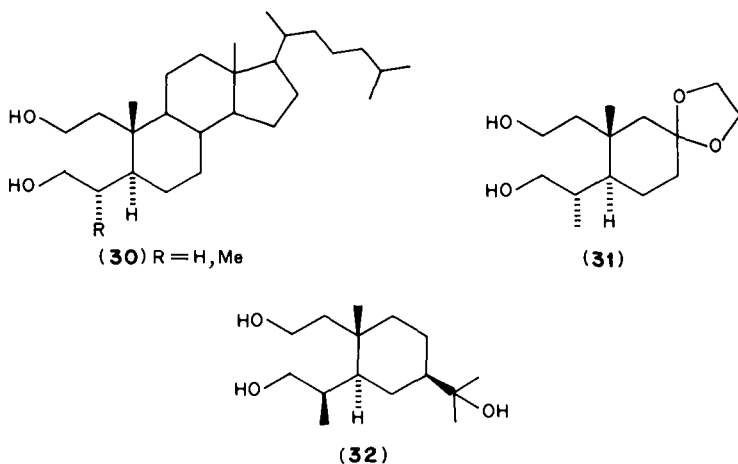
Although the reaction is slower, a secondary OH group can be replaced by an arylseleno group using this procedure, as already mentioned in Scheme 2 and 3. Another example was found in the conversion of benzyl alcohol derivatives to β-aminostyrene derivatives (**33**) (equation 61)[133]. This reaction was utilized in the synthesis of cyclic and acyclic peptide alkaloids, zizyphine A (**34**)[133] and celenamide A (**35**)[134], respectively (the double bonds introduced are shown by arrows).

(61)

(**34**)

(**35**)
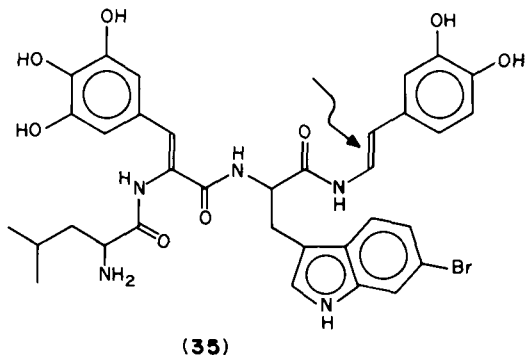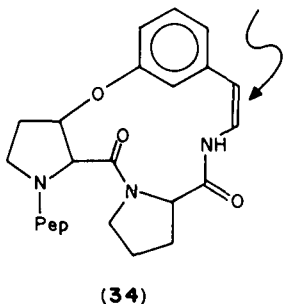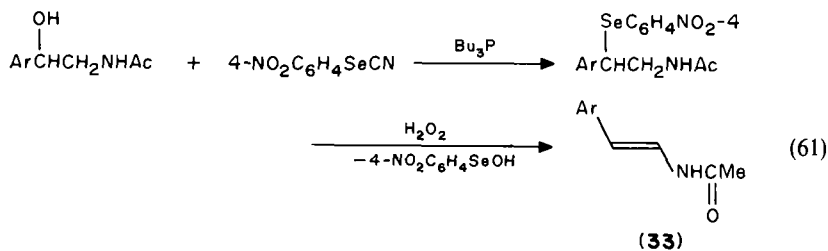
The preparation of thermally unstable oxete was also carried out using this procedure (equation 62)[135]. The formation of **36** was detected by NMR spectroscopy.

$$(62)$$

(36)
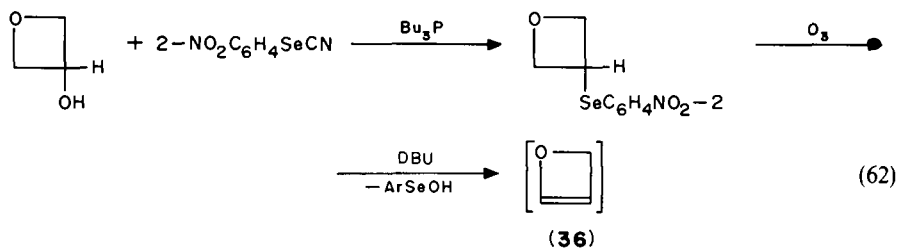
In other numerous examples of this double bond-forming reaction, primary alcohols were used as substrates. Replacement by an arylseleno group and subsequent selenoxide elimination produced terminal olefins. During the synthesis of the skeleton of lycorine alkaloids, the 1-aminobutadiene derivative **37** was prepared by this selenenylation–elimination sequence, indicating the compatibility of this procedure with reactive functional groups (equation 63)[136]. In the preparation of the irregular monoterpene (R)-santolinatriene, the selenoxide elimination was also carried out in the presence of a non-conjugated diene group in the molecule (equation 64)[137].

$$(63)$$

(37)

$$(64)$$
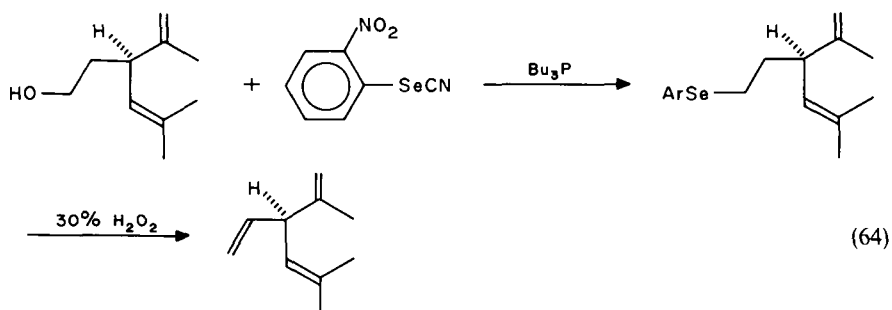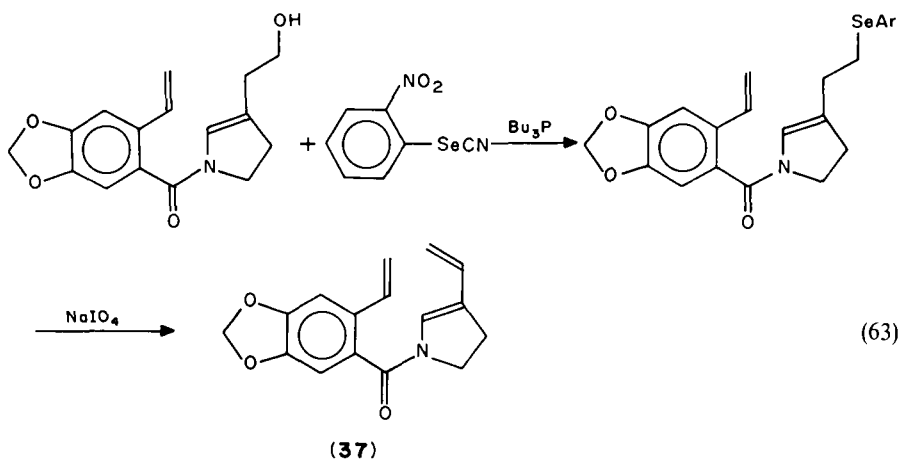
Terminal double bonds were introduced using this procedure in the syntheses of estradiol[138,139], the sex pheromone of the pine sawflies[140], dl-3β-bromo-8-epicaparrapi oxide[141], the ionophore calimycin (A-23187)[142], (+)-8-deoxyvernolepin[143,144], erythromycin[145], Prelog–Djerassi lactone[146], monoterpene, semburin and isosemburin[147], the wing gland pheromone of the African sugar-cane borer[148] and miyaginin, p-allylphenyl glycoside[149].

This procedure was also utilized in the preparation of the starting materials for the studies of the tandem Cope–Claisen rearrangement, namely **38** (equation 65)[150], and for the photochemical rearrangement, namely **39**[151].

$$\text{(65)}$$

(38)

(39)
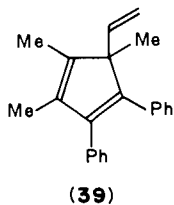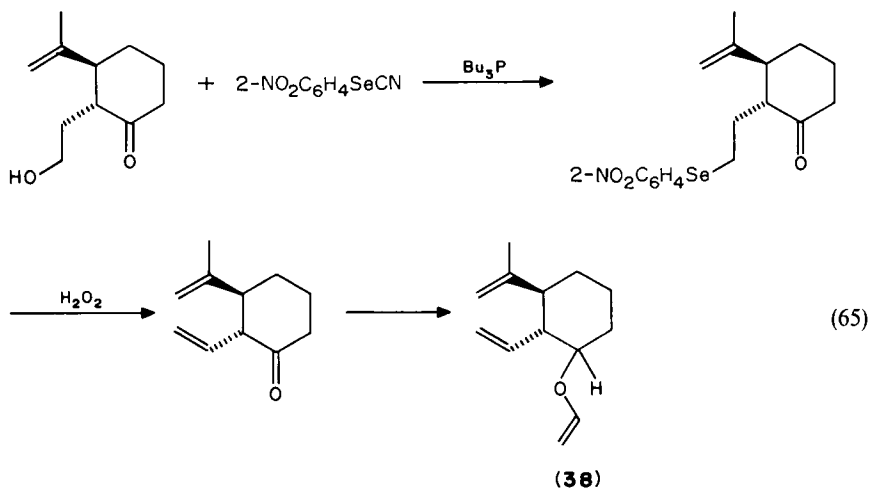
The procedure was also effective for the preparation of an exocyclic double bond. For example, in the total synthesis of (±)-β-chamigrene, the ester function was converted to an exocyclic methylene group in three steps, viz. reduction, selenenylation and elimination (equation 66)[152]. Similar procedures were used in the total syntheses of pederin[153,154], (±)-atractylon and (±)-lindestrene[155]. The exocyclic double bonds of **40**[156] and **41**[157] were also prepared using this procedure.

In the case of highly strained polycyclic compounds, the procedure was also shown to be effective for the introduction of exocyclic methylene groups. Isocomene, which was isolated from a toxic plant, was synthesized using this procedure (equation 67)[158]. The polycyclic alcohols **42**[159], **43**[160] and **44**[161] were converted to the corresponding exomethylene compounds by treatment with o-nitrophenyl selenocyanate and subsequent oxidation (ozone or 30% H_2O_2).

(66)

(40)   (41)

(67)

(42)   (43)   (44)
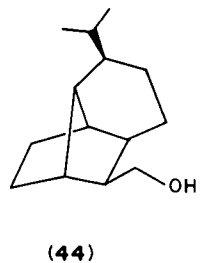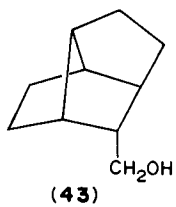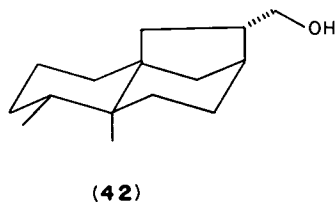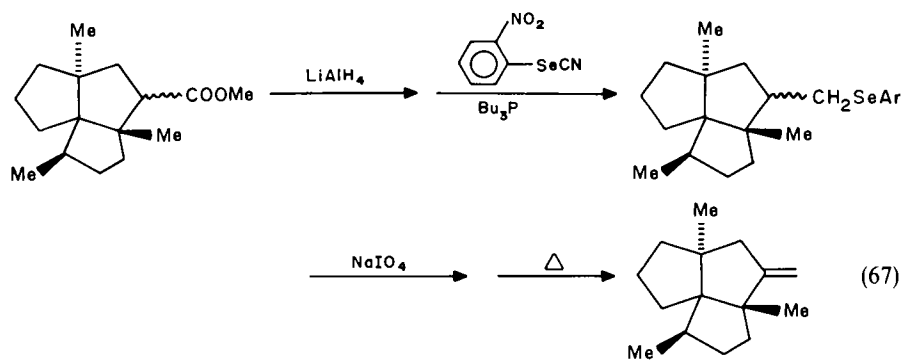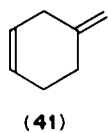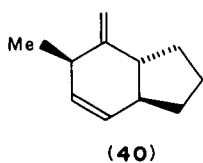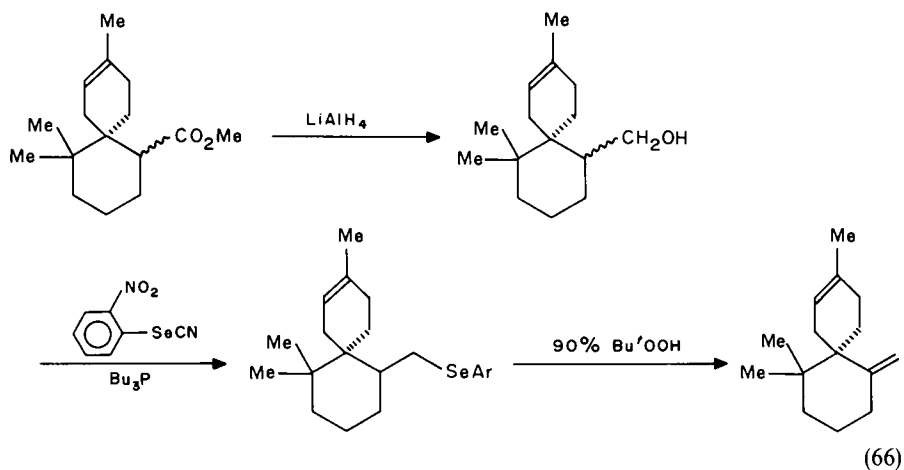
The formation of an exocyclic double bond conjugated with an endocyclic double bond was also achieved similarly. Examples are found in the total syntheses of ($\pm$)-periplanone-B[162], which is the sex excitant pheromone of the American cockroach (equation 68), and in the total synthesis of the sesquiterpene ($\pm$)-silphiperfol-6-ene (equation 69)[163].

$$(68)$$

$$(69)$$
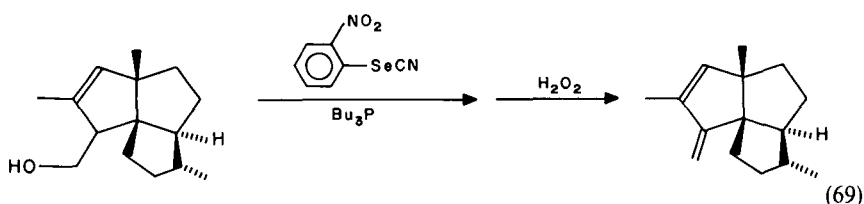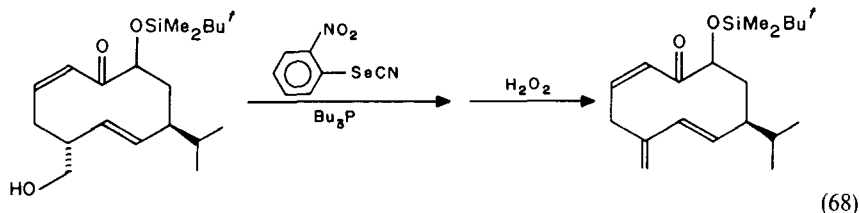
An elegant application is the preparation of α-(methylenecyclopropyl)glycine, which shows significant biological activity (equation 70)[164].

$$(70)$$
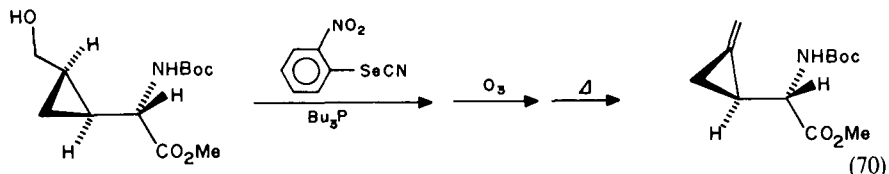
In carbohydrate chemistry the selenenylation–elimination sequence was used in the preparation of a key intermediate (45) for the synthesis of antibiotics related to angustmycin A and nucleocidine (equation 71)[165–168]. This reaction was also carried out without protection of the secondary OH groups.

$$(71)$$

(45)

$$\text{Ar} = \qquad \text{Ad} =$$
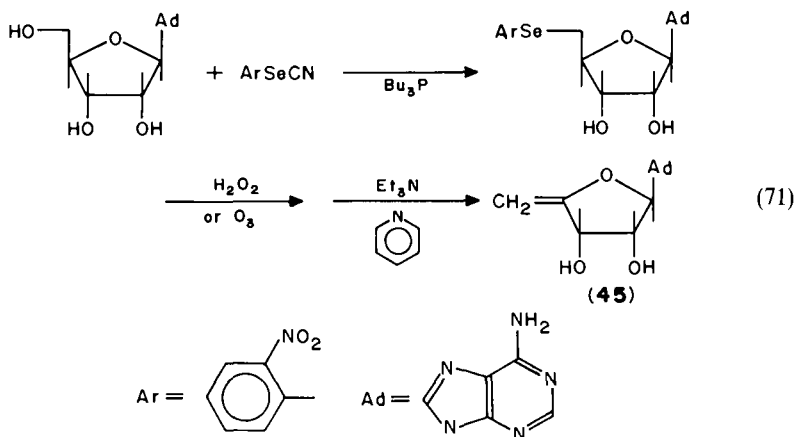
When conversion of an alcohol to a selenide is combined with reductive removal of the introduced arylseleno group, the overall reaction is the replacement of a hydroxy group by hydrogen[169]. This was carried out in the presence of a lactone group in the preparation of (R)- and (S)-α-benzylidene-γ-butyrolactone from the readily available (S)- and (R)-glutamic acids (equation 72)[170].

$$(72)$$
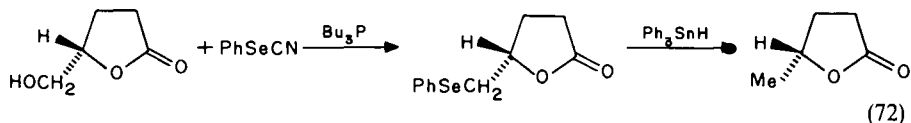
Allylic alcohols are prepared by the [2,3] sigmatropic rearrangement of allylic selenoxides[97]. If allylic selenides are prepared using the so far described reaction, the overall reaction results in the transposition of allylic alcohols. The advantage of this selenium methodology is shown by the contrathermodynamic transposition in equation 73 under very mild conditions[171]. Stereospecific replacement of secondary alcohols (Scheme 2) and the subsequent [2,3] sigmatropic rearrangement of the resulting selenoxides afforded stereospecifically generated allylic alcohols in the cyclic compounds shown in equation 74[172]. The stereospecific formation of tertiary alcohols (46) was also reported. When this reaction was applied to geraniol, the [2,3] sigmatropic rearrangement was accompanied by epoxidation of the isolated double bond to afford 47 in the presence of pyridine. In the absence of pyridine, the product was found to be a tetrahydrofuran derivative (48), which was independently prepared from 47 by the action of p-toluenesulphonic acid (Scheme 4)[173,174]. Arylseleninic acid or its peracid, which were formed during the course of the reaction, may be responsible for the cyclization and epoxidation shown in Scheme 4.

$$Ar = 4\text{-}NO_2C_6H_4 \qquad (73)$$

$$Ar = 2\text{-}NO_2C_6H_4 \qquad (74)$$

SCHEME 4

(46)
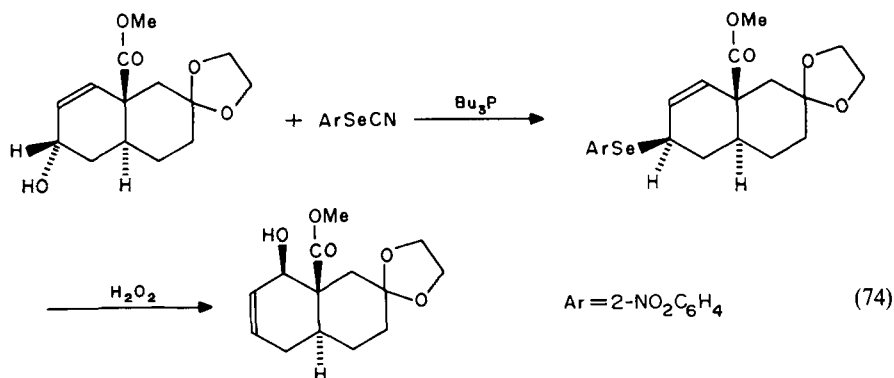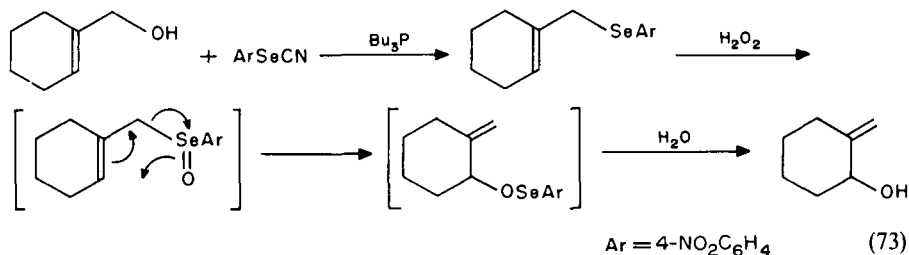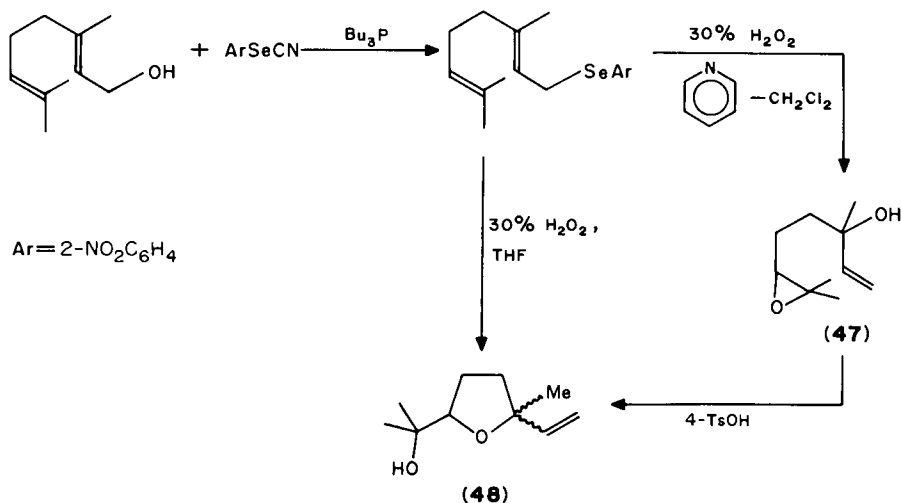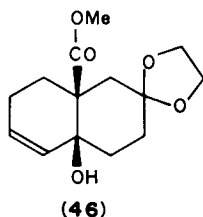
d. Selenenylation of olefins and acetylenes. The reactions described in this section are formally a substitution of the cyano group of the —SeCN moiety by a carbon atom similarly to the reactions in the previous sections (II.C.2.b and c). These reactions are, however, best described as an electrophilic addition of organoselenium reagents to carbon—carbon multiple bonds. This methodology constitutes one of the most important branches in the selenenylation reactions.

When the reactions are carried out in hydroxylic solvents in the presence of metal catalysts, phenylseleno and alkoxy groups are added to the olefins to form β-alkoxyalkyl phenyl selenides (49) (equation 75)[175,176]. Cu^{I}, Cu^{II} and Ni^{II} were found to be most effective when used in the form of their chlorides or bromides. The stereochemistry of the addition reaction was confirmed to be *trans*. Oxidation of 49 produces allylic ethers, acetates and alcohols[97]. When non-conjugated dienes were used as substrates, cyclic ethers bearing two phenylseleno groups were produced (Scheme 5)[177-179].

$$\text{>C=C<} + \text{PhSeCN} \xrightarrow[\text{MX}_n]{\text{ROH}} \text{PhSe>C—C<OR} \qquad (75)$$

R = alkyl, MeCO, H   (49)
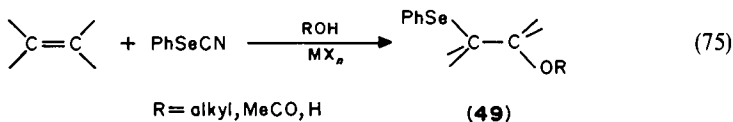
Two bicyclic ethers, 50 and 51, were produced from cycloocta-1,5-diene, the reaction being highly solvent-dependent; 50 was produced selectively (95:5) in methanol and 51 was
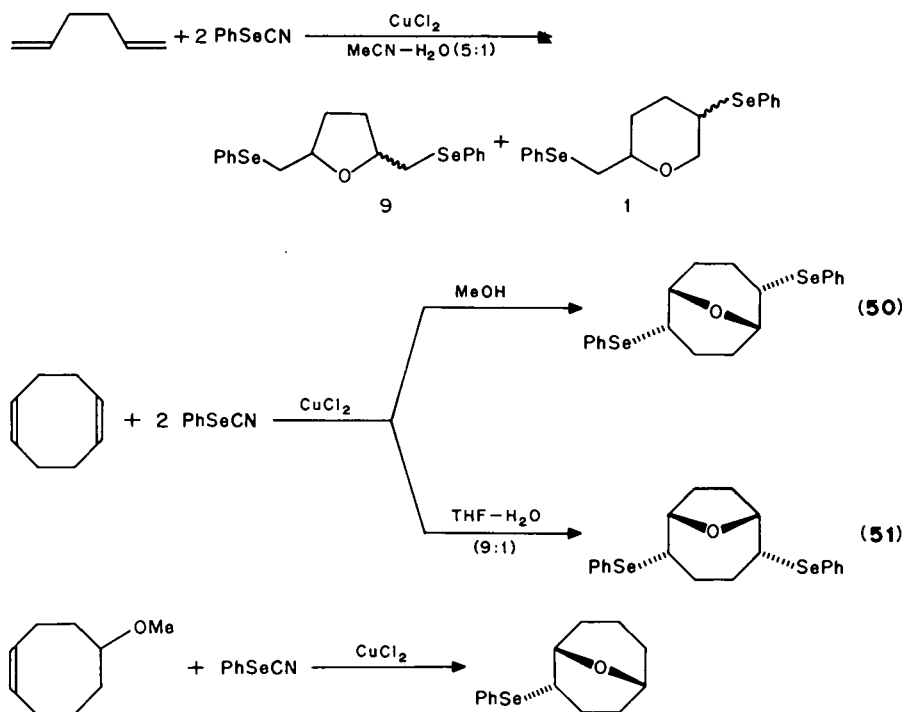
SCHEME 5

the sole product in acetonitrile–water (5:1). The second step of these reactions is an intramolecular oxyselenation and it was confirmed that a methoxy group reacted with an episelenonium ion to form cyclic ethers (Scheme 5). By the application of equation 20 to non-conjugated dienes, selenium-containing cyclic compounds were produced (equation 76)[43]. The second step of this reaction was also an oxyselenation as described above.
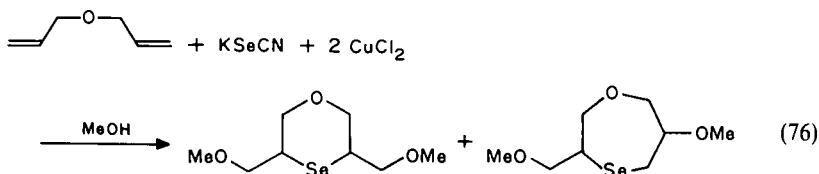
The reaction of acetylenes with phenyl selenocyanate proceeds in the presence of copper(II) halide and triethylamine to afford addition products (Scheme 6)[180]. Reactions with internal alkynes afford a mixture of regio-isomers (both *trans* adducts), while a mixture of geometrical isomers is produced from terminal alkynes having a phenylseleno group at the internal carbon atom.

In other cases, both phenylseleno and cyano groups add to olefins. Thus, in the reaction of phenyl selenocyanate with enamines, addition products were obtained almost quantitatively (equation 77)[181]. The ethanol solvent did not attach the double bond, but

$$R^1C{\equiv}CR^2 + PhSeCN \xrightarrow[Et_3N-CH_2Cl_2]{CuX_2}$$

$$R^3C{\equiv}CH + PhSeCN \xrightarrow[Et_3N-CH_2Cl_2]{CuX_2}$$

$$R^1, R^2, R^3 = alkyl; X = Cl, Br$$
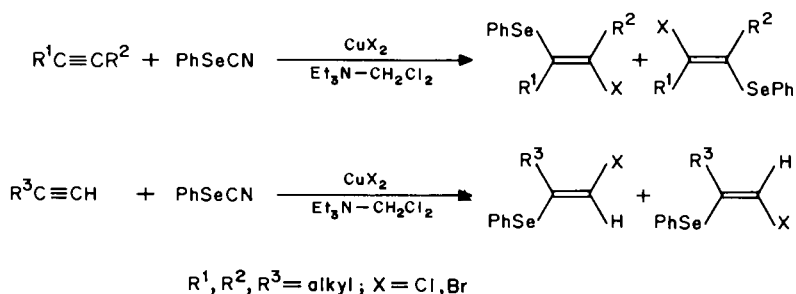
SCHEME 6

the cyano group was incorporated in the products. As the products were found to consist of one isomer, the *trans* addition of the shown regioselectivity was strongly suggested. The addition also proceeded when ketene dialkyl acetals or ketene alkyl silyl acetals were used as olefins (equation 78)[182]. In this case, non-stereoselective addition was observed. Oxidation of **52** afforded β,γ-unsaturated-α,α-dioxycarbonitriles via selenoxide elimination. Alkenes bearing only alkyl substituents were less reactive than the olefins described above, and the addition of Lewis acid catalysts was necessary, tin(IV) chloride giving the best results (equation 79)[183]. Stereospecific addition was observed in this case (see **53**) and this was utilized in the stereoselective syntheses of α,β-unsaturated nitriles by selenoxide *syn* elimination. From unsymmetrical olefins, a mixture of regioisomers was produced.

(77)

(78)

(**52**)

(**53**)

(79)
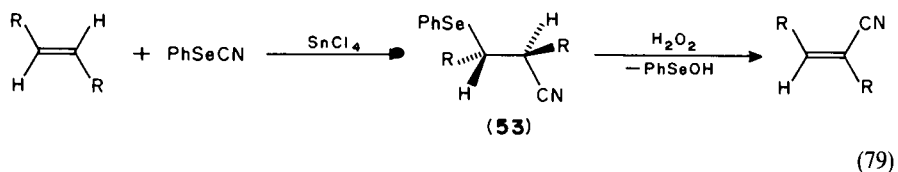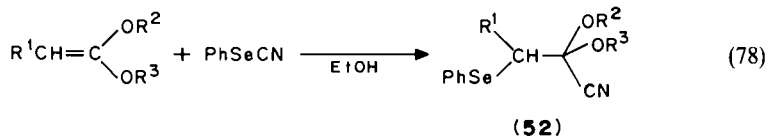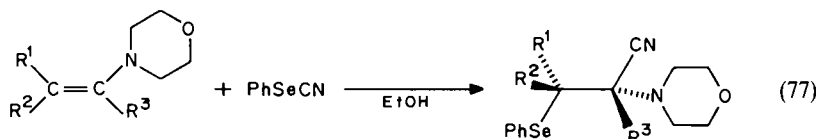
3. Elimination of the CN group

The oxaselenole **57** was produced by the reaction of the selenocyanate **54** with sodium hydride (equation 80)[13]. This reaction was explained to proceed through the selenoketone intermediate **56**, which was formed by base-induced elimination of HCN from **54**. The intermediate **56** then reacted with another mole of **55** to give the cyclization product.

$$\underset{(54)}{\underset{|}{PhCHCOPh}}^{SeCN} \xrightarrow[-H^+]{NaH} \left[\underset{(55)}{\underset{|}{PhC\!\!\!\!\!\!-\!\!\!\!\!\!COPh}}^{SeCN} \right] \xrightarrow{-CN^-} \left[\underset{\underset{O}{\overset{||}{}}}{PhCCPh}^{\overset{Se}{\overset{||}{}}} \right]$$

(56)

$$(55) \longrightarrow \left[\underset{Ph}{\overset{Ph}{}}\!\!\!\diagdown\!\!\!\!\underset{O^-}{\overset{Se}{C}}\!\!\!\diagup^{\overset{SeCN}{\diagdown COPh}}_{Ph} \right] \xrightarrow{-SeCN^-} \left[\underset{Ph}{\overset{Ph}{}}\!\!\!\diagdown\!\!\!\!\underset{O^-}{\overset{\overset{+}{Se}}{C}}\!\!=\!\!\underset{Ph}{\overset{COPh}{C}} \right]$$

$$\longrightarrow \underset{(57)}{\underset{Ph}{\overset{Ph}{}}\!\!\!\diagdown\!\!\!\!\underset{O}{\overset{Se}{C}}\!\!\!\!\underset{Ph}{\overset{\overset{O}{\overset{||}{CPh}}}{}}} \qquad\qquad (80)$$
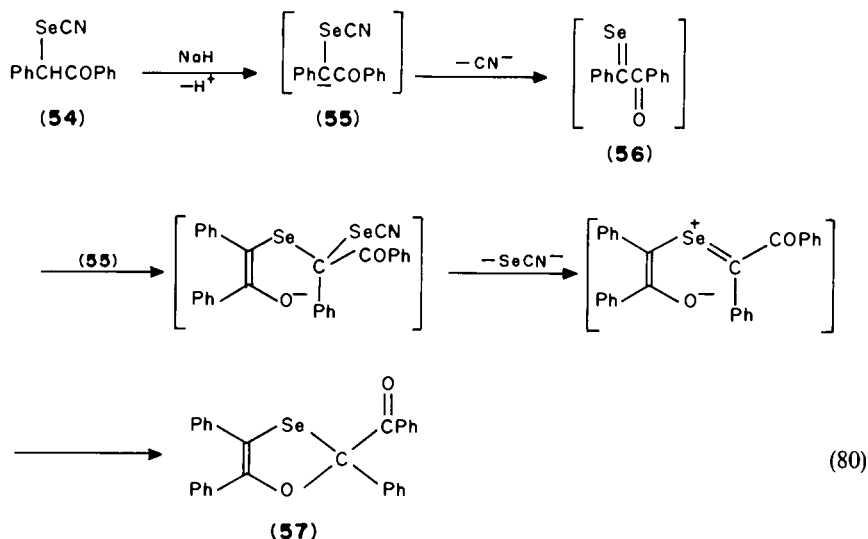
The formation of selenoketones was observed as the metal complex with chromium or tungsten carbonyls. By the treatment of [aryl(phenyl)carbene]pentacarbonyl complexes (58) with potassium selenocyanate, selenium was inserted to the metal—carbene bond to give the complex (59) (equation 81)[184].

$$\underset{(58)}{CO\!\!-\!\!M\!\!=\!\!C\diagup^{Ar}_{\diagdown Ph}} + KSeCN \longrightarrow \underset{(59)}{CO\!\!-\!\!M\!\!-\!\!Se\diagup^{Ar}_{C}\!\!-\!\!Ph} \qquad (81)$$

$$M = Cr, W$$

$$Ar = -\!\!\!\bigcirc\!\!\!-OMe, \quad -\!\!\!\bigcirc\!\!\!-CF_3, etc.$$
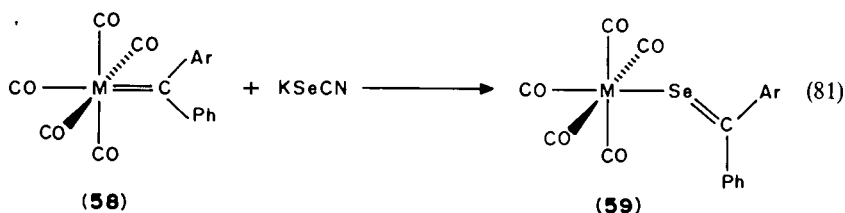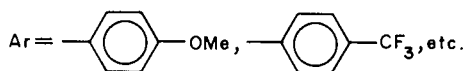
The first cationic selenoformaldehyde complex (61) was prepared by the reaction of the rhenium complex 60 with potassium selenocyanate (equation 82)[185]. Elimination of the cyano group occurred in these reactions.

The pyrolysis of methyl selenocyanate was reported to produce selenoformaldehyde, which was detected by photoelectron spectra[186]. Recently, selenoformaldehyde, produced by fluorine-induced elimination of phenyldimethylsilyl and cyano groups from 62 (R = H), was trapped with cyclopentadiene to give the Diels–Alder adducts (63, R = H) (equation 83)[23]. Selenoacetaldehyde and its homologues as well as selenobenzaldehyde were produced and trapped effectively by this procedure.

In the formation of alkyl isoselenocyanates by the reaction of carboimidoyl dichlorides with potassium selenocyanate, the elimination of cyanogen chloride from the intermediate (64) was postulated (equation 84)[187].

(82)

(83)

(84)
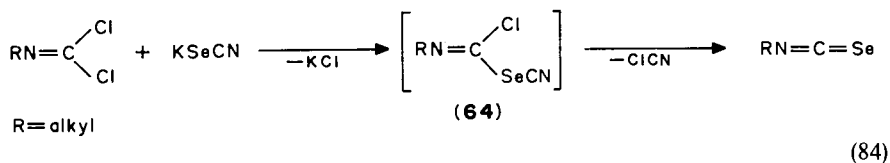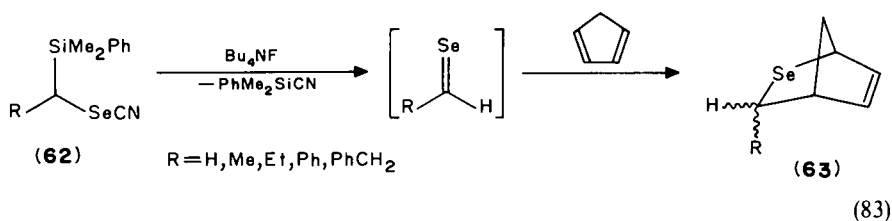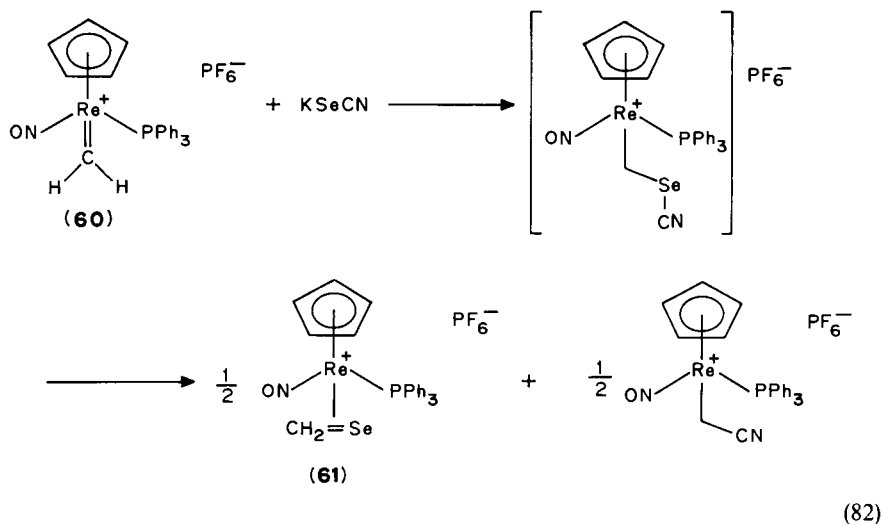
4. Formation of complexes.

Organic selenocyanate complexes, $M(CO)_5(RSeCN)$ $(M = Cr, Mo)$, were prepared by abstraction of an iodide ion from the anion $[M(CO)_5I]^-$ by a silver ion, followed by the addition of $RSeCN^{188}$. It was concluded from the ^1H and ^{13}C NMR and IR spectra that the ligands coordinated through the cyano-N rather than the Se atom. Palladium complexes of either the formula $PdCl_2 \cdot RSeCN$ or $PdCl_2 \cdot 2RSeCN$ were prepared, depending on the preparation procedure[189]. The IR and far IR spectra of these complexes were discussed.

The charge-transfer spectra of the 1:1 TCNE $[(NC)_2C{=}C(CN)_2]$ complex with RC_6H_4SeCN $(R = H, o\text{-}, m\text{-} \text{ or } p\text{-Me, Cl, Br, MeO}, p\text{-NH}_2, Me_2N)$ were examined[190,191]. The energies of the first charge-transfer transitions were linearly correlated with σ^+ constants. The formation of 1:1 $RSeCN\text{--}I_2$ complexes $(R = Me, Ph)$ was established from

electronic and photoelectronic spectroscopic data[192]. Mutual analysis of these data with the results of quantum chemical calculations of the electronic structure of donors indicated that the coordinating centre in RSeCN was the Se atom.

III. ORGANIC ISOSELENOCYANATES

Since Bulka's review[1] appeared, only five reactions have been reported for the preparation of organic isoselenocyanates.

Primary amines formed a 1:1 adduct with mercury(II) chloride in an inert solvent. This complex reacted with carbon diselenide in the presence of triethylamine to give the isoselenocyanates (equation 85)[193]. The role of mercury is not only to reduce the reactivity of the intermediate diselenocarbamate (65) but also to catalyse the elimination reaction. The reaction of phenylselenenyl selenocyanate with diazomethane or ethyl α-diazoacetate was reported to afford the isoselenocyanates (equation 86)[194]. This insertion reaction did not proceed when phenyl selenocyanate was used as the substrate. A photochemical route to some benzyl isoselenocyanates was reported[195]. The isomerization of benzyl selenocyanates (66) to the isoselenocyanates (67) was facilitated by irradiation using a high-pressure mercury lamp to afford a 9:1 mixture of 67 and 66 within 20 min (equation 87). Compound 67 was isolated by column chromatography. To investigate the ambident nature of the SeCN group, alkyl halides were treated with mercury(II) selenocyanate in hexane as solvent[196], when alkyl isoselenocyanates were obtained from secondary or tertiary alkyl halides. The same halides afforded alkyl selenocyanates or a mixture of isomers when treated with potassium selenocyanate. Reaction 84 may also be used for the preparation of alkyl isoselenocyanates[187].

$$RNH_2 + HgCl_2 + CSe_2 + 2\ Et_3N \longrightarrow RN{=}C{=}Se + HgSe + 2\ [Et_3N.HCl]$$

(85)

$$\left[\begin{array}{c} Se \\ \parallel \\ RNHCSe^- \end{array} \right]$$

(65)

$$PhSeSeCN + RCHN_2 \longrightarrow PhSe\overset{\displaystyle R}{\underset{\displaystyle |}{C}}HNCSe$$

(86)

R=H,COOEt

(87)

(66)   (67)
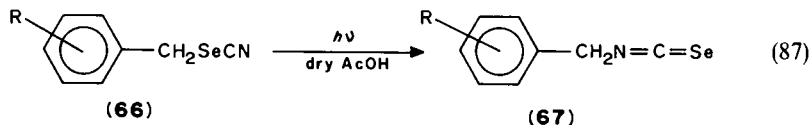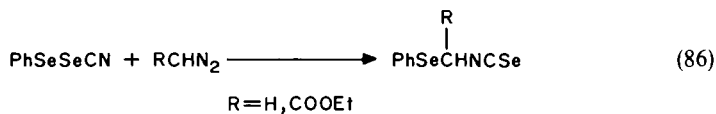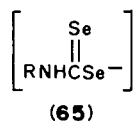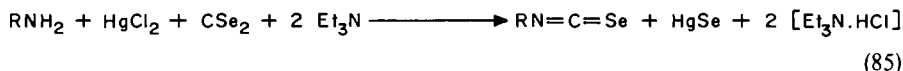
The photoelectron spectra of $Ph_2CHNCSe$ and Ph_3CNCSe have been reported[66]. Although the spectra were dominated by the presence of strong benzenoid bands, some general trends related to structural effects can be recognized.

The reactions of isoselenocyanates with amines to form selenoureas are well known. By the reaction of benzoyl chloride with potassium selenocyanate in the presence of diisopropylamine, the selenourea 68 was produced through the addition of the amine to

the intermediate isoselenocyanate (equation 88)[197]. In the case of acetylenic amines, the amine addition to a N=C bond was accompanied by the selenium addition to the triple bond to afford the selenazolines 69 (equation 89)[198]. If the solvent of the reaction described in equation 9 was changed from diethyl ether–tetrahydrofuran to dimethoxyethane–dioxane, the product became the isoselenocyanate, which was trapped by the addition of amine to give the selenourea 70[25].

$$
\text{PhCCl} + \text{KSeCN} + \text{Bu}_2'\text{NH} \longrightarrow
\qquad\qquad\qquad (88)
$$

(68)

$$
\text{H}_2\text{NCRR}^1\text{C}\equiv\text{CH} + \text{R}^2\text{NCSe} \longrightarrow
\qquad\qquad\qquad (89)
$$

R, R^1 = alkyl

R^2 = Et, PhCO, 3-ClC$_6$H$_4$

(69)

R^1 = Ph, R^2 = H or

R^1, R^2 =

(70)
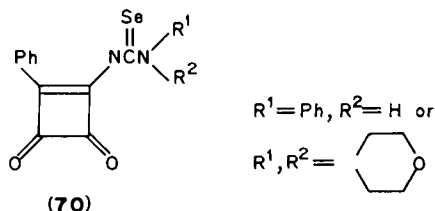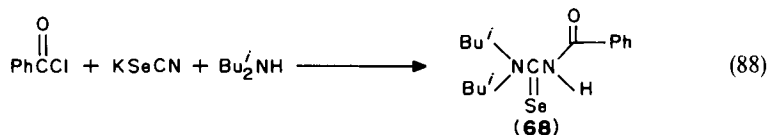
By the reaction of N-acylchloroformamidine (71) with potassium selenocyanate, a cyclic compound (72) was produced by the addition of oxygen to the carbon atom of the introduced isoselenocyanate group (equation 90)[199].

(71)   + KSeCN ⟶

$$
\longrightarrow \qquad\qquad\qquad\qquad\qquad\qquad (90)
$$

(72)
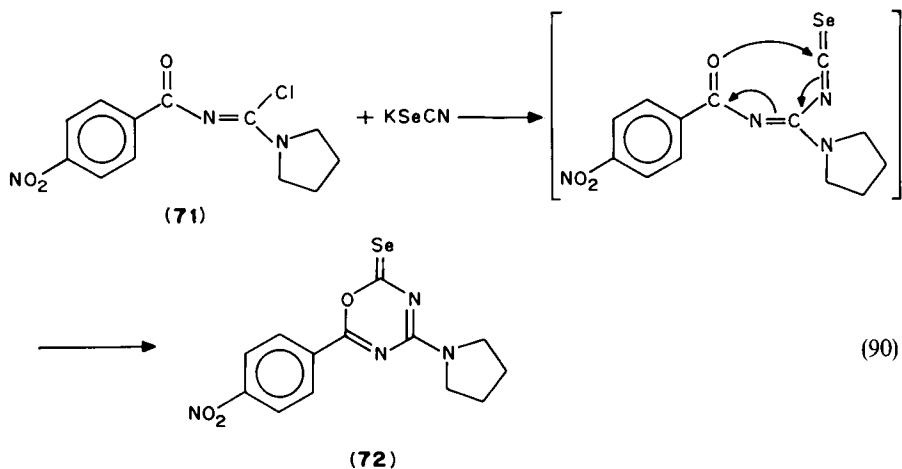
The addition of phosphorus to an isoselenocyanato group was reported. Addition products (73) were obtained by the reaction of trimethyl or triethyl phosphite with acetyl isoselenocyanate, which was, in turn, prepared from acetyl chloride and potassium selenocyanate and was used without isolation (equation 91)[200].

$$
\underset{\substack{\parallel \\ \text{MeCCl}}}{\overset{\text{O}}{}} + \text{KSeCN} \longrightarrow \left[\underset{\substack{\parallel \\ \text{MeCN}}}{\overset{\text{O}}{}}=\text{C}=\text{Se} \right]
$$

$$
\xrightarrow{\text{P(OR)}_3} \underset{\substack{\parallel \\ \text{MeCN}}}{\overset{\text{O}}{}}=\text{C} \overset{\text{SeR}}{\underset{\underset{\parallel}{\overset{}{\text{P(OR)}_2}}}{\diagdown}} \qquad\qquad R = \text{Me, Et} \qquad (91)
$$
$$
\qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{O}
$$

(73)
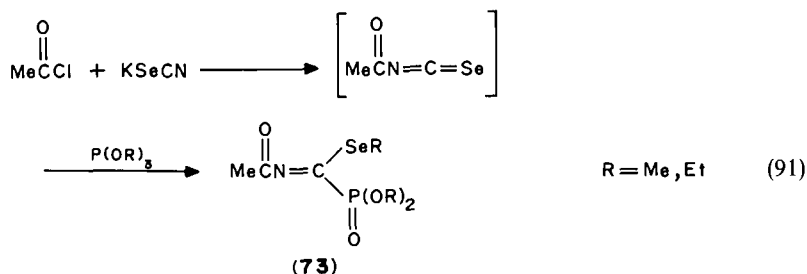
Two examples of cyclization by carbon—carbon bond formation in an isoselenocyanato group were reported. In the formation of selenoimidazolidone (74) by the reaction of aziridine with potassium selenocyanate, the intramolecular attack of a carbanion on the central carbon of the isoselenocyanate was postulated (Scheme 7)[201]. By the reaction of N-vinylchloroformamidines with potassium selenocyanate, a heterocyclic compound (75) was produced through carbon—carbon bond formation (equation 92)[202].

SCHEME 7

$$
\underset{\substack{| \\ \text{N} \\ | \\ \text{O}}}{\overset{}{\text{PhCH}=\text{CRN}=\text{C}}} \overset{\diagup \text{Cl}}{\diagdown} + \text{KSeCN} \longrightarrow (75) \qquad (92)
$$

R = H, Ph   (75)
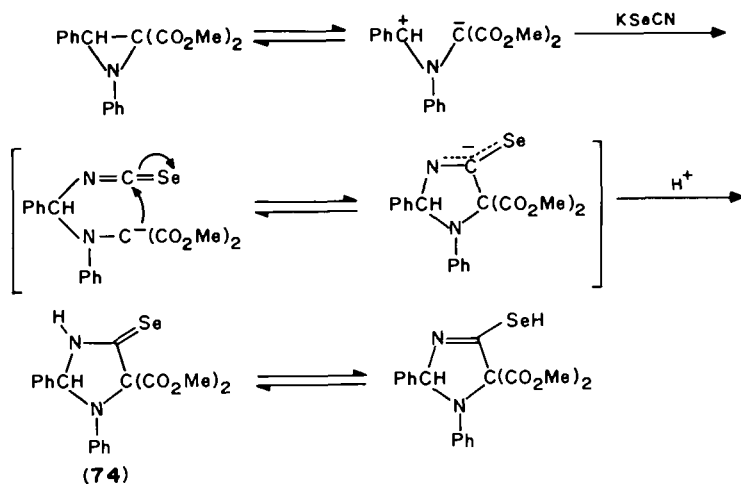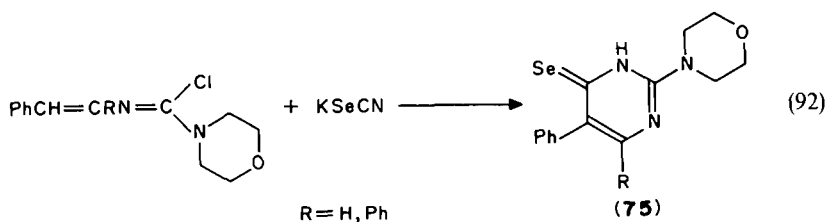
The complex **59** in equation (81) was also prepared by the reaction of **58** with PhNCSe instead of KSeCN. A selenium atom was transferred from the isoselenocyanate to the metal complex, leaving phenyl isocyanide[184].

IV. ORGANIC TELLUROCYANATES

Compared with selenocyanates, organic tellurocyanates (RTeCN) are little known. Although the formation of various such compounds has been claimed in many patents[203,204], none of them has been characterized. The first concrete example of an organic tellurocyanate seems to be 1-azulenyl tellurocyanate (**76**), prepared by Nefedov in 1968[205]. The compound (fine violet needles, m.p.80–81 °C) was synthesized in 7% yield by treatment of azulene with a combination of copper(II) acetate and potassium telluro-cyanate (KTeCN) in acetonitrile at reflux temperature (equation 93), KTeCN being produced separately by heating potassium cyanide and tellurium at 100–250 °C. The *in situ* formation of copper(II) tellurocyanate [$Cu(TeCN)_2$] and the direct replacement of hydrogen in azulene by this species were proposed. This substitution method, however, does not seem to have been applied to any other aromatic compound. Another method for aryl tellurocyanates was developed by Renson and coworkers, who treated stable aryltellurium(II) halides with silver cyanide to produce substitution of halide by cyanide (equation 94)[206,207]. Similar reactions also proceeded with potassium cyanide (equation 95)[208]. In these reactions a carbonyl-containing function or a nitro group was necessary at the position *ortho* to the tellurium atom to obtain remarkably stable aryl tellurocyanates, attributed to the interaction of the tellurium with the carbonyl or nitro oxygen atom, which is then coordinatively less unsaturated[209]. Another route to aryl tellurocyanates is a carbon—tellurium bond cleavage of 3-oxo-2,3-dihydrobenzotellurophene by aqueous hydrogen cyanide (equation 96)[210].

(93)

(**76**)

(94)

(**77**)R=H
(**78**)R=Ph

(95)

(**79**)

(96)

(80)
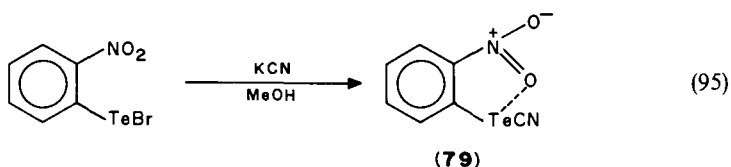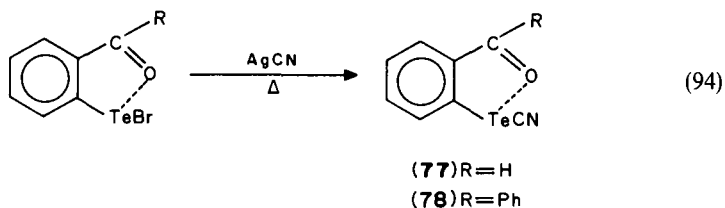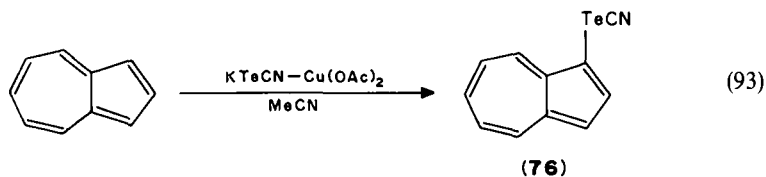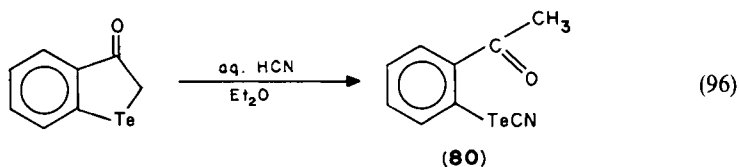
These methods, unfortunately, are of limited applicability for the synthesis of aryl tellurocyanates because aryltellurium(II) halides are normally unstable polymeric species, unless stabilized by a group such as *o*-formyl, *o*-acetyl, *o*-benzoyl or *o*-nitro, and also available tellurophenes are very limited.

It was later proved, however, that *ortho*-substituents are not necessarily required for the preparation of phenyl tellurocyanates. Thus, Falcone and Cava[208] succeeded in syntheses of tellurocyanates by two procedures. One is a direct nucleophilic attack by a cyanide ion on one of the tellurium atoms of a diaryl ditelluride, the reaction being carried out in DMSO at room temperature (equation 97). By this method phenyl tellurocyanate (81) and 4-methoxyphenyl tellurocyanate (82) were prepared, but the yield never surpassed 20%. The other method consists in partial reduction of aryltellurium trihalides with aqueous sodium metabisulphite ($Na_2S_2O_5$) to aryltellurium(II) halides (84), followed by the addition of potassium cyanide (equation 98). By this method 81 and 82 were prepared in 86% and 93% yields respectively. The reaction conditions are critical, and the best results were obtained when the trihalide was first stirred with 2 equiv. of sodium hydrogen carbonate to yield an aryltellurinyl halide (83), and then about 4 equiv. each of sodium metabisulphite and potassium cyanide were added.

$$\text{ArTeTeAr} + \text{CN}^- \xrightarrow{\text{DMSO}} \text{ArTe}^- + \text{ArTeCN}$$

(81) Ar = Ph   (97)

(82) Ar = 4-MeOC$_6$H$_4$

$$\text{ArTeX}_3 \xrightarrow[\text{aq. NaHCO}_3]{} \text{ArTe}\overset{\displaystyle O}{\underset{\displaystyle X}{\diagdown}} \xrightarrow[\text{aq. Na}_2\text{S}_2\text{O}_5]{} [\text{ArTeX}] \xrightarrow{\text{KCN}} \textbf{81,82}$$

(X = Cl, Br)   (83)   (84)

(98)
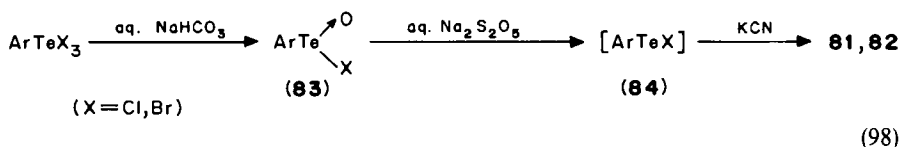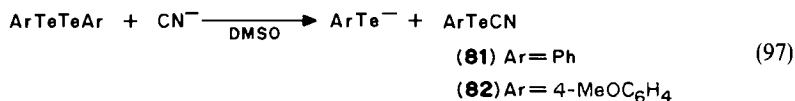
Compound 81 was also prepared by treatment of benzenetellurolate anion (PhTe⁻) with cyanogen bromide in ethanol (equation 99)[211]. Sodium borohydride reduction of diphenyl ditelluride in ethanol under nitrogen followed by addition of an ethanolic solution of commercial cyanogen bromide afforded 81 in 58% isolated yield. The tellurocyanate thus prepared could be converted to various alkyl phenyl tellurides in moderate to good yields by treating it with alcohol in dichloroethane or tetrahydrofuran at room temperature in the presence of tributylphosphine (equation 99)[211]. Such a transformation did not occur by using other organophosphorus compounds such as triphenylphosphine or triethyl phosphite. Although details are not known, this telluride formation may proceed via a nucleophilic attack of a benzenetellurolate anion on an alkyl group of the phosphonium salt of the alcohol, as proposed in a similar reaction of aryl selenocyanate[114].

$$\text{PhTeTePh} \xrightarrow[\text{EtOH}]{\text{NaBH}_4} [\text{PhTeNa}] \xrightarrow[\text{EtOH}]{\text{BrCN}} \textbf{81} \xrightarrow[\substack{\text{Bu}_3\text{P,} \\ \text{CH}_2\text{Cl}_2}]{\text{ROH}} \text{PhTeR} \qquad (99)$$
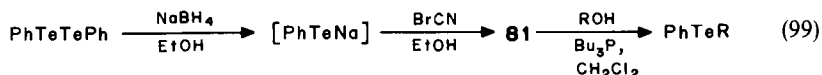
Compound **81** has also been used as a source of introduction of phenyltellurium species to other organic compounds. For example, treatment of cyclohexene with **81** in methanol in the presence of copper(II) chloride afforded (2-methoxycyclohexyl)phenyltellurium dichloride in 62% yield (equation 100)[212,213]. The reaction is the so-called oxytelluriation of olefins, with the phenyltellurium species acting as an electrophile. A contrasting example is a nucleophilic substitution by the species for preparation of tellurium-containing amino acid[214]. Thus, treatment of **81** with β- or γ-halogenoamino acids in the presence of sodium borohydride in ethanol gave the corresponding phenyltelluroamino acids in ca. 30% yield (equation 101).

$$
\text{cyclohexene} \xrightarrow[\substack{CuCl_2, \\ MeOH}]{\textbf{81}} \text{(2-methoxycyclohexyl with OMe and ''''TePh, Cl}_2\text{)}
\tag{100}
$$

$$
\overset{\overset{\displaystyle NH_3Cl}{|}}{X(CH_2)_nCHCO_2H} \xrightarrow[\substack{NaBH_4, \\ EtOH}]{\textbf{81}} \overset{\overset{\displaystyle NH_3Cl}{|}}{PhTe(CH_2)_nCHCO_2H}
\tag{101}
$$

$$X = Cl, Br$$
$$n = 1, 2$$
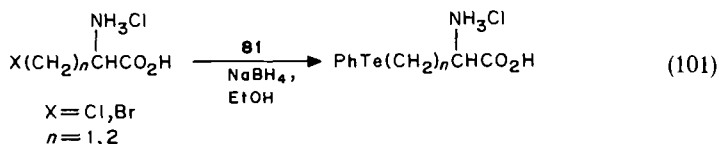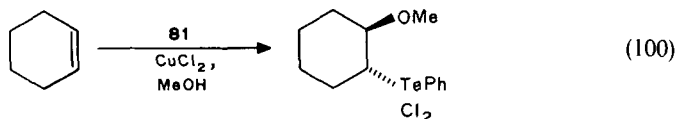
Two aryl tellurocyanates were recently prepared as by-products in the synthesis of diaryl tellurides from aromatic amines[215]. Aryldiazonium tetrafluroroborates were converted to symmetrical diaryl tellurides in moderate yields by treatment with potassium tellurocyanate in DMSO (for KTeCN–DMSO, see below). Although the expected aryl tellurocyanates are seldom stable enough to be isolable under the reaction conditions, in two cases they were isolated by chromatography in addition to diaryl tellurides, viz., **79** and 2,6-dimethylphenyl tellurocyanate (**85**), in 11% and 40% yields, respectively (equation 102). The main reaction course was the disproportionation of the intermediate aryl tellurocyanates to diaryl tellurides and tellurium dicyanide, the latter of which decomposed instantly to elemental tellurium and dicyanogen (equation 103).

$$
ArN_2^+BF_4^- + KTeCN \xrightarrow{DMSO} ArTeCN + KBF_4 + N_2
\tag{102}
$$

$$\textbf{(79)}\, Ar = 2\text{-}NO_2C_6H_4$$

$$\textbf{(85)}\, Ar = 2,6\text{-}Me_2C_6H_3$$

$$
2\,ArTeCN \xrightarrow{DMSO} Ar_2Te + Te(CN)_2
\tag{103}
$$
$$\downarrow$$
$$Te + (CN)_2$$
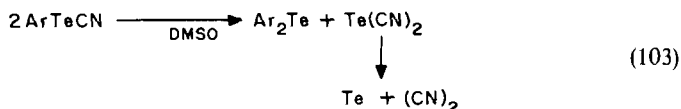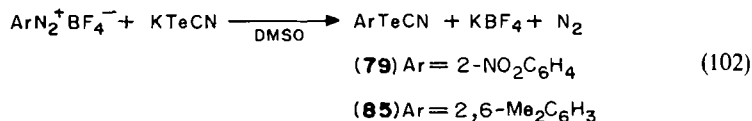
An attempt to prepare 2,3,5,6-tetramethylphenyl tellurocyanate by the reaction of the corresponding aryl iodide with KTeCN in a mixture of hexamethylphosphoramide and DMSO in the presence of copper(I) iodide resulted in the formation of the corresponding aryl cyanide as the sole identifiable product[31]. The initially formed copper(I) tellurocyanate decomposed immediately to elemental tellurium and copper(I) cyanide, the latter being the reactive species for the aryl cyanide. In contrast, the corresponding aryl selenocyanate was obtained in 45–61% yields by a similar procedure.

Although a tellurocyanate ion has been shown to be a much stronger nucleophile than selenocyanate and thiocyanate ions by kinetic studies using benzylic halides[18,216] and

dichloromethane[217] as substrates, the preparation of organic tellurocyanates by nucleophilic substitution by the tellurocyanate ion was not known until a decade ago, probably because of the instability of the ion and the products towards air and/or water. Thus, alkali metal tellurocyanates and their solutions were decomposed instantly by water with the liberation of elemental tellurium[218,219] and a sterically large counter cation was necessary to stabilize the tellurocyanate anion[18,216,219]. By using the stabilized tellurocyanate ion, Austad *et al.*[216] succeeded in isolating from benzyl bromide in acetonitrile a stable and almost colourless crystalline substance, which was suggested to be tetraphenylarsonium bromocyanobenzyl tellurate (86) (equation 104). Tetraphenylarsonium tellurocyanate was prepared by the reaction of tetraphenylarsonium cyanide with tellurium in acetonitrile and shown to be fairly stable when properly dried[219]. Freshly prepared 86 had no odour, but on storage at room temperature an unpleasant odour was produced. On crystallization of 86, tetraphenylarsonium bromide crystallized out as a minor product. The authors suggested that an equilibrium as shown in equation 104 exists and the unpleasant odour is due to traces of benzyl tellurocyanate (87) or subsequent products, but they could not isolate and characterize it[216]. A complex similar to 86 was also prepared in high yield[18] from 4-nitrobenzyl chloride and bis(triphenylphosphine)iminium tellurocyanate [m.p. 190–193 °C (decomp.)][220] in acetone namely 88 [yellow–brownish needles, m.p. ca. 120 °C (decomp.)] (equation 105). Structural determination of the anionic part of 88 by X-ray crystallography indicated that the C—Te—C bond angle is 87.4° and the Te—Cl bond is approximately *trans* to the Te—C (cyano) bond. In contrast Spencer *et al.*[221] succeeded in isolating (61% yield) and characterizing 87 (white needles, m.p. 126–127 °C), the first alkyl tellurocyanate ever isolated, by the reaction of benzyl chloride with potassium or sodium tellurocyanate in DMSO at room temperature (equation 106). The key problem in the reaction was to prepare stable alkali metal tellurocyanates or their solutions, which were known to be very sensitive to air and water as described above. Although it was already known that KTeCN was produced in the solid state by heating potassium cyanide and tellurium at 100–250 °C and it could be dissolved in acetonitrile[205,222*], Spencer *et al.*[221] found that stable solutions of potassium or sodium tellurocyanate were readily prepared by stirring together 1 equiv. each of powdered tellurium and dry, powdered alkali metal cyanide in dry DMSO at 100 °C under an inert atmosphere until all of the tellurium dissolved. The resulting pale yellow solution decomposed instantly if added to water, with the formation of elemental tellurium, and also attempts to precipitate the alkali metal tellurocyanates by addition of acetone or diethyl ether resulted in the formation of a tellurium mirror. A detailed IR spectrum of 87

$$Ph_4As^+TeCN^- + PhCH_2Br \xrightarrow{\text{MeCN}} Ph_4As^+PhCH_2Te^- \quad (104)$$

(86)

(87)
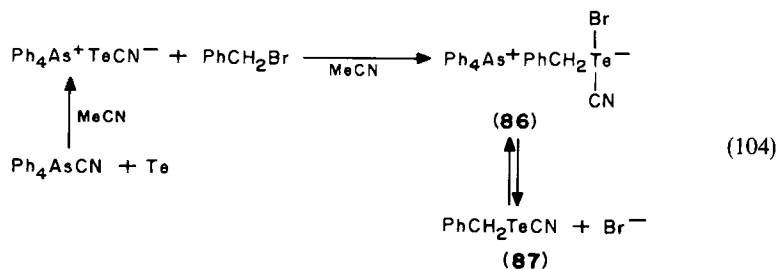
*Contrary to Ref. 205, Greenwood *et al.*[222] could not observe any reaction of powdered tellurium with fused NaCN–KCN eutectic, with aqueous or methanolic KCN under reflux or with a suspension of KCN in benzene.

in the solid state was recorded together with those of the corresponding thiocyanate and selenocyanate and tentative assignments, based on force fields transferred from similar molecules, were proposed[63].

$$[(Ph_3P)_2N]^+ \; TeCN^- \; + \; O_2N\!\!-\!\!\langle\bigcirc\rangle\!\!-\!\!CH_2Cl$$

$$\downarrow acetone \qquad\qquad (105)$$

$$[(Ph_3P)_2N]^+ \; O_2N\!\!-\!\!\langle\bigcirc\rangle\!\!-\!\!CH_2\!\!\overset{Cl}{\underset{CN}{\mid}}\!\!Te^-$$

$$\textbf{(88)}$$

$$MCN \; + \; Te \; \xrightarrow[\text{DMSO}]{\Delta} \; [MTeCN] \; \xrightarrow{PhCH_2Cl} \; \textbf{87} \qquad (106)$$

$$(M = K, Na)$$
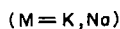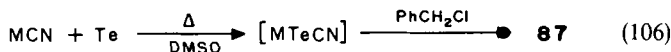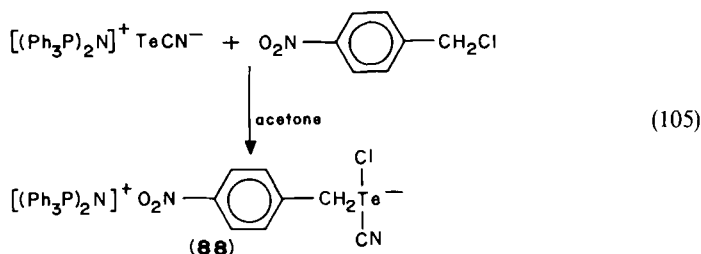
The reaction shown in equation 106 was also applied to 4-chloro-, 4-methoxy- and 1, 2, 3, 4, 5-pentamethyl-benzyl chlorides, and the corresponding ring-substituted benzyl tellurocyanates (89)–(91) were produced in 46–64% yields (equation 107)[223]. All these tellurocyanates are light sensitive and thermally unstable white to pale yellow solids. When 4-nitrobenzyl chloride was treated under similar conditions, 4-nitrobenzyl tellurocyanate (92) could not be isolated, but it changed to the corresponding ditelluride during the work-up procedure. However Maartmann-Moe et al.[224] succeeded in isolating 92 in 49% yield by a similar treatment and they claimed that the compound is a stable solid and can be stored for months even in daylight and moist air.

$$ArCH_2Cl \; \xrightarrow[\text{DMSO}]{[KTeCN]} \; ArCH_2TeCN$$

$$\textbf{(89)} \; Ar = 4\text{-}ClC_6H_4$$

$$\textbf{(90)} \; Ar = 4\text{-}MeOC_6H_4 \qquad\qquad (107)$$

$$\textbf{(91)} \; Ar = 1,2,3,4,5\text{-}Me_5C_6$$

$$\textbf{(92)} \; Ar = 4\text{-}O_2NC_6H_4$$
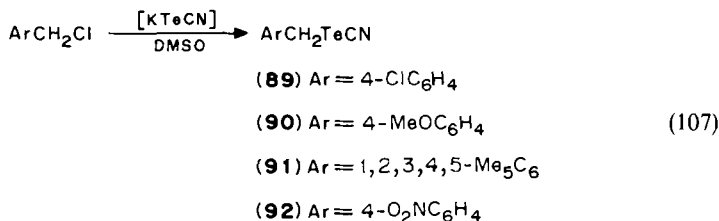
The X-ray crystal structural determination of 92 revealed the following[67,224]. There are two distinctly different Te—C bond lengths in the molecule, Te—C_1 (benzylic) and Te—C_2 (cyano) being 2.167 and 2.06 Å, respectively. The C_1—Te—C_2 bond angle is 90.6°. The tellurium atom forms two strong intermolecular 'secondary bonds' to oxygen atoms of 2.949 and 3.182 Å, these two bonds and the two Te—C bonds being strictly coplanar. The compound may be considered as a distorted square-planar tellurium(II) complex and must owe its stability in the crystalline state to intermolecular contacts between the tellurium atom and the two oxygen atoms. The corresponding selenocyanate has been shown to have a similar structure[67].

Tellurenyl halides (93) obtained by halogenolysis of tellurophthalide reacted with ethanol and then potassium cyanide to give a 33–69% yield of 2-carbethoxybenzyl tellurocyanate (94) (equation 108), which was also synthesized independently from 2-

carbethoxybenzyl bromide in 85% yield by treatment with KTeCN in DMSO (equation 109)[225].

(93)   **(94)**

X = Cl, Br, I

(108)

(109)
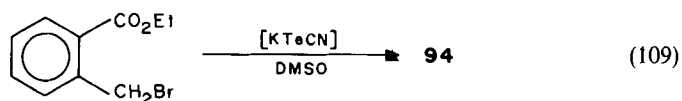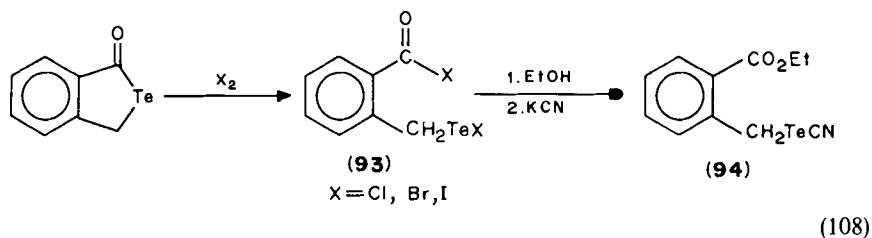
Organic tellurocyanates so far isolated and characterized are summarized in Table 1.
The tellurocyanate **87** was stable to light alone in the absence of oxygen, but darkened in the presence of air with the precipitation of a black solid. Organic products were revealed to be benzaldehyde (60%) and benzyl alcohol (40%). Several other reactions of **87** were also examined by Cava and coworkers, as follows[221,226]. Crystallization of an equimolar mixture of **87** and tetraphenylarsonium bromide afforded the complex **86**, but the properties of this substance suggested that it is probably a loose molecular complex of its two components, rather than a compound[216] containing an anionic tellurium in the form of **86** as previously suggested. Chromatography of the complex on silica gel in the dark afforded **87** with a recovery of 90%. The reaction of **87** with methanolic sodium hydroxide

TABLE 1. Organic tellurocyanates isolated and characterized

Compound	Equation[a]	Isolated yield (%)	M.p. (°C) (colour)	Spectral data: ^{1}HNMR δ(ppm), IR v(cm^{-1}), mass m/e	Ref.
76	93	7	80–81 (violet)	IR 2148, 778, 743	205
77	94	—[b]	104		206
78	94	80	135	NMR 7.3–7.7 (m, 7H), 7.85–8.5 (m, 2H)	207
79	95	65	148–149 (red–brown)	IR 2400, 1600, 1580, 1500, 1320 Mass 278 (M$^+$), 250 (M$^+$ − CN)	208
79	102	11	160	NMR 7.62 (t, 1H), 7.74 (t, 1H), 8.46–8.52 (m, 2H) IR 2150	215
80	96	50	117		210
81	98	86	74–75 (white)	IR 2170, 1400, 1170, 730, 690 Mass 233 (M$^+$), 207 (M$^+$ − CN)	208

Table 1. (Contd.)

Compound	Equation[a]	Isolated yield(%)	M.p. (°C) (colour)	Spectral data: ^{1}HNMR δ(ppm), IR v(cm^{-1}), mass m/e	Ref.
81	97	20	74–75		208
81	99	58	67–70 (decomp.) (colourless)		211
82	98	93	75–77 (white)	IR 2160, 1590, 1500, 1400, 1260, 1190 Mass 263 (M$^+$), 237 (M$^+$ − CN)	208
82	97	18	75–77		208
85	102	40	114–115	NMR 2.69 (s, 6H), 7.23–7.26 (m, 3H) IR 2140	215
87	106 (M = K)	61	126–127 (white)	NMR 4.52 (s, 2H), 7.38 (br, s, 5H) Mass 247 (M$^+$), 91	221
87	106 (M = Na)	57			221
87	107	72	126–127 (decomp.)	NMR 4.48 (s, 2H), 7.26 (s, 5H) IR 2150, 1600, 1495, 1455, 1140, 1060, 760, 695	223
89	107	46	75–80 (decomp.)	NMR 4.36 (s, 2H), 7.14 (s, 4H) IR 2150, 1485, 1410, 1150, 1140, 1090, 1015, 835, 805	223
90	107	59	76–79 (decomp.)	NMR 3.80 (s, 3H), 4.52 (s, 2H), 6.92 (d, 2H, J = 9 Hz), 7.22 (d, 2H, J = 9 Hz) IR 2140, 1605, 1500, 1460, 1300, 1240, 1175, 1030, 830–815, 795, 735	223
91	107	64	161–162 (decomp.) (white–pale yellow)	NMR 2.22 (s, 9H), 2.32 (s, 6H), 4.72 (s, 2H) IR 2130, 1430, 1140, 1050, 990, 840, 760	223
92	107	49	123 (decomp.) (green– yellow)	NMR 4.36 (s, 2H), 7.91 (m, 4H) IR 2157, 430 Mass 292 (13)^c, 290 (11), 288 (7), 136 (100) UV(MeCN) ∼ 342 nm (log ε ⩽ ∼ 3.33)	224
94	109	85	72–73 (dark)	NMR 1.41 (t, 3H), 4.22 (s, 2H), 4.36 (q, 2H), 7.32–7.41 (m, 2H), 7.54 (t, 1H), 7.98 (d, 1H) IR 2110, 1660 Mass 391 (1)^c, 163 (27), 135 (100), 118 (15), 105 (11)	225
94	108 (X = Br)	69			225
94	108 (X = Cl)	33			225
94	108 (X = I)	44			225

[a]Equation number employed for synthesis.
[b]Not determined.
[c]The value in parentheses is a relative intensity.

O₂/hν → PhCH₂OH + PhCHO + Te

NaOH–MeOH or H₃PO₂ → PhCH₂TeTeCH₂Ph (95)

Br₂/CH₂Cl₂ → [PhCH₂Te(Br₂)CN] →Br₂→ PhCH₂TeBr₃

87

excess Br₂/CCl₄ → [PhCH₂TeBr₃] →excess Br₂→ PhCH₂Br

PhCH₂SH → PhCH₂TeSCH₂Ph (96)

(with 2-nitrophenyllithium) → 2-nitrophenyl benzyl telluride

SCHEME 8

(87) →O₂/hν→ [PhCH₂Te⁺CN, ⁻O—O] (97) → [PhCH₂ TeCN, O——O] (98) → [PhCH₂O•] → PhCH₂OH + PhCHO
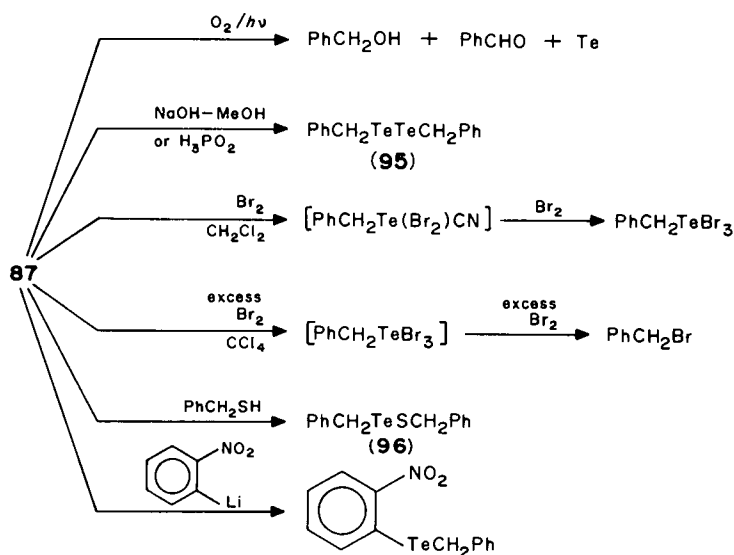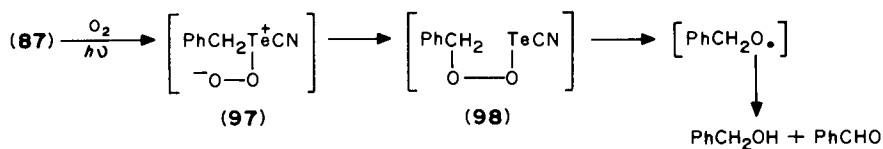
SCHEME 9

under argon gave a photosensitive dibenzyl ditelluride (95) in fair yield (29%), which was produced more effectively and almost quantitatively by treatment of 87 with warm hypophosphorous acid(H₃PO₂). Similar transformations were also observed with 89–91[223]. Treatment of 87 with excess of bromine produced benzyl bromide via a benzyltellurium tribromide. The reaction of 87 with benzyl thiol in carbon tetrachloride afforded dibenzyl thiotelluride (96). The attack of a carbanion on the tellurium atom of 87 was also expected and, in fact, 2-nitrophenyllithium reacted smoothly with 87 to give the organe–red benzyl 2-nitrophenyl telluride in 72% yield at −100 °C. All the results are summarized in Scheme 8. The proposed mechanism of the photooxidation of 87 is shown in Scheme 9[221]. The major reaction pathway may involve singlet oxygen, which could attack the tellurium atom to give a 1,3-dipolar peroxide (97). Rearrangement of 97 to an unstable benzylperoxytellurocyanate (98) might occur in which an oxygen—oxygen bond fission gives benzyloxy radicals, leading to the alcohol and the aldehyde. It was proposed that reduction of 87 with hypophosphorous acid may give a very unstable benzyl tellurol (PhCH₂TeH) rather than benzyltellurium radical (PhCH₂Te•) and the former reacts instantaneously with another mole of 87 to give 95. This assumption is consistent with the facile formation of 96 when treated with benzyl thiol.

$$TeCN^- - e^- \rightleftharpoons TeCN^\bullet$$

$$2\,TeCN^\bullet \longrightarrow (TeCN)_2$$

$$(TeCN)_2 + TeCN^- \rightleftharpoons (TeCN)_3^-$$

$$2(TeCN)_3^- - 2e^- \rightleftharpoons 3(TeCN)_2$$

$$(TeCN)_2 \longrightarrow 2Te + (CN)_2$$
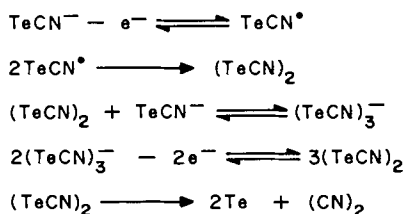
SCHEME 10

The electrochemical oxidation of tetraethylammonium tellurocyanate in acetonitrile produced tellurocyanogen, $(TeCN)_2$, via the $(TeCN)_3^-$ ion as an intermediate[227]. This compound was unstable and decomposed to tellurium and dicyanogen (Scheme 10). The instability of $(TeCN)_2$ will make it difficult to use this compound as a reagent to introduce the TeCN group into organic molecules and there seems to be no report of such attempts.

V. ORGANIC ISOTELLUROCYANATES

Organic isotellurocyanates $(RN{=}C{=}Te)$ have not been prepared so far, in spite of several attempts at their synthesis from isonitriles or organocyanosilanes and tellurium[228-230] and also by photoinduced isomerization of organic tellurocyanates[223]. When organic tellurocyanates were subjected to photolysis, only tellurium precipitation was observed[223], as expected from the reaction shown in Scheme 8.

VI. REFERENCES

1. E. Bulka, in *The Chemistry of Cyanates and Their Thio Derivatives, Part 2* (Ed. S. Patai), Wiley, Chichester, 1977, Ch. 19.
2. B. Lindgren, *Chem. Scr.*, **16**, 24 (1980).
3. M. V. Lakshmikantham and M. P. Cava, *J. Org. Chem.*, **45**, 2632 (1980).
4. T. Hori and K. B. Sharpless, *J. Org. Chem.*, **43**, 1689 (1978).
5. K. Alzbeta, V. Konecny, M. Fandlova and J. Kovac, *Czech. Pat.*, 169352; *Chem. Abstr.*, **88**, P152599g (1978).
6. A. Krutosikova, V. Konecny, M. Fandlova and J. Kovac, *Czech. Pat.*, 170750; *Chem. Abstr.*, **89**, P101858d (1978).
7. A. P. Kozikowski and A. Krief, *Tetrahedron Lett.*, 2709 (1975).
8. R. C. Cambie, P. S. Rutledge, V. Y. Y. Tan and P. D. Woodgate, *J. Chem. Res. (S)*, 392 (1984).
9. A. P. Arnold and A. J. Canty, *Aust. J. Chem.*, **36**, 815 (1983).
10. B. Lindgren, *Acta Chem. Scand., Ser. B*, **30**, 941 (1976).
11. B. Lindgren, *Acta Chem. Scand., Ser. B*, **31**, 1 (1977).
12. F. Asinger and M. K. Schmitz, *Monatsh. Chem.*, **113**, 1191 (1982).
13. J. Gramza, R. B. Mitchell and D. C. Ditter, *J. Org. Chem.*, **49**, 2057 (1984).
14. V. N. Bodner, M. O. Lozinskii and P. S. Pel'kis, *Ukr. Khim. Zh.*, **47**, 424 (1981); *Chem. Abstr.*, **95**, 80775f (1981).
15. A. Halvorsen and J. Songstad, *J. Chem. Soc., Chem. Commun.*, 327 (1978).
16. T. Thorstenson and J. Songstad, *Acta Chem. Scand., Ser. A*, **32**, 133 (1978).
17. T. Thorstenson, R. Eliason and J. Songstad, *Acta Chem. Scand., Ser. A*, **31**, 276 (1977).
18. K. Maartmann-Moe, K. A. Sanderud and J. Songstad, *Acta Chem. Scand., Ser. B*, **36**, 211 (1982).
19. L. M. Yagupol'skii, I. I. Maletina, N. V. Kondratenko and V. V. Orda, *Synthesis*, 835 (1978).
20. P. D. Woodgate, H. H. Lee and P. S. Rutledge, *Synthesis*, 152 (1978).
21. Y. Tamura, M. Adachi, T. Kawasaki and Y. Kita, *Tetrahedron Lett.*, 2251 (1979).
22. C. H. Banks, J. R. Daniel and R. A. Zingaro, *J. Med. Chem.*, **22**, 572 (1979).

23. G. A. Krafft and P. T. Meinke, *J. Am. Chem. Soc.*, **108**, 1314 (1986).
24. H. G. Werchan, G. Dittrich and H. Lehmann, *East Ger. Pat*; DD 202699; *Chem. Abstr.*, **100**, P138785z (1984).
25. W. Ried and H. Dietschmann, *Justus Liebigs Ann. Chem.*, 1003 (1981).
26. Z. Ejmocki, *Pr. Nauk. Politech. Warz., Chem.*, **17**, 93 (1975); *Chem. Abstr.*, **86**, 42730u (1977).
27. C. Paulmier and F. Outurquin, *J. Heterocycl. Chem.*, **20**, 113 (1980).
28. A. V. El'tsov, A. N. Frolov, E. V. Smirnov and V. V. Yunnikov, *USSR Pat.*, 520354; *Chem. Abstr.*, **85**, P94065e (1976): A. N. Frolov, A. V. El'tsov, E. V. Smirnov and O. V. Kul'bitskaya, *Zh. Org. Khim.*, **13**, 2007 (1977); *Chem. Abstr.*, **88**, 6482x (1978).
29. A. N. Frolov, E. V. Smirnov, O. V. Kul'bitskaya and A. V. El'tsov, *Zh. Org. Khim.*, **16**, 2302 (1980); *Chem. Abstr.*, **94**, 174536k (1981).
30. H. Suzuki and M. Shinoda, *Synthesis*, 640 (1977).
31. H. Suzuki, K. Miyoshi and M. Shinoda, *Bull. Chem. Soc. Jpn.*, **53**, 1765 (1980).
32. V. A. Nafedov, L. K. Tarygina, L. V. Kryuchkova and Yu. S. Ryabokobylko, *Zh. Org. Khim.*, **17**, 570 (1981); *Chem. Abstr.*, **95**, 41864 (1981).
33. W. H. H. Gunther, *US Pat.*, 3905958; *Chem. Abstr.*, **84**, P37310m (1976).
34. D. Herrmann and R. Gollmick, *Z. Chem.*, **17**, 290 (1977).
35. H. J. Reich, *US Pat.*, 4242285; *Chem. Abstr.*, **94**, P139188b (1981).
36. D. E. Ames, A. G. Singh and W. F. Smith, *Tetrahedron*, **39**, 831 (1983).
37. G. H. Schmid and D. G. Garratt, *J. Org. Chem.*, **48**, 4169 (1983).
38. C. Paulmier, *Bull. Soc. Chim. Fr. II*, 237 (1979).
39. M. Kato, R. Michels and W. Heitz, *J. Polym. Sci., Polym. Lett.*, **14**, 413 (1976); M. Kato, *Ger. Offen.*, 2649163; *Chem. Abstr.*, **87**, 53851f (1977).
40. S. Uemura, A. Toshimitsu, M. Okano and K. Ichikawa, *Bull. Chem. Soc. Jpn.*, **48**, 1925 (1975).
41. S. Uemura, H. Miyoshi, M. Wakasugi, M. Okano, O. Itoh, T. Izumi and K. Ichikawa, *Bull. Chem. Soc. Jpn.*, **53**, 553 (1980).
42. S. Uemura, A. Toshimitsu, Y. Kozawa and M. Okano, *Bull. Inst. Chem. Res. Kyoto Univ.*, **59**, 354 (1981).
43. A. Toshimitsu, S. Uemura and M. Okano, *J. Chem. Soc., Perkin Trans. 1*, 1206 (1979).
44. A. Arase and Y. Masuda, *Chem. Lett.*, 785 (1976).
45. A. Arase and Y. Masuda, *Chem. Lett.*, 1115 (1976).
46. C. Paulmier, *Tetrahedron Lett.*, 1797 (1978).
47. C. Paulmier, *Bull. Soc. Chim. Fr. II*, 592 (1979).
48. R. Michels, M. Kato and W. Heitz, *Makromol. Chem.*, **177**, 2311 (1976).
49. G. Cauquis and G. Pierre, *Tetrahedron*, **34**, 1475 (1978).
50. A. Toshimitsu, S. Uemura and M. Okano, *J. Chem. Soc., Perkin Trans. 1*, 1273 (1978).
51. G. Simchen and G. Entenmann, *Justus Liebigs Ann. Chem.*, 1249 (1977).
52. S. Braverman, M. Freund and I. Goldberg, *Tetrahedron Lett.*, **21**, 3617 (1980).
53. A. Haas, B. Koch and N. Welcman, *Chem.-Ztg.*, **98**, 511 (1974).
54. A. Haas, B. Koch and N. Welcman, *Z. Anorg. Alg. Chem.*, **427**, 114 (1976).
55. B. Lindgren, *Tetrahedron Lett.*, 4347 (1979).
56. M. R. Bryce, C. D. Reynolds, P. Hanson and J. M. Vernan, *J. Chem. Soc., Perkin Trans. 1*, 607 (1981).
57. Y. H. Kang and J. L. Kice, *J. Org. Chem.*, **49**, 1507 (1984).
58. S. Tomoda, Y. Takeuchi and Y. Nomura, *Chem. Lett.*, 1069 (1981).
59. S. Tomoda, Y. Takeuchi and Y. Nomura, *Synthesis*, 212 (1985).
60. M. Tiecco, L. Testaferri, M. Tingoli, D. Chianelli and M. Montanucci, *J. Org. Chem.*, **48**, 4289 (1983).
61. E. G. Yarkova, N. R. Safiullina, G. A. Chmutova and I. V. Bautina, *Zh. Obshch. Khim.*, **49**, 2025 (1979); *Chem. Abstr.*, **92**, 75714 (1980).
62. S. Giorgianni, A. Passerini and R. Passerini, *Spectrosc. Lett.*, **16**, 775 (1983).
63. C. E. Sjøgren, *Acta Chem. Scand., Ser. A*, **38**, 657 (1984).
64. W. J. Franklin, R. L. Werner and R. A. Ashby, *Spectrochim. Acta, Part A*, **30**, 387 (1974).
65. F. Ritschl, *Z. Chem.*, **18**, 411 (1978); *Chem. Abstr.*, **90**, 120811v (1979).
66. M. V. Andreocci, M. Bossa, C. Furlani, M. N. Piancastelli and T. Tarantelli, *J. Chem. Soc., Faraday Trans. II*, **75**, 105 (1979).
67. K. Maartmann-Moe, K. A. Sanderud and J. Songstad, *Acta Chem. Scand., Ser. A*, **38**, 187 (1984).
68. B. M. Landsberg, *Z. Naturforsch., Teil A*, **33**, 1333 (1978).

69. T. Sakaizumi, Y. Kohri, O. Ohashi and I. Yamaguchi, *Bull. Chem. Soc. Jpn.*, **51**, 3411 (1978).
70. T. Sakaizumi, T. Itakura and O. Ohashi, *Koen Yoshishu-Bunshi Kozo Toronkai*, 524 (1979); *Chem. Abstr.*, **93**, 176230j (1980).
71. G. A. Chmutova, I. V. Bautina and A. N. Vereshchagin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2469 (1976); *Chem. Abstr.*, **86**, 120659u (1977).
72. G. A. Chmutova, I. V. Bautina and A. N. Vereshchagin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1554 (1981); *Chem. Abstr.*, **95**, 149826t (1981).
73. G. A. Chmutova, I. V. Bautina, R. U. Belyzlov and A. N. Vereshchagin, *Zh. Org. Khim.*, **17**, 2249 (1981); *Chem. Abstr.*, **96**, 34149c (1982).
74. A. Benedetti C. Preti, L. Tassi and G. Tosi, *Aust. J. Chem.*, **35**, 1365 (1982).
75. A. Croisy, P. Jacquignon and L. Christiaens, *Org. Mass. Spectrom.*, **10**, 1084 (1975).
76. L. Christiaens, J. L. Piette, L. Laitem, M. Baiwir, J. Denoel and G. Llabres, *Org. Magn. Reson.*, **8**, 354 (1976).
77. W. H. Pan and J. P. Fackler, Jr., *J. Am. Chem. Soc.*, **100**, 5783 (1978).
78. G. A. Kalabin, D. F. Kushnarev, G. A. Chmutova and L. V. Kashurnikova, *Zh. Org. Khim.*, **15**, 24 (1979); *Chem. Abstr.*, **90**, 167514r (1979).
79. P. Granger, S. Chapelle and C. Paulmier, *Org. Magn. Reson.*, **14**, 240 (1980).
80. R. B. Valeef, G.A. Kalabin and D. F. Kushnarev, *Zh. Org. Khim.*, **16**, 2482 (1980); *Chem. Abstr.*, **94**, 120695t (1981).
81. G. Llabres, M. Baiwir, J. L. Piette and L. Christiaens, *Org. Magn. Reson.*, **15**, 152 (1981).
82. G. A. Kalabin and D. F. Kushnarev, *Zh. Strukt. Khim.*, **20**, 617 (1979); *Chem. Abstr.*, **92**, 110126c (1980).
83. G. Llabres, M. Baiwir, L. Christiaens and J. L. Piette, *Org. Magn. Reson.*, **21**, 461 (1983).
84. H. M. Hassaneen, A. Shetta and A. S. Shawali, *J. Heterocycl. Chem.*, **17**, 1185 (1980).
85. M. Takahashi and M. Kurosawa, *Bull. Chem. Soc. Jpn.*, **53**, 1185 (1980).
86. H. M. Hassaneen, A. O. Abdelhamid, A. Shetta and A. S. Shawali, *Gazz. Chim. Ital.*, **112**, 545 (1982).
87. A. O. Abdelhamid, H. M. Hassaneen and A. S. Shawali, *J. Heterocycl. Chem.*, **20**, 719 (1983).
88. K. Peseke and N. C. Catanedo, *East Ger. Pat.*, 147361; *Chem. Abstr.*, **95**, P203939x (1981).
89. J. M. Bahan, R. A. W. Johnstone and M. J. Wright, *J. Chem. Soc., Perkin Trans. 1*, 1216 (1975).
90. Meiji Seika Kaisha, *Jpn. Kokai Tokkyo Koho*, JP 5852299 [8352299]; *Chem. Abstr.*, **99**, P53972u (1983).
91. A. Lobert and A. Le Marechal, *J. Chem. Soc., Chem. Commun.*, 447 (1978).
92. J. Liebscher and H. Hartmann, *Synthesis*, 273 (1976).
93. E. R. Clark and M. A. S. Al-Turahi, *J. Organomet. Chem.*, **134**, 181 (1977).
94. J. T. Groves, S. M. Lindenauer, B. J. Haywood, J. A. Knol and J. S. Schultz, *J. Med. Chem.*, **17**, 902 (1974).
95. D. Herrmann and M. Schlenzig, *Z. Chem.*, **18**, 94 (1978).
96. R. H. Mitchell, *Can. J. Chem.*, **54**, 238 (1976).
97. For reviews, see D. L. J. Clive, *Tetrahedron*, **34**, 1049 (1978); H. J. Reich, in *Oxidation of Organic Compounds, Part C* (Ed. W. Trahanovsky), Academic Press, New York, 1978, pp. 1–130.
98. K. B. Sharpless and M. W. Young, *J. Org. Chem.*, **40**, 947 (1975).
99. P. A. Grieco, J. A. Noguez and Y. Masaki, *Tetrahedron Lett.*, 4213 (1975).
100. H. J. Reich, S. Wollowitz, J. E. Trend, F. Chow and D. F. Wendelborn, *J. Org. Chem.*, **43**, 1697 (1978).
101. K. Mori, S. Masuda and T. Suguro, *Tetrahedron*, **37**, 1329 (1981).
102. H. J. Reich and S. Wollowitz, *J. Am. Chem. Soc.*, **104**, 7051 (1982).
103. T. Otsubo, F. Ogura, H. Yamaguchi, Y. Sakata and S. Misumi, *Bull. Chem. Soc. Jpn.*, **55**, 182 (1982).
104. K. Furuichi, S. Yogai and T. Miwa, *J. Chem. Soc., Chem. Commun.*, 66 (1980).
105. G. P. Mullen, N. P. Luthra, R. B. Dunlap and J. D. Odom, *J. Org. Chem.*, **50**, 811 (1985).
106. H. J. Reich, S. K. Shah, P. M. Gold and R. E. Olson, *J. Am. Chem. Soc.*, **103**, 3112 (1981).
107. T. Otsubo, F. Ogura, H. Yamaguchi and S. Misumi, *Synth. Commun.*, **10**, 595 (1980).
108. H. Higuchi and S. Misumi, *Tetrahedron Lett.*, **23**, 5571 (1982).
109. N. Esaki, H. Tanaka, S. Uemura, T. Suzuki and K. Soda, *Biochemistry*, **18**, 407 (1979).
110. M. V. Lakshmikantham, M. P. Cava and A. F. Garito, *J. Chem. Soc., Chem. Commun.*, 383 (1975).
111. N. X. Hu, Y. Aso, T. Otsubo and F. Ogura, *Chem. Lett.*, 603 (1985).

112. J. P. Battioni, D. Mansuy and J. C. Chottard, *Inorg. Chem.*, **19**, 791 (1980).
113. S. Tomoda, Y. Takeuchi and Y. Nomura, *Chem. Lett.*, 253 (1982).
114. P. A. Grieco, S. Gilman and M. Nishizawa, *J. Org. Chem.*, **41**, 1485 (1976).
115. M. Sevrin and A. Krief, *J. Chem. Soc., Chem. Commun.*, 656 (1980).
116. P. A. Grieco, J. Y. Jaw, D. A. Claremon and K. C. Nicolaou, *J. Org. Chem.*, **46**, 1215 (1981).
117. T. G. Back and D. J. McPhee, *J. Org. Chem.*, **49**, 3842 (1984).
118. P. A. Grieco and Y. Yokoyama, *J. Am. Chem. Soc.*, **99**, 5210 (1977).
119. P. A. Grieco, Y. Yokoyama and E. Williams, *J. Org. Chem.*, **43**, 1283 (1978).
120. P. A. Grieco, J. A. Noguez and Y. Masaki, *J. Org. Chem.*, **42**, 495 (1977).
121. J. A. Marshall and G. A. Flynn, *J. Org. Chem.*, **44**, 1391 (1979).
122. P. A. Grieco, T. Takigawa and W. Shillinger, *J. Org. Chem.*, **45**, 2247 (1980).
123. W. R. Roush and T. E. D'Ambra, *J. Org. Chem.*, **46**, 5045 (1981).
124. S. L. Schreiber and K. Satake, *J. Am. Chem. Soc.*, **105**, 6723 (1983).
125. K. Nagao, M. Chiba and S.-W. Kim, *Chem. Pharm. Bull.*, **31**, 414 (1983).
126. S. Takano, M. Takahashi and K. Ogasawara, *J. Am. Chem. Soc.*, **102**, 4282 (1980).
127. P. A. Grieco and M. Nishizawa, *J. Org. Chem.*, **42**, 1717 (1977).
128. M. Nishizawa, P. A. Grieco, S. D. Burke and W. Metz, *J. Chem. Soc., Chem. Commun.*, 76 (1978).
129. M. Arnó, B. Garciá, J. R. Pedro and E. Seoane, *Tetrahedron Lett.*, **24**, 1741 (1983).
130. M. Arnó, G. M. Begona, J. R. Pedro and E. Seoane, *Steroids*, **43**, 305 (1984).
131. G. Majetich, P. A. Grieco and M. Nishizawa, *J. Org. Chem.*, **42**, 2327 (1977).
132. J. P. Cutney and A. K. Singh, *Can. J. Chem.*, **61**, 1111 (1983).
133. U. Schmidt, A. Lieberknecht, H. Bökens and H. Griesser, *J. Org. Chem.*, **48**, 2680 (1983).
134. U. Schmidt and J. Wild, *Angew. Chem. Int. Ed. Engl.*, **23**, 991 (1984).
135. L. E. Friedrich and P. Y. -S. Lam, *J. Org. Chem.*, **46**, 306 (1981).
136. G. Stork and D. J. Morgans, Jr., *J. Am. Chem. Soc.*, **101**, 7110 (1979).
137. S. Takano, M. Tanaka, K. Seo, H. Hirama and K. Ogasawara, *J. Org. Chem.*, **50**, 931 (1985).
138. T. Kametani, H. Matsumoto, H. Nemoto and F. Fukumoto, *J. Am Chem. Soc.*, **100**, 6218 (1978).
139. T. Kametani, *Jpn. Kokai Tokkyo Koho* Jp 79125639; *Chem. Abstr.*, **92**, P128474 (1980).
140. K. Mori and S. Masuda, *Agric. Biol. Chem.*, **42**, 1015 (1978).
141. T. R. Hoye and M. J. Kourth, *J. Org. Chem.*, **44**, 3461 (1979).
142. P. A. Grieco, E. Williams, H. Tanaka and S. Gilman, *J. Org. Chem.*, **45**, 3537 (1980).
143. Y. Fujimoto, H. Miura, T. Shimidzu and T. Tatsuno, *Tetrahedron Lett.*, **21**, 3409 (1980).
144. Institute of Physical and Chemical Research, *Jpn. Kokai Tokkyo Koho*, JP 81139487; *Chem. Abstr.*, **96**, P104552 (1982).
145. R. B. Woodward, E. Logusch, K. P. Nambier, K. Sakan, D. E. Ward, B.-W. Au-Yeung, P. Balaram, L. J. Browne, P. J. Card, C. H. Chen, R. B. Chênevert, A. Fliri, K. Frobel, H.-J. Gais, D. G. Garratt, K. Hayakawa, W. Heggie, D. P. Hesson, D. Hoppe, J. A. Hyatt, D. Ikeda, P. A. Jacobi, K. S. Kim, Y. Kobuke, K. Kojima, K. Krowicki, V. J. Lee, T. Leutert, S. Malchenko, J. Martens, R. S. Matthews, B. S. Ong, J. B. Press, T. V. Rajan Babu, G. Rousseau, H. M. Sauter, M. Suzuki, K. Tatsuta, L. M. Tolbert, E. A. Truesdale, I. Uchida, Y. Ueda, T. Uyehara, A. T. Vasella, W. C. Vladuchick, P. A. Wade, R. M. Williams and H. N.-C. Wong, *J. Am. Chem. Soc.*, **103**, 3210 (1981).
146. D. J. Morgans, Jr., *Tetrahedron Lett.*, **22**, 3721 (1981).
147. S. Takano, M. Morimoto, K. Masuda and K. Ogasawara, *Chem. Pharam. Bull.*, **30**, 4238 (1982).
148. T. Uematsu, T. Umemura and K. Mori, *Agric. Biol. Chem.*, **47**, 597 (1983).
149. M. Ojika, H. Kuyama, H. Niwa and K. Yamada, *Bull. Chem. Soc. Jpn.*, **57**, 2893 (1984).
150. F. E. Ziegler and J. J. Piwinsky, *J. Am. Chem. Soc.*, **104**, 7181 (1982).
151. H. E. Zimmerman and W. D. Ramsden, *Can. J. Chem.*, **62**, 2592 (1984).
152. R. E. Ireland, W. C. Dow, J. D. Godfrey and S. Thaisrivongs, *J. Org. Chem.*, **49**, 1001 (1984).
153. M. A. Adams, A. J. Duggan, J. Smolanoff and J. Meinwald, *J. Am. Chem. Soc.*, **101**, 5364 (1979).
154. T. Nakata, S. Nagao and T. Oishi, *Tetrahedron Lett.*, **26**, 6465 (1985).
155. M. C. Hanan, *Tetrahedron Lett.*, **26**, 6393 (1985).
156. W. R. Roush, H. R. Gillis and A. I. Ko, *J. Am. Chem. Soc.*, **104**, 2269 (1982).
157. P. G. Gassman and S. M. Bonser, *Tetrahedron Lett.*, **24**, 3431 (1983).
158. W. Oppolzer, K. Baettig and T. Hudlicky, *Helv. Chim. Acta*, **62**, 1493 (1979).
159. R. L. Funk, L. H. M. Horcher, II, J. U. Daggett and M. M. Hansen, *J. Org. Chem.*, **48**, 2632 (1983).
160. A. Nickon and A. G. Stern, *Tetrahedron Lett.*, **26**, 5915 (1985).

162. W. C. Still, *J. Am. Chem. Soc.*, **101**, 2493 (1979).
163. P. A. Wender and S. K. Singh, *Tetrahedron Lett.*, **26**, 5987 (1985).
164. N. Kurokawa and Y. Ohfune, *Tetrahedron Lett.*, **26**, 83 (1985).
165. H. Takaku, T. Nomoto and K. Kimura, *Chem. Lett.*, 1221 (1981).
166. Sankyo Chemical Industries, *Jpn. Kokai Tokkyo Koho*, JP 5804780 [8304780]; *Chem. Abstr.*, **98**, P161120c (1983).
167. Sankyo Kagaku K. K., *Jpn. Kokai Tokkyo Koho*, JP 5804797 [8304797]; *Chem. Abstr.*, **98**, P161121d (1983).
168. C. Boullais, N. Zylber, J. Zylber, J. Guilhem and A. Gaudemer, *Tetrahedron*, **39**, 759 (1983).
169. D. L. J. Clive, G. J. Chittattu, V. Farina, W. A. Kiel, S. M. Menchen, C. G. Russell, A. Singh, C. K. Wong and N. J. Curtis, *J. Am Chem. Soc.*, **102**, 4483 (1980).
170. T. Uematsu, N. Matsuo and Y. Sanemitsu, *Agric. Biol. Chem.*, **48**, 2477 (1984).
171. D. L. J. Clive, G. Chittattu, N. J. Curtis and S. M. Menchen, *J. Chem. Soc., Chem. Commun.*, 770 (1978).
172. P. A. Zoretie, R. J. Chambers, G. D. Marbury and A. A. Riebiro, *J. Org. Chem.*, **50**, 2981 (1985).
173. T. Kametani, H. Nemoto and K. Fukumoto, *Heterocycles*, **6**, 1365 (1977).
174. T. Kametani, H. Nemoto and K. Fukumoto, *Bioorg. Chem.*, **7**, 215 (1978).
175. A. Toshimitsu, S. Uemura and M. Okano, *J. Chem. Soc., Chem. Commun.*, 166 (1977).
176. A. Toshimitsu, T. Aoai, S. Uemura and M. Okano, *J. Org. Chem.*, **45**, 1953 (1980).
177. S. Uemura, A. Toshimitsu, T. Aoai and M. Okano, *J. Chem. Soc., Chem. Commun.*, 610 (1979).
178. S. Uemura, A. Toshimitsu, T. Aoai and M. Okano, *Chem. Lett.*, 1359 (1979).
179. A. Toshimitsu, T. Aoai, S. Uemura and M. Okano, *J. Org. Chem.*, **46**, 3021 (1981).
180. S. Tomoda, Y. Takeuchi and Y. Nomura, *Chem. Lett.*, 1715 (1981).
181. S. Tomoda, Y. Takeuchi and Y. Nomura, *Tetrahedron Lett.*, **23**, 1361 (1982).
182. S. Tomoda, Y. Takeuchi and Y. Nomura, *Chem. Lett.*, 1733 (1982).
183. S. Tomoda, Y. Takeuchi and Y. Nomura, *J. Chem. Soc., Chem. Commun.*, 871 (1982).
184. H. Fischer and S. Zeuner, *Z. Naturforsch., Teil B*, **38**, 1365 (1983).
185. F. B. McCormick, *Organometallics*, **3**, 1924 (1984).
186. H. Bock, S. Augen, P. Rasmus, B. Solouki and E. Weissflog, *Chem. Ber.*, **117**, 187 (1984).
187. S. Tanaka, S. Uemura and M. Okano, *Bull. Chem. Soc. Jpn.*, **50**, 722 (1977).
188. M. H. Quick and R. J. Angelici, *Inorg. Chem.*, **15**, 160 (1976).
189. S. Uemura, A. Toshimitsu, Y. Kozawa and M. Okano, *Bull. Inst. Chem. Res. Kyoto Univ.*, **59**, 350 (1981).
190. G. A. Chmutova and I. V. Bautina, *Zh. Obshch. Khim.*, **49**, 465 (1979); *Chem. Abstr.*, **90**, 186237u (1979).
191. G. A. Chmutova and I. V. Bautina, *Zh. Obshch. Khim.*, **51**, 1657 (1981); *Chem. Abstr.*, **95**, 167972s (1981).
192. G. A. Chmutova, M. A. Kazymova and L. V. Ermolaeva, *Zh. Obschch. Khim.*, **55**, 422 (1985); *Chem. Abstr.*, **102**, 211792x (1985).
193. L. Henrikson and U. Ehrbar, *Synthesis*, 519 (1976).
194. T. G. Back and R. G. Kerr, *J. Organomet. Chem.*, **286**, 171 (1985).
195. H. Suzuki, M. Usuki and T. Hanafusa, *Synthesis*, 705 (1979).
196. S. Uemura, N. Watanabe, A. Toshimitsu and M. Okano, *Bull. Chem. Soc. Jpn.*, **51**, 1818 (1978).
197. R. Herzschuh, B. Birner, L. Beyer, F. Dietze and E. Hoyer, *Z. Anorg. Allg. Chem.*, **464**, 159 (1980).
198. I. N. Azerbaev, L. A. Tsoi, A. D. Salimbaeva, S. T. Cholpankulova, G. A. Ryskieva, L. T. Kalkabaeva and M. Zh. Aitkhozhaeva, *Tr. Inst. Khim. Nauk Akad. Nauk Kaz. SSR*, **52**, 128 (1980); *Chem. Abstr.*, **94**, 208766c (1981).
199. W. E. Ried and E. Hanns, *Justus Liebigs Ann. Chem.*, 201 (1982).
200. W. J. Stec, K. Lesiak and M. Sudol, *Synthesis*, 785 (1975).
201. M. Vaultier and R. Carrie, *Tetrahedron*, **32**, 2525 (1976).
202. W. Reid and H. E. Erle, *Chem. Ber.*, **112**, 640 (1979).
203. A. von Wasserman, *Br. Pat.*, 978; *Chem. Abstr.*, **7**, 2286 (1913).
204. J. N. Barglin, *US Pat.*, 2209184; *Chem. Abstr.*, **35**, 272 (1941); *US Pat.*, 2217611, 2217612, 2217613, 2217614, 2217615; *Chem. Abstr.*, **35**, 1156 (1941); *US Pat.*, 2227058, 2227059, 2227061; *Chem. Abstr.*, **35**, 2646 (1941); *US Pat.*, 2239495; *Chem. Abstr.*, **35**, 4781 (1941); *US Pat.*, 2263716; *Chem. Abstr.*, **36**, 1730 (1942); *US Pat.*, 2275606; *Chem. Abstr.*, **36**, 4240 (1942); *US Pat.*, 2400095; *Chem. Abstr.*, **40**, 4747 (1946).
205. V. A. Nefedov, *Zh. Obshch. Khim.*, **38**, 2191 (1968); *Chem. Abstr.*, **70**, 28556 (1969).

206. J.-L. Piette, R. Lysy and M. Renson, *Bull. Soc. Chim. Fr.*, 3559 (1972).
207. J.-L. Piette, P. Thibaut and M. Renson, *Tetrahedron*, **34**, 655 (1978).
208. S. J. Falcone and M. P. Cava, *J. Org. Chem.*, **45**, 1044 (1980).
209. M. Baiwir, G. Llabres, J. Denoel and J.-L. Piette, *Mol. Phys.*, **25**, 1 (1973).
210. J.-M. Talbot, J.-L. Piette and M. Renson, *Bull. Soc. Chim. Fr.*, 294 (1976).
211. F. Ogura, H. Yamaguchi, T. Otsubo and K. Chikamatsu, *Synth. Commun.*, **12**, 131 (1982).
212. S. Uemura, S. Fukuzawa, A. Toshimitsu and M. Okano, *Tetrahedron Lett.*, **23**, 1177 (1982).
213. S. Uemura, S. Fukuzawa and A. Toshimitsu, *J. Organomet. Chem.*, **250**, 203 (1985).
214. Ajinomoto Co., *Jpn. Kokai Tokkyo Koho*, JP 59 216868 [84216868]; *Chem. Abstr.*, **102**, P185497h (1985).
215. L. Engman, *J. Org. Chem.*, **48**, 2920 (1983).
216. T. Austad, S. Esperås and J. Songstad, *Acta Chem. Scand.*, **27**, 3594 (1973).
217. S. Bekkevoll, I. Svorstøl, H. Høiland and J. Songstad, *Acta Chem. Scand., Ser. B*, **37**, 935 (1983).
218. A. W. Downs, *Chem. Commun.*, 1290 (1968).
219. T. Austad, J. Songstad and K. Åse, *Acta Chem. Scand.*, **25**, 331 (1971).
220. A. Martinsen and J. Songstad, *Acta Chem. Scand., Ser. A*, **31**, 645 (1977).
221. H. K. Spencer, M. V. Lakshmikantham and M. P. Cava, *J. Am. Chem. Soc.*, **99**, 1470 (1977).
222. N. N. Greenwood, R. Little and M. J. Spraque, *J. Chem. Soc.*, 1292 (1964).
223. H. Suzuki, K. Miyoshi and A. Osuka, *Nippon Kagaku Kaishi*, 472 (1981).
224. K. Maartmann-Moe, K. A. Sanderud and J. Songstad, *Acta Chem. Scand., Ser. A*, **35**, 151 (1981).
225. L. Engman and M. P. Cava, *J. Org. Chem.*, **46**, 4194 (1981).
226. P. Wiriyachitra, J. S. Falcone and M. P. Cava, *J. Org. Chem.*, **44**, 3957 (1979).
227. G. Cauquis and G. Pierre, *Bull. Soc. Chim. Fr.*, 736 (1976).
228. M. Lipp, F. Dallacker and I. Meier zu Köcker, *Monatsh. Chem.*, **90**, 41 (1959).
229. W. J. Franklin and R. L. Werner, *Tetrahedron Lett.*, 3003 (1965).
230. J. S. Thayer, *Inorg. Chem.*, **7**, 2599 (1968).

CHAPTER **15**

Organic compounds containing bonds between Se or Te with P, As, Sb and Bi

WOLF-WALTHER DU MONT, RALPH HENSEL, SILVIA KUBINIOK AND LUTZ LANGE

Fachbereich Chemie, Universität Oldenburg, Carl-von-Ossietzky-Strasse 9–11, D-2900 Oldenburg, FRG

I. INTRODUCTION

Recently, considerable interest has been focused on the properties of compounds containing single, double or triple bonds or secondary bonding involving the heavier main group elements. As far as bonds between chalcogens and Group VA (Group 15) elements (pnictogens) are concerned, the basic chemistry of compounds with P—S and P—Se bonding is well covered in books and recent reviews[1-5], whereas only scattered information is available on compounds with P—Te bonds and on organic compounds containing bonds between Se or Te and As, Sb or Bi. The main concern of this chapter will be the presentation of recent work on P^{III}, As^{III}, Sb^{III} and Bi^{III} compounds with organylseleno and organyltelluro substituents or generally with biscoordinate Se or Te (Sections II–IV). Organylseleno- and organyltelluro-substituted compounds with four-coordinate P and As are treated in Sections V (organylseleno- and -telluro-phosphonium ions) and VI (phosphinic, phosphonic or phosphoric acid *Se*- or *Te*-esters and anhydrides). As far as compounds with (at least formally) double bonds between Se or Te and P, As and Bi are concerned, which do not contain Se—C or Te—C bonds, only very selected results

on structures, bonding and reactivity will be presented. Among these are the formation of novel seleno-metaphosphinates, -metaphosphonates and -metaphosphates (Section VII, selenoxo-phosphoranes of P^V with coordination number 3) and novel chalcogen transfer reactions between four-coordinate P^V, As^V and Sb^V compounds with double (or ylidic) bonds to Se or Te and the corresponding phosphanes, arsanes and stibanes (Section VIII). The mainly preparative Sections II–VIII are followed by a discussion of spectroscopic and structural features of compounds of Se or Te with bonds to P, As, Sb or Bi and of chemical reactions involving these bonds (Section IX). Finally, all compounds of Se or Te with bonds to P, As, Sb or Bi contain lone pairs of electrons that give them the ability to coordinate with Lewis acids via lone pairs at Se/Te or the main Group V element or both. Recent results on these Lewis base to Lewis acid interactions will also be presented in Section VIII; for general coordination chemistry of organic Se and Te compounds, the review[6] by Gysling and also his chapter in this volume can be consulted.

TABLE 1. Classification and naming of organic compounds of Se or Te with bonds to P, As, Sb and Bi

Structure	Section	Compounds
—C—Se—P<	II	Organylselenophosphanes (seleno-phosphinous, -phosphonous and -phosphorus esters) and related Te and As, Sb, Bi compounds
—C—Se—P—P<	III	Organylselenodiphosphanes (and related Te and As compounds)
>P—Se—P<	IV	Selenobisphosphanes (seleno-phosphinous, -phosphonous and -phosphorous anhydrides) (and related compounds, including seleno- or telluro-cyclophosphanes)
—C—Se—P⁺—	V	Organylselenophosphonium ions (and related Te and As compounds)
—C—Se—P(=X)<	VI	Seleno-phosphinic, -phosphonic and -phosphoric acid and Se-esters
—P(=X)=Se	VII	Selenometa-phosphinates, -phosphonates and -phosphates (imino- or methylene-selenoxophosphoranes)
—P=Se	VIII	Selenophosphinic, selenophosphonic and selenophosphoric acids, esters and amides; selenophosphoranes ('phosphane selenides') with P=Se bonds and related compounds

A note on nomenclature may be useful as the nomenclature of P, As, Sb and Bi compounds is somewhat confused[1,7]. To find comparable names for structurally comparable P, As, Sb and Bi compounds, the trivalent derivatives will preferably be named phosphanes, arsanes, stibanes or bismuthanes, but classification as derivatives of phosphinous, phosphonous or phosphorous acid derivatives (arsinous, etc) will also be mentioned. Few selenium and no tellurium compounds of pentavalent As and Sb are known. P^V compounds will preferably be named as derivatives of phosphinic, phosphonic and phosphoric acids.

The classification and naming of the compounds concerned are outlined in Table 1.

It should be mentioned that various inorganic phosphorus selenides are known as molecular compounds, but a phosphorus telluride has not yet been well characterized. Arsenic gives both molecular and polymeric chalcogenides, and antimony and bismuth chalcogenides are known to have lattice structures with interesting solid-state properties[8]. Electronegativity differences between Se or Te heavier main Group V elements are generally low (close to zero in the case of P/Te). Owing to increasing atomic radii, the single bond strengths decrease from P to Bi, and this is even more true for the tendency to form double bonds; π-overlap seems to be very poor between Te and As, Sb and Bi and generally in all cases where Bi would be involved in (formal) double bonding (see Section IX).

II. PREPARATION OF ORGANYL-SELENO- AND -TELLURO-PHOSPHANES, -ARSANES, -STIBANES AND -BISMUTHANES

A. Organyl-seleno- and -telluro-phosphinous Acid Esters and Related Arsenic, Antimony and Bismuth Compounds.

1. Phosphinous acid esters, $R_2^1PER^2$ (E = Se, Te)

a. Organylseleno(diorganyl)phosphanes. Early work on the formation of seleno-phosphanes and -arsanes was based on the reaction of bis(trifluoromethylseleno)mercury with iodophosphanes and iodoarsanes[9]. Bis(trifluoromethyl)-trifluoromethylselenophosphane(1) was isolated in quantitative yield by trap to trap condensation as colourless liquid by Emeleus et al.[9].

$$2\ (CF_3)_2PI + Hg(SeCF_3)_2 \longrightarrow 2\ (CF_3)_2PSeCF_3 + HgI_2 \tag{1}$$

(1)

$$Ph_2PI + MSeCF_3 \longrightarrow Ph_2PSeCF_3 + MI \tag{2}$$

$$M = Cs,\ Tl \qquad\qquad (2)$$
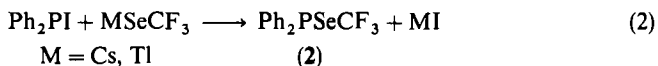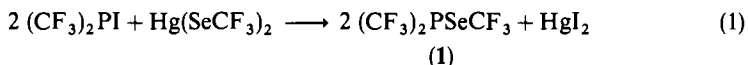
In a similar manner, trifluoromethylselenolates of Cs and Tl^I react with iododiphenylphosphane to give diphenyl(trifluoromethylseleno)phosphane (2)[10] as a reddish–yellow oil that is fairly soluble in pentane. Various reactions which lead to diphenyl(phenylseleno)phosphane (3) as an intermediate have been described by Petragnani et al.[11]. Air oxidation and hydrolysis led in all cases to the oxidized species 4. The basic types of P—Se bond formation were the reactions of chlorodiphenylphosphane with phenylselenomagnesium bromide, with phenylselenol or with diphenyl diselenide. Diphenyl diselenide is also cleaved by diphenylphosphinomagnesium bromide, and finally phenylselenyl bromide reacts with diphenylphosphane or with the phosphorus Grignard reagent[11].

$$Ph_2PCl + PhSeMgBr \xrightarrow[-'MgBrCl']{} [Ph_2PSePh] \tag{3}$$

(3)

$$Ph_2PCl + PhSeH \xrightarrow[-HCl]{} \quad [3] \qquad\qquad (4)$$

$$Ph_2PMgBr + PhSeBr \xrightarrow[-MgBr_2]{} \quad [3] \qquad\qquad (5)$$

$$Ph_2PH + PhSeBr \xrightarrow[-HBr]{} \quad [3] \qquad\qquad (6)$$

$$Ph_2PCl + PhSeSePh \longrightarrow \quad [3] + PhSeCl \qquad\qquad (7)$$

$$Ph_2PMgBr + PhSeSePh \longrightarrow \quad [3] + PhSeMgBr \qquad\qquad (8)$$

$$[3] \xrightarrow{\frac{1}{2}O_2} Ph_2P\begin{array}{c}\nearrow O\\\searrow SePh\end{array} \qquad\qquad (9)$$
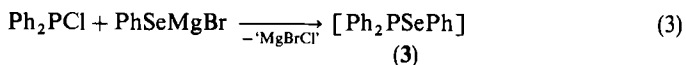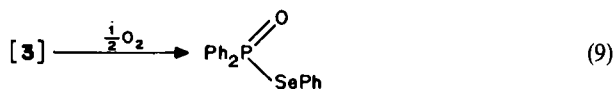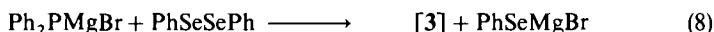
(4)

Compound [3] is halogenated by phenylselenyl halides, but hydrolysis of the postulated halogenophosphoranes led also to 4, which was isolated in all cases as colourless crystals (see Section VI)[11]. Pure [3] was obtained by adding chlorodiphenylphosphane to an equimolar quantity of phenylselenol and a slight excess of triethylamine in diethyl ether under inert gas at −10 °C. Distillation led to the pure, pale yellow product. The compound is oxidized in air within a few hours. It was reported to isomerize to $Ph_3P{=}Se$ within 3–4 h at 100 °C, but no details were given on the evidence for this isomerization[12]. The attempted preparation of [3] by reaction of sodium phenylselenolate with chloro-diphenylphosphane lead mainly to Ph_3PSe, even at lower temperatures. It was proposed that the selenophosphane to selenophosphorane (phosphaneselenide) rearrangement is due to the weaker Se—C bond in [3] compared with the S—C bond of the corresponding sulphur compound, which did not rearrange under comparable conditions[12]. A versatile method for the formation of methylseleno derivatives of phosphorus and arsenic is the reaction of trimethyl(methylseleno)silane with chlorophosphanes (and chloroarsanes) which gives quantitative yields of chloro(trimethyl)silane[13].

$$Ph_2PCl + PhSeH + Et_3N \longrightarrow Ph_2PSePh + Et_3NH^+Cl^- \qquad\qquad (10)$$

$$Ph_2PCl + PhSeNa \longrightarrow Ph_3P = Se + NaCl \qquad\qquad (11)$$

$$Ph_2PCl + MeSeSiMe_3 \longrightarrow Ph_2PSeMe + Me_3SiCl \qquad\qquad (12)$$
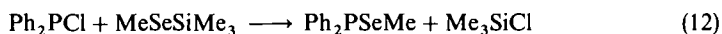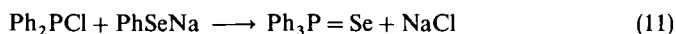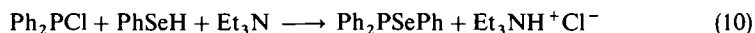
(5)

Compound 5 was characterized by performing the reaction in an NMR tube. Removal of the volatile material containing chlorotrimethylsilane and excess of trimethyl(methylseleno)silane led to 5 as viscous yellow oil that is thermally stable. In a similar manner, the reaction of disilylselane with bromodifluorophosphane lead to P—Se bond formation; an NMR study of the reaction showed that with excess of bromodifluoro-phosphane, disilylselane was completely consumed in the equilibrium, but digermylselane was not[14] (see also Section IV).

$$F_2PBr + (H_3Si)_2Se \rightarrow H_3SiSePF_2 + H_3SiBr \qquad\qquad (13)$$

(6)

$$2H_3SiSePF_2 \rightleftharpoons (H_3Si)_2Se + Se(PF_2)_2 \qquad\qquad (14)$$
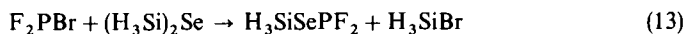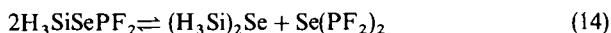
(7)

A detailed study on reaction paths to thio-, seleno- and telluro-phosphinous esters and related arsenic compounds by Dehnert, Grobe *et al.*[15] showed that so-called $(2 + 2)$ dismutation reactions of diorganyldichalcogenides with tetraorganyl-diphosphanes or -diarsanes[16-19] are very effective for the formation of bonds between sulphur, selenium or tellurium and phosphorus or arsenic.

$$R_2^1PPR_2^1 + R^2SeSeR^2 \longrightarrow 2\,R_2^1PSeR^2 \qquad (15)$$
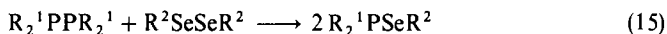
R^1	R^2	Compound	Ref.
Me	Ph	Me_2PSePh **(8)**	16
Me	Me	Me_2PSeMe **(9)**	15
CF_3	Me	$(CF_3)_2PSeMe$ **(10)**	15
CF_3	CF_3	$(CF_3)_2PSeCF_3$ **(1)**	15
Me	CF_3	Me_2PSeCF_3 **(11)** (unstable above $-30\,°C$)	15

All these P—P/Se—Se dismutation reactions give quantitatively crude yields of the P—Se-bonded species (as do most diphosphane/disulphide reactions). The dismutation can even occur when one phosphorus atom of the diphosphane is coordinated to pentacarbonyl chromium, molybdenum or tungsten[20,21]. Bis (trifluoromethyl) diselenide is more reactive in dismutation reactions than dimethyl diselenide.

$$(CO)_5M—PMe_2—PMe_2 + MeSeSeMe$$

$$\xrightarrow[\substack{40-50\,°C\,(C_6D_6)}]{>5\,d} (CO)_5M—PMe_2SeMe + Me_2PSeMe \qquad (16)$$
$$\textbf{(9)}$$

$$M = Cr\ \textbf{(12)}$$
$$M = Mo\ \textbf{(13)}$$
$$M = W\ \textbf{(14)}$$

$$(CO)_5Mo—PMe_2PMe_2 + CF_3SeSeCF_3$$

$$\xrightarrow[\substack{(C_6D_5CD_3)}]{-10\,°C} (CO)_5Mo—PMe_2SeCF_3 + Me_2PSeCF_3 \qquad (17)$$
$$\textbf{(15)} \qquad\qquad \textbf{(11)}$$
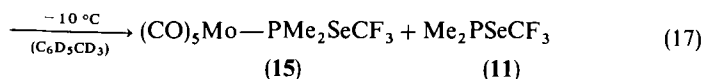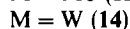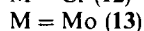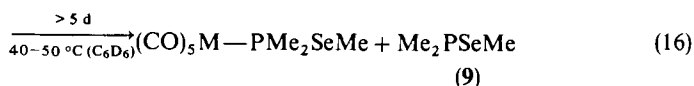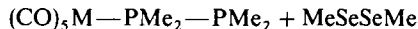
The molybdenum complex **15** is significantly more thermally stable than non-coordinated dimethyl(trifluoromethylseleno)phosphane (**11**). The complexes **12–15** were easily separated from the volatile ligands **9** and **11**[21]. Dismutation reactions of coordinated tetramethyldiphosphane are generally slower than with tetramethyldiphosphane itself; double coordination of the diphosphane (as bridging bidentate ligand between pentacarbonyl-chromium, -molybdenum and -tungsten moieties) leads to complete loss of the ability to undergo $(2 + 2)$ dismutations even with very reactive bis(trifluoromethyl) disulphide[21].

$$
\begin{array}{c}
\text{Me}\quad\ \text{Me} \\
|\qquad | \\
(CO)_5M—P——P—M(CO)_5 \quad + \quad REER \quad \nrightarrow \\
|\qquad | \\
\text{Me}\quad\ \text{Me} \qquad\qquad E = S, Se \\
\qquad\qquad\qquad R = CH_3, CF_3
\end{array}
\qquad (18)
$$
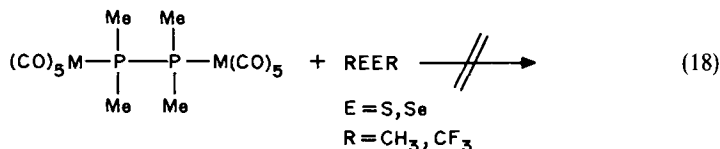
A novel way to make P—Se bonds is the selenation or hydroselenation of phosphenes (alkylidenephosphanes). Addition of methyselenol to difluoromethylidene-(trifluoromethyl)phosphane leads to chiral difluoromethyl(trifluoromethyl)-(methylseleno)phosphane (16), i.e. hydroselenation across the P$=$C double bond occurs via nucleophilic attack at phosphorus in this (first) case[22].

$$CF_3P{=}CF_2 \ + \ MeSeH \ \longrightarrow \ CF_3{-}\underset{\underset{CF_2H}{|}}{\overset{\overset{P}{\diagup\,\diagdown}}{|}}{-}SeCH_3 \qquad (19)$$

$$(16)$$
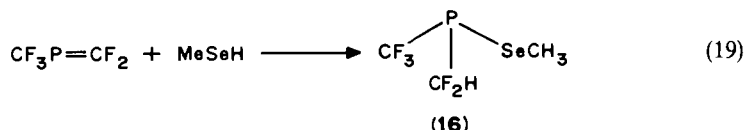
With elemental selenium (as with sulphur), alkylidenephosphanes react to give either 1,2-λ^3-selenophosphiranes or the isomeric alkylideneselenoxophosphoranes (see Section VII).

A decision between the two types of structures A and B can easily be made with help of ^{31}P NMR spectroscopy. Typically, ^{31}P NMR shifts of phosphiranes A are upfield compared with open-chain phosphanes (effect of small ring size on ^{31}P resonance), and the NMR coupling constant $^nJ(^{77}Se^{31}P)$ is much less than 200 Hz in all known phosphiranes and diphosphiranes. Imino- or alkylidene selenoxophosphoranes B also give ^{31}P resonances at comparatively high field in most cases, but $^1J(^{77}Se^{31}P)$ is very large (available values are all more than 800 Hz) (for details, see Sections VII and IX).

$$RP{\overset{\diagup Se}{\underset{\diagdown CR^1R^2}{|}}} \qquad\qquad RP{\overset{\diagup\!\!\diagup Se}{\diagdown CR^1R^2}}$$

A   B
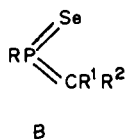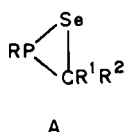
1,2-di-t-butylmethylenephosphane reacts with elemental sulphur or selenium at room temperature within 2 weeks (S) or 3 days (Se). Only phosphirane formation was observed in each case[23].

$$t\text{-BuP}{=}C{\overset{\diagup Bu\text{-}t}{\diagdown H}} \ + \ 1/n\ E_n \ \longrightarrow \ t\text{-Bu}{\overset{\diagup E \diagdown}{\underset{P{-}C}{}}}{\overset{\diagup Bu\text{-}t}{\diagdown H}} \qquad (20)$$

$$(17)\ E = S$$

$$(18)\ E = Se$$
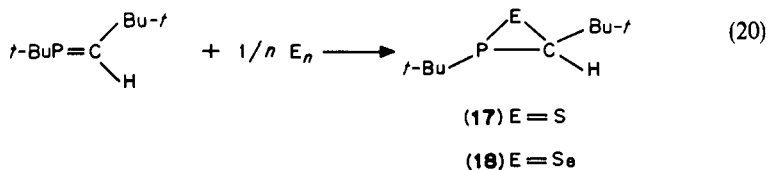
The preference for the three-membered rings 17 and 18 over the isomeric methylene(thioxo and selenoxo)phosphoranes (type B) was rationalized by molecular orbital calculations by Schoeller and Niecke[24], which predict a non-polar π-system with a low-energy LUMO for the parent 1,2-di-t-butylmethylenephosphane (see Section VII). Similarly, bis(trimethylsilyl)methylene(trimethylsilylethinyl)phosphane gives '(2 + 1) cycloaddition' with S and Se leading to 1,2-λ^3-thia- and -selena-phosphiranes[25].

$$Me_3SiC{\equiv}CP{=}C(SiMe_3)_2 \ \overset{+E}{\longrightarrow} \ Me_3SiC{\equiv}CP{\overset{\diagup E \diagdown}{}}{-}C(SiMe_3)_2 \qquad (21)$$

$$(19)\ E = S$$

$$(20)\ E = Se$$
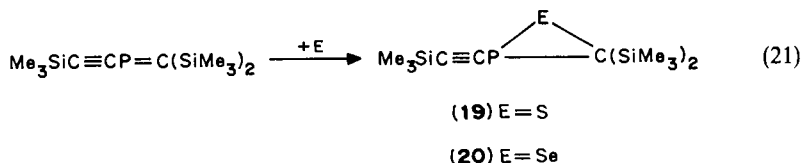
Compounds **19** and **20** are yellow liquids that partially decompose to the starting materials at room temperature, but purification has been achieved by distillation *in vacuo*. Both compounds can be desulphurated or deselenated with triphenylphosphane (regeneration of the alkylidenephosphane). With 2,3-dimethylbutadiene, cycloaddition occurs with initial loss of sulphur or selenium; NMR evidence for the cycloreversion of **19** was provided by NMR identification of the tetrahydrophosphabenzene intermediate that is sulphurated to give the final product **21**.

$$(22)$$

(21) E = S

(22) E = Se
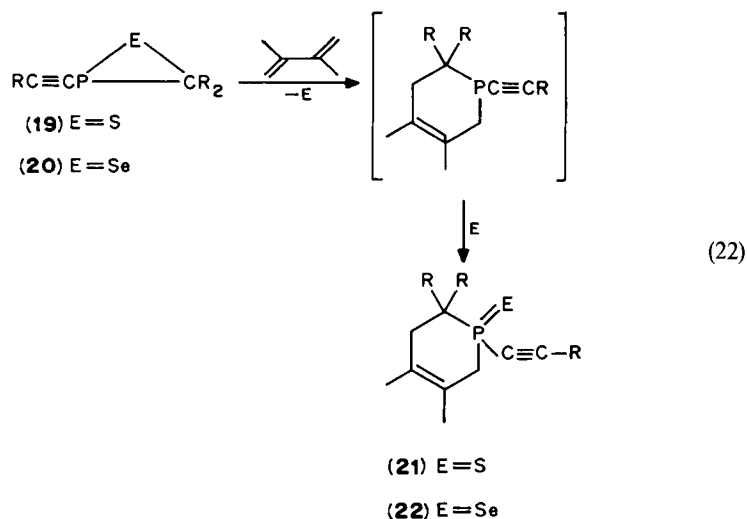
These findings indicate that thia- and selena-phosphiranes may be useful precursors of species with doubly bonded phosphorus that are easily formed by desulphuration and deselenation reactions. Selenaphosphiranes **20** and **22** are apparently more stable than seleniranes, which decompose thermally with alkene formation (see Section IX).

b. Organyltelluro(diorganyl)phosphanes. The dismutation reaction of dimethylditelluride with tetramethyldiphosphane leads only to an equilibrium mixture of dimethyl(methyltelluro)phosphane (**23**) with the starting materials; **23** cannot be separated from Me_2Te_2 and Me_4P_2. Quite differently, the dismutation of dimethylditelluride with tetrakis(trifluoromethyl)diphosphane is quantitative after 4 days at 50 °C and methyltellurobis(trifluoromethyl)phosphane (**24**) was the first tellurophosphane that could be obtained in pure state as an orange–yellow liquid that boils at 118 °C[15].

$$Me_2PPMe_2 + MeTeTeMe \rightleftharpoons 2\ Me_2PTeMe \tag{23}$$

(23)

$$(CF_3)_2PP(CF_3)_2 + MeTeTeMe \rightarrow 2\ (CF_3)_2PTeMe \tag{24}$$

(24)
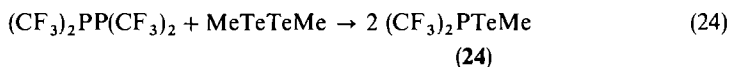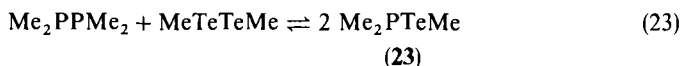
Bulky substituents at the diphosphane appear to favour dismutations with di-*p*-tolylditelluride. Dismutation with tetra-*t*-butyldiphosphane is complete after heating the educts for 1 h in boiling toluene, but with tetra-*i*-propyldiphosphane the (2 + 2) dismutations with the same ditelluride leads to a reaction mixture that contains the tellurophosphane **25** as the main product with a few percent of the educts still present in

the equilibrium. Compounds **25** and **26** were obtained as pure compounds by distillation *in vacuo*[26] as yellow liquids.

$$R_2PPR_2 + p\text{-TolTeTeTol-}p \longrightarrow 2\ R_2PTeTol\text{-}p \qquad (25)$$

$$\text{(25) } R = i\text{-Pr}$$
$$\text{(26) } R = t\text{-Bu}$$
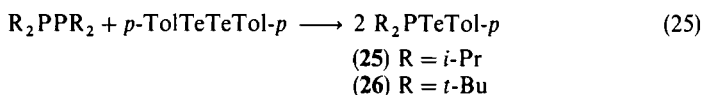
Older (originally distilled) samples of **25** contain, again, small amounts of di-*p*-tolyl-ditelluride and tetra-*i*-propyldiphosphane. Re-dismutation leading to the educts is not a fast process on the NMR time-scale, since $^1J(^{125}\text{Te}^{31}\text{P})$ is well resolved in the ^{31}P and ^{125}Te NMR spectra of **25**, nor does one tolytelluro substituent at phosphorus lead to a low barrier of inversion, since diastereotopic carbon atoms are well resolved in the (25 °C) ^{13}C NMR spectrum of **25**[26]. Re-dismutation does not occur when **25** is coordinated to pentacarbonyltungsten[27].

$$2\ \mathbf{25} \ \rightleftharpoons\ p\text{-TolTeTeTol-}p \quad + \quad \qquad (26)$$

$$\mathbf{(CO)_5WPTeTol\text{-}p} \quad \overset{/\!/}{\longrightarrow} \quad (CO)_4WP\!\!-\!\!PW(CO)_5 \quad + \quad p\text{-TolTeTeTol-}p \qquad (27)$$
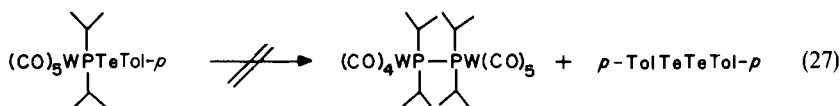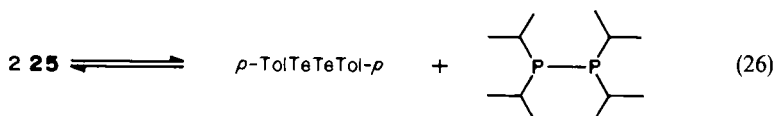
This finding is consistent with Grobe and Le Van's observation[21] that the reverse reaction (of coordinated tetramethyldiphosphane as bridging bidentate ligand with disulphides and diselenides) does not occur. Di-*t*-butyl(trimethyl-silyl, -germyl and -stannyl)tellurophosphanes are formed by insertion of elemental tellurium into the P—Si, P—Ge and P—Sn bonds of di-*t*-butyl(trimethyl-silyl, -germyl and -stannyl)phosphane[28]. *n*-Bu$_3$P=Te may also serve as source of tellurium atoms; in each case, the short-lived intermediates $R_2P(\rightleftharpoons Te)MMe_3$ rearrange with migration of the trimethyl-silyl, -germyl and -stannyl groups from phosphorus to tellurium (a kind of retro-Arbuzov rearrangement). Subsequently, a rearrangement centred at tellurium leads to equilibrium mixtures of **27–29** with the symmetrically substituted tellurium compounds (equation 29). In this case, no significant retro-(2 + 2) dismutation (which would give the ditellurides $Me_3MTeTeMMe_3$, M = Si, Ge, Sn)[28] occurs.

$$R_2PMMe_3 + Te \longrightarrow \left[R_2P\!\!\overset{/\!\!/Te}{\underset{\diagdown MMe_3}{}} \right] \longrightarrow R_2PTeMMe_3$$

R = *t*-Bu, M = Si, Ge, Sn

$$\textbf{(27)}\ R = t\text{-Bu, M = Si} \qquad (28)$$
$$\textbf{(28)}\ R = t\text{-Bu, M = Ge}$$
$$\textbf{(29)}\ R = t\text{-Bu, M = Sn}$$

$$2\ R_2PTeMMe_3 \rightleftharpoons (Me_3M)_2Te + Te(PR_2)_2 \qquad (29)$$
$$\textbf{(27–29)} \qquad\qquad M = Si,\ Ge,\ Sn\ \textbf{(30)}\ R = t\text{-Bu}$$
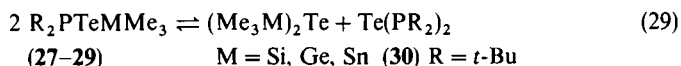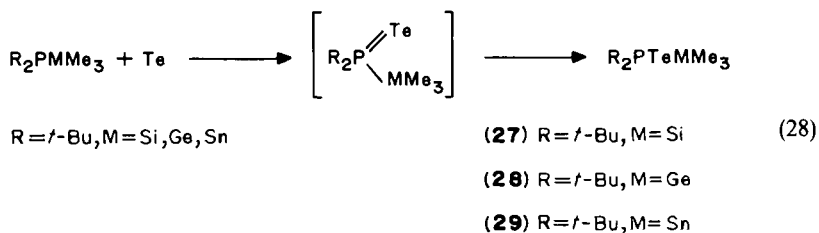
Compounds **27–29** are not further oxidized by excess of tellurium; in contrast, excess of sulphur or selenium oxidizes R_2PSiMe_3 to the pentavalent phosphorus compounds t-$Bu_2P(=E)ESiMe_3 (E=S, Se)^{29}$. NMR spectra of compounds related to **27–29** have also been recorded after reacting $(H_3M)_2Te$ (M = Si, Ge) with bromodifluorophosphane[14]. Compounds **31–33** decomposed thermally by precipitation of elemental tellurium[14].

$$(H_3M)_2Te \xrightarrow[-H_3MBr]{F_2PBr} F_2PTeMH_3 \xrightarrow[-H_3MBr]{F_2PBr} F_2PTePF_2 \qquad (30)$$

$$(31)\ M = Si \qquad\qquad (33)$$

$$(32)\ M = Ge$$
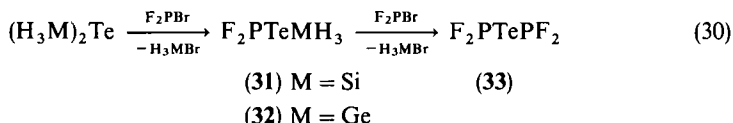
P—Te bonds may also be formed by metal halide elimination from a telluromagnesium or tellurolithium reagent with di-t-butylchlorophosphane. Thus **26** is obtained conveniently in high yield with p-tolyltelluromagnesium bromide[30,31]:

$$t\text{-}Bu_2PCl + p\text{-}TolTeMgBr \xrightarrow{(THF)} t\text{-}Bu_2PTeTol\text{-}p + \text{'}MgBrCl\text{'} \qquad (31)$$

$$(26)$$

$$(t\text{-}Bu)_2PCl + (Me_3Si)_3CTeLi \xrightarrow[-LiCl]{(THF)} (Me_3Si)_3CTeP(Bu\text{-}t)_2 \qquad (32)$$

$$(34)$$
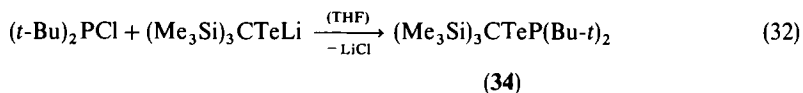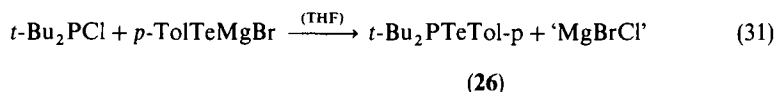
In contrast to the thermally stable **26**, the bulky **34** rearranges at room temperature with formation of the corresponding symmetrically substituted tellurium compounds[32]:

$$2\ 34 \longrightarrow (Me_3Si)_3CTeC(SiMe_3)_3 + (t\text{-}Bu)_2PTeP(Bu\text{-}t)_2 \qquad (33)$$

$$(30)$$
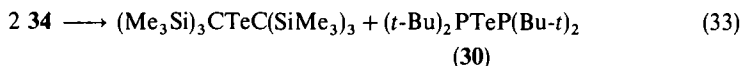
Starting with the tris(trimethylsilyl)methyl ditelluride anion, the first ditellurophosphane (**35**) was characterized by NMR spectroscopy as a thermally labile compound that disproportionates into an organic tritelluride and **34**[32].

$$(t\text{-}Bu)_2PCl + (Me_3Si)_3CTeTeLi \xrightarrow[-LiCl]{(THF)} (Me_3Si)_3CTeTeP(Bu\text{-}t)_2$$

$$(35)$$

$$2\ 35 \longrightarrow 34 + (Me_3Si)_3CTeTeTeC(SiMe_3)_3 \qquad (34)$$
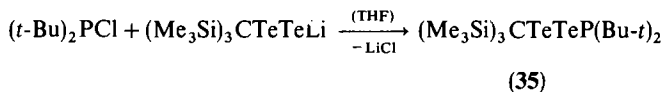
Extremely bulky substituents at tellurium disfavour $(2 + 2)$ dismutation reactions with tetra-t-butyldiphosphane and tetra-i-propyldiphosphane, but P—Te bonds can be made with 2, 4, 6-tri-t-butylphenyltellurolithium[33]:

$$(36)$$

$$(36)$$
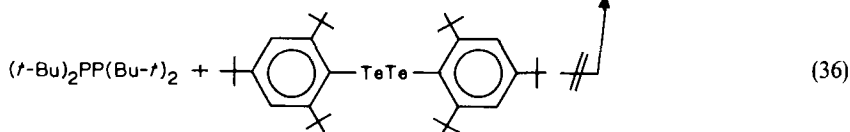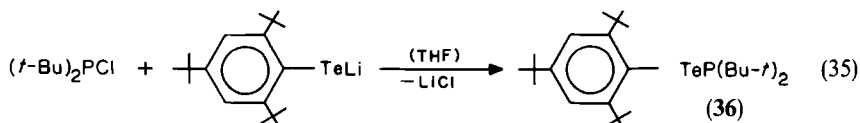
2. Arsinous acid esters, $R_2{}^1$ AsER^2 (E = Se, Te)

   a. Organylseleno(diorganyl)arsanes. As mentioned previously (Section II.A.1.a), the first perfluoroalkylselenoarsanes were prepared by Emeleus *et al.*[9] from mercury-selenium compounds with two equivalents of iodobis(trifluoromethyl)arsane. Vacuum fractionation of the volatile products gave the pure colourless compounds **37** and **38**.

$$2\,(CF_3)_2AsI + Hg(SeR)_2 \longrightarrow 2\,(CF_3)_2AsSeR + HgI_2 \tag{37}$$

$$\textbf{(37)}\ R = CF_3$$
$$\textbf{(38)}\ R = n\text{-}C_3F_7$$
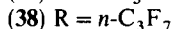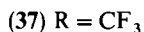
Sagan *et al.*[34] found that protolysis of dialkyl(diethylamino)arsanes with alcohols, thiols and selenols is a convenient method for the synthesis of compounds that contain As—O, As—S and As—Se bonds. Qualitative observation of the progress of amine formation showed the selenols to be most reactive and alcohols to be least reactive, suggesting that the reaction rate depends on the acidity of the protic agents.

$$R_2{}^1AsNEt_2 + R^2SeH \longrightarrow R_2{}^1AsSeR^2 + Et_2NH \tag{38}$$

$$\textbf{(39)}\ R^1 = Me,\ R^2 = Et$$
$$\textbf{(40)}\ R^1 = Me,\ R^2 = Ph$$
$$\textbf{(41)}\ R^1 = Me,\ R^2 = CH_2Ph$$
$$\textbf{(42)}\ R^1 = Me,\ R^2 = 1\text{-}C_{10}H_7$$
$$\textbf{(43)}\ R^1 = Et,\ R^2 = Ph$$
$$\textbf{(44)}\ R^1 = Et,\ R^2 = CH_2Ph$$
$$\textbf{(45)}\ R^1 = Pr,\ R^2 = Ph$$
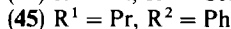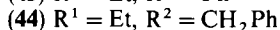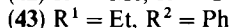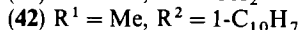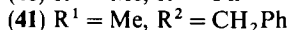
After expelling the amine by refluxing the reaction mixture and removing excess of the selenol by distillation, **39–45** were obtained in nearly quantitative yield (excess of the selenol leads to precipitation of diethylammonium alkaneselenolates)[34]. Compounds **39–45** are fairly inert towards air and moisture, but on extended exposure to air dialkylarsinic acids are formed. Dialkyl (alkoxy)arsanes are much more sensitive and the reactivity of dialkyl(alkylthio)arsanes towards moist air is intermediate. Infrared spectra confirmed that Arbuzov-like rearrangements did not occur with **39–45**.

   Trimethyl(methylseleno)silane reacts with chlorodiphenylarsane to give methylselenodiphenylarsane (**46**) under mild conditions. The preparation and characterization of **46** are identical with that of the corresponding phosphane **5**[13].

$$Ph_2AsCl + MeSeSiMe_3 \longrightarrow Ph_2AsSeMe + Me_3SiCl \tag{39}$$

$$\textbf{(46)}$$
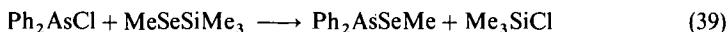
Dehnert, Grobe *et al.*[15] used both substitution and (2 + 2) dismutation reactions for the preparation of dialkyl(alkylseleno)arsanes:

$$R_2{}^1AsAsR_2{}^1 + R^2SeSeR^2 \longrightarrow 2\,R_2{}^1AsSeR^2 \tag{40}$$

$$\textbf{(37)}\ R^1 = \qquad R^2 = CF_3$$
$$\textbf{(47)}\ R^1 = \qquad R^2 = Me$$
$$\textbf{(48)}\ R^1 = Me,\ R^2 = CF_3$$
$$\textbf{(49)}\ R^1 = CF_3,\ R^2 = Me$$
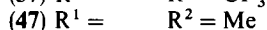
The diarsane/diselenide reactions lead to complete dismutation in all cases; **47** was also obtained in satisfactory yield by the dehydrohalgenation method from chlorodimethylarsane and methylselenol in the presence of trimethylamine[15]. For **37**, the Emeleus synthesis was found to be the most convenient. Compounds **37** and **47–49** are distillable yellow liquids.

In the course of a synthetic study on biologically active glucose esters of dimethylarsinous acid, Zingaro and coworkers[35,36] used the $(2 + 2)$ dismutation of tetramethyldiarsane with 6,6-diselenobis(1,2,3,4-tetra-O-acetyl-α- or -β-D-glucopyranose) to give 1,2,3,4-tetra-O-acetyl-6-Se-dimethylarsino-6-seleno-α- and -β-D-glucopyranose (50 and 51). 6-Se-Dimethylarsino-6-seleno-β-D-glucopyranose (52) was prepared as a yellow solid in the same manner. Under alkaline conditions, it is possible to deacetylate thio sugar esters of dimethylarsinous acid, but under similar conditions the C—Se—AsMe$_2$ linkage is also subject to hydrolysis (in these cases, hydrolysis of the As—Se compound under aerobic conditions is about six times faster than hydrolysis of the corresponding sulphur compound).

$$(41)$$

$$(42)$$

$$Me_2AsXR \xrightarrow[\;H_2O\;]{\;OH^-\;} ROH + HX^- + [Me_2AsOH]$$

$$(or\ RX^-)$$

$$X = S, Se;\ R = sugar\ moiety$$

$$\downarrow O_2 \quad (rapid) \qquad (43)$$

$$Me_2As\overset{\displaystyle O}{\underset{\displaystyle OH}{\diagup\hspace{-0.3em}\diagdown}}$$
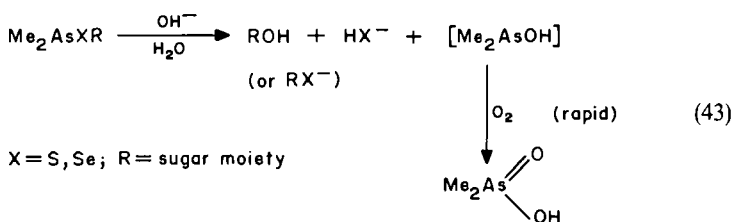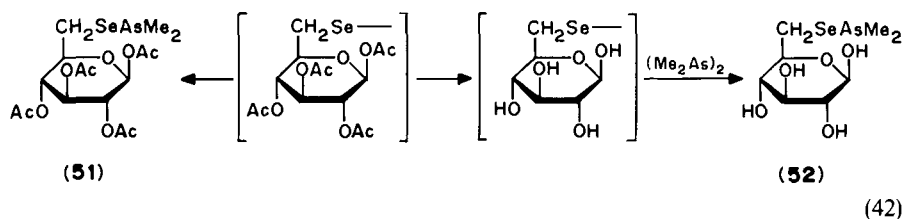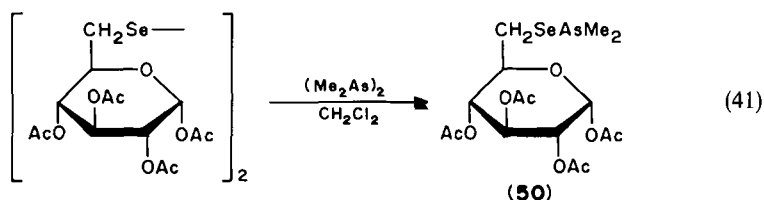
A further remarkable difference in the reactivity of 6-seleno and 6-thio sugars is that unlike the 6,6-diselenobis(β-D-glucopyranose), the corresponding 6,6-dithiobis(β-D-glucopyranose) did not react with tetramethyldiarsane.

b. Organyltelluro(diorganyl)arsanes. The $(2 + 2)$ dismutations of diarsanes with dimethylditelluride are very similar to those with diphosphanes: with tetramethyldiarsane only an equilibrium mixture is obtained, but with tetrakis(trifluoromethyl)diarsane, methyltellurobis-(trifluoromethyl)arsane (54) is formed as a pure orange-yellow compound[15].

$$Me_2AsAsMe_2 + MeTeTeMe \rightleftharpoons 2Me_2AsTeMe \qquad (44)$$

$$(53)$$

$$(CF_3)_2AsAs(CF_3)_2 + MeTeTeMe \longrightarrow 2(CF_3)_2AsTeMe \tag{45}$$
$$(54)$$
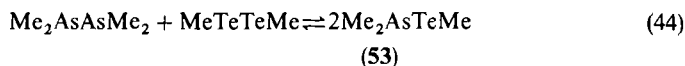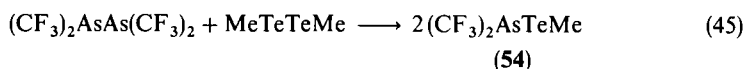
Aryltelluro-dimethyl- and -diethyl-arsanes (55–57) are formed in about 90% yield from diphenyl ditelluride or di-p-tolyl ditelluride with the corresponding diarsanes (equation 46) or with excess of dimethylarsane [37] (equation 47).

$$R_2AsAsR_2 + ArTeTeAr \longrightarrow 2R_2AsTeAr \tag{46}$$
$$\text{(55) R = Me, Ar = Ph}$$
$$\text{(56) R = Me, Ar = }p\text{-Tol}$$
$$\text{(57) R = Et, Ar = Ph}$$

$$Me_2AsH + ArTeTeAr \longrightarrow Me_2AsTeAr + ArTeH \tag{47}$$
$$\text{(55) Ar = Ph}$$
$$\text{(56) Ar = }p\text{-Tol}$$
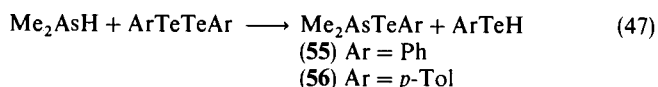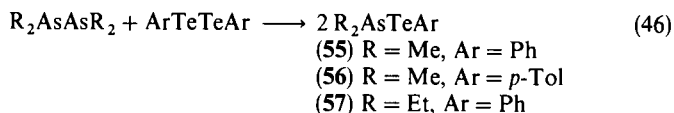
Evidence for As—Te bond formation was provided by NMR, mass and UV–visible spectroscopy. Compounds 55–57 are orange to red solids (56) or oils (55, 57) that are thermally fairly labile. They decompose on attempted vacuum distillation.

3. Organyl-seleno- and -telluro-(diorganyl)stibanes, $R_2{}'SbER^2 (E = Se, Te)$

Molecular compounds with Sb—Se or Sb—Te bonds were unknown until recently. The striking change in colour between liquid and solid tetramethyldistibane and the fact that organic ditellurides are generally coloured compounds lead to the question of whether the Sb—Te moiety would be a chromophore comparable to the Sb—Sb and Te—Te moieties, and if thermochromic behaviour, which may be related to weak intermolecular interactions in the solid state, would also occur in heterodiatomic heavy non-metal moieties. Surprisingly, $(2 + 2)$ dismutations of di-p-tolyl ditelluride with tetramethyldistibane[38] and tetraethyldistibane[39] are fast and quantitative, whereas equilibrium mixtures are formed from non-strained diphosphanes with ditellurides[15]. The reaction between di-p-tolyl ditelluride and tetraalkyldistibanes can be carried out like a titration, with the liquid distibane added to the red solid ditelluride. The reaction is complete when the colour of the reaction mixture changes from red to yellow. At this stage the educts are completely consumed, NMR spectra, mass spectra and analytical data confirm the presence of pure liquid tellurostibanes 58 and 59.

$$R_2SbSbR_2 + p\text{-TolTeTeTol-}p \longrightarrow 2R_2SbTeTol-p \tag{48}$$
$$\text{(58) R = Me}^{[38]}$$
$$\text{(59) R = Et}^{[39]}$$
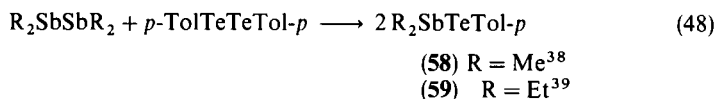
Yellow 58 and orange 59 are less coloured than both educts and they do not show significant temperature-dependent colour changes. Both compounds are sensitive to air; among the oxidation products is red di-p-tolyl ditelluride. The $(2 + 2)$ dismutation of diphenyldiselenide with tetramethyldistibane is also quantitative, leading to dimethyl(phenylseleno)stibane (60)[40], which is a yellowish compound and non-thermochromic.

4. Organyl-seleno- and -telluro-(diorganyl)bismuthanes, $R_2{}'BiER^2 (E = Se, Te)$

˙ Tetraorganyldibismuthanes were regarded as being unstable until recently. After the characterization of the first pure dibismuthanes, it became clear that the colour of such compounds in the solid state can be completely different from that in the liquid[41–44]. Secondary bonding in the solid state is at present a point of discussion when coloured

dibismuthanes, distibanes and ditellurides are concerned and has led to the search for heteronuclear bonds between Bi, Sb and Te.

Tetramethyldibismuthane reacts with diphenyl disulphide, diphenyl diselenide and diphenyl ditelluride in diethyl ether solution below 0 °C (equation 49)[45]. Similarly, tetra-n-propyldibismuthane reacts quantitatively with di-p-tolyl ditelluride to give p-tolyltellurodi-n-propylbismuthane (equation 50)[46].

$$Me_2BiBiMe_2 + PhEEPh \longrightarrow 2\,Me_2BiEPh \qquad\qquad (49)$$
$$\text{yellow crystals}$$
$$(\mathbf{61})\ E = S$$
$$(\mathbf{62})\ E = Se$$
$$(\mathbf{63})\ E = Te$$

$$Pr_2BiBiPr_2 + p\text{-TolTeTeTol-}p \longrightarrow 2\,Pr_2BiTeTol\text{-}p$$
$$\qquad\qquad\qquad\qquad\qquad (\mathbf{64}) \qquad\qquad\qquad\qquad (50)$$
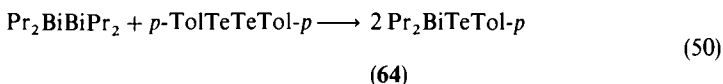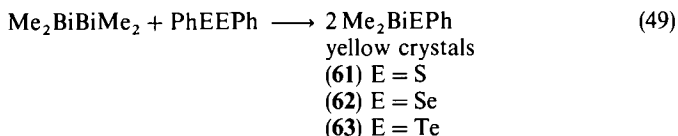
The thermal stability of **61–63** depends strongly on the chalcogen: the tellurobismuth ane **63** decomposes (slowly) even at $-30\,°C$, whereas dimethyl(phenyl-thio and -seleno)bismuthane appears to be stable at this temperature. Thermal decomposition of **61–63** leads in the first step to methylbis(phenylchalcogeno)bismuthanes[45].

$$2\,Me_2BiEPh \longrightarrow Me_3Bi + MeBi(EPh)_2 \qquad\qquad (51)$$
$$(\mathbf{61\text{–}63}) \qquad\qquad\quad (\mathbf{65})\ E = S$$
$$(\mathbf{66})\ E = Se$$
$$(\mathbf{67})\ E = Te$$
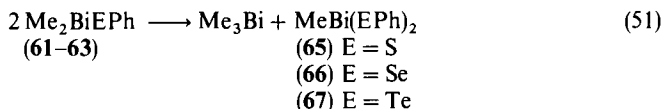
For **65** and **66**, this disproportionation can be used as a preparative method (see Section II.B.2.c); **67** cannot be isolated owing to further decomposition. In solution, only PhTeMe could be characterized, and the unsoluble black residue seemed to contain mainly polymeric $(BiCh_3)_x$. Formation of PhTeMe is due to a dismutation of trimethyl-bismuth with diphenyl ditelluride[45].

$$BiMe_3 + PhTeTePh \longrightarrow PhTeMe + Me_2BiTePh \qquad\qquad (52)$$
$$(\mathbf{63})$$
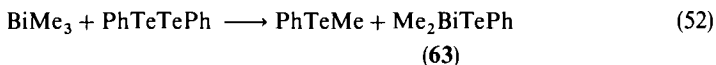
Red–brown liquid **64** (orange in solution) appears to be thermally more stable than **63** neither of them showing typical thermochromic behaviour. Compound **64** was stable enough in C_6D_6 solution to allow the recording of a ^{125}Te NMR spectrum (acquisition time several hours)[46]. Alkyl scrambling occurred when mass spectra of the tellurobismuth-anes were run. The (2 + 2)dismutations with dichalcogenides belong to the first reactions of dibismuthanes that lead selectively to Bi—Bi bond cleavage.

B. Organyl-seleno and -telluro Esters of Phosphonous Acids and Related Arsenic, Antimony and Bismuth Compounds

1. Seleno- and telluro-phosphonous esters, $R^1P(ER^2)_2$ $(E = Se, Te)$

a. Organylbis(organylseleno)phosphanes. Phenylbis(methylseleno)phosphane (**69**) and chloro(phenyl)(methylseleno)phosphane (**68**) are formed from dichlorophenylphosphane, depending on the amount of added trimethyl(methylseleno)silane, shown by ^1H NMR spectra in sealed tubes[13]. Diiodo(phenyl)phosphane reacts with bis(trifluoro-methylseleno)mercury in benzene to give phenylbis(trifluoromethyl-seleno)phosphane (**70**) in 87% yield as the pure compound[47]. Alternatively, **70** is

prepared by reaction of pentaphenylcyclopentaphosphane with bis(trifluoromethyl)-diselenide for 10h at 40°C in a sealed vessel; **70** is also formed when 1,2-diiodo-1,2-diphenyldiphosphane reacts with $Hg(SeCF_3)_2$ in C_6H_6 for 1h at 0°C. One of the products of these reactions is CF_3SeHgI[47].

$$PhPCl_2 \xrightarrow[-Me_3SiCl]{MeSeSiMe_3} PhP\!\!\begin{array}{c} ^{\diagup Cl} \\ ^{\diagdown SeMe} \end{array} \xrightarrow[-Me_3SiCl]{MeSeSiMe_3} PhP(SeMe)_2 \qquad (53)$$

$$\mathbf{(68)} \qquad\qquad\qquad\qquad\qquad \mathbf{(69)}$$

$$PhPI_2 + Hg(SeCF_3)_2 \xrightarrow{-HgI_2} PhP(SeCF_3)_2 \qquad (54)$$

$$\mathbf{(70)}$$

$$1/5\,(PhP)_5 + CF_3SeSeCF_3 \longrightarrow \qquad \mathbf{(70)} \qquad\qquad (55)$$

$$\begin{array}{c} Ph \diagdown \qquad \diagup Ph \\ PP \\ I \diagup \qquad \diagdown I \end{array} \xrightarrow{Hg(SeCF_3)_2} \mathbf{(70)} + \text{other products} \qquad (56)$$
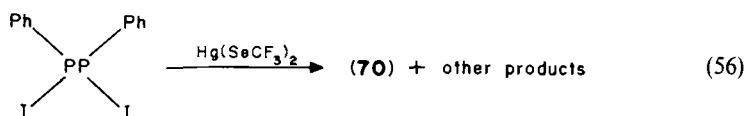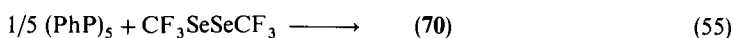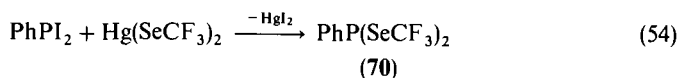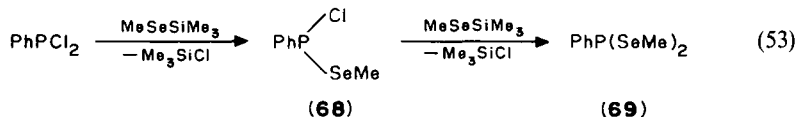
Compound **70** is fairly soluble in pentane and benzene and is thermally stable up to 80°C.

    b. Organylbis(organyltelluro)phosphanes. The cleavage of tri-*t*-butylcyclotriphosphane with ditolyl ditelluride did not lead to *t*-butylbis(*p*-tolyltelluro) phosphane **(71)**, but a ditolyldiphosphane was formed (see Section III). 1,2-Di-*t*-butyl-1,2-dichlorodiphosphane did not react with di-*p*-tolyl ditelluride to give a simple (2 + 2) dismutation that should lead to *t*-butyl(chloro)(*p*-tolyltelluro)phosphane **(72)**, but disproportionation occurred and diphosphanes were obtained (Section III) with only traces of **72** (NMR evidence)[30,31]. Finally, reaction of *t*-butyldichlorophosphane with two equivalents of *p*-tolyltelluromagnesium bromide in THF led again to disproportionation and **71** was only observed as a byproduct [$\delta(^{31}P) = +51.7$ ppm]; which was enriched in pentane solution and characterized by MS (molecular ion at *m/e* 526 with correct isotopic distribution)[30,31].

$$t\text{-}BuPCl_2 \xrightarrow[THF, -'MgBrCl']{2\ p\text{-}TolTeMgBr} t\text{-}BuP(TeTol\text{-}p)_2 + \begin{array}{c} t\text{-}Bu\diagdown \qquad \diagup Bu\text{-}t \\ P\!-\!P \\ p\text{-}TolTe\diagup \qquad \diagdown TeTol\text{-}p \end{array}$$

$$\mathbf{(71)} \qquad\qquad\qquad\qquad \mathbf{(73)}$$

$$+ p\text{-}TolTeTeTol\text{-}p \quad + \quad t\text{-}BuP(Cl)TeTol\text{-}p \qquad (57)$$

$$\mathbf{(72)}$$

2. Seleno- and telluro-arsonous esters and related Sb and Bi compounds

a. Reaction of dichloro(phenyl)arsane with trimethyl(methylseleno)silane[13].

$$PhAsCl_2 \xrightarrow[-Me_3SiCl]{MeSeSiMe_3} PhAs\!\!\begin{array}{c} ^{\diagup Cl} \\ ^{\diagdown SeMe} \end{array} \xrightarrow[-Me_3SiCl]{MeSeSiMe_3} PhAs(SeMe)_2 \qquad (58)$$

$$\mathbf{(74)} \qquad\qquad\qquad\qquad\qquad \mathbf{(75)}$$

The formation and characterization of **74** and **75** were similar to those of the related phosphorus compounds **68** and **69**.

b. Organylbis(organyl-seleno or -telluro)stibanes. These appear to be unknown at present (see also Section IV.B.3).

c. Methylbis(phenyl-seleno- and -telluro)bismuthane. Wieber and Sauer[45] used the thermal decomposition of dimethyl(phenylseleno)bismuthane (**62**) in a stream of nitrogen at 80 °C for the preparation of methylbis(phenylseleno)bismuthane (**66**) (equation 51); **66** is an orange powder and the monomeric compound (mass spectrometry) decomposes with melting at 120 °C. The corresponding bismuth compound decomposes at room temperature[45] (see Section II.A.4).

C. Organyl-seleno and -telluro Esters of Phosphorous Acid and Related Arsenic, Antimony and Bismuth Compounds

1. Phosphorous acid esters, $P(ER)_3$ $(E = Se, Te)$

a. Tri(organylseleno)phosphanes and halogeno(organylseleno)phosphanes. Phenylse-lenol reacts with phosphorus trichloride with evolution of hydrogen chloride in cold benzene to give tri(phenylseleno)phosphane (**76**); spontaneous oxidation leads to the isolation of triselenophosphoric acid *Se,Se,Se*-triphenyl ester (**77**)[11]. Pure **76** was obtained as yellow crystals from finely divided white phosphorus suspended in acetone with diphenyl diselenide in the presence of few drops of concentrated KOH. Pure tri(methylseleno)phosphane (**78**) was prepared similarly as a yellow oil with a very repulsive odour (b.p. 45–50 °C/0.1 Torr)[48].

$$PCl_3 + 3\,PhSeH \xrightarrow{-3\,HCl} [P(SePh)_3] \xrightarrow{1/2\,O_2} (PhSe)_3P = O \qquad (59)$$

$$\text{(76)} \qquad\qquad\qquad \text{(77)}$$

$$P_4 + 6\,RSeSeR \xrightarrow[\text{acetone}]{\text{(KOH)}} 4\,P(SeR)_3 \qquad (60)$$

$$\text{(76) } R = Ph$$
$$\text{(78) } R = Me$$

Compound **76** is only slightly soluble in organic solvents, but **78** is fairly soluble in inert solvents and was studied by ^{31}P NMR (Section IX). NMR and Raman spectra served to confirm the formation of **78** when phosphorus trichloride reacted with excess of trimethyl(methylseleno)silane[13]. With a deficit of trimethyl(methylseleno)silane, mixed species were detected in equilibrium by ^1H NMR[13]:

$$PCl_3 + 3\,MeSeSiMe_3 \longrightarrow P(SeMe)_3 + 3\,Me_3SiCl \qquad (61)$$

$$\text{(78)}$$

$$PCl_3 \xrightarrow[-\,Me_3SiCl]{MeSeSiMe_3\ (deficit)} Cl_2PSeMe + ClP(SeMe)_2 \qquad (62)$$

$$\text{(79)} \qquad\qquad \text{(80)}$$

$$2\,Cl_2PSeMe \rightleftharpoons ClP(SeMe)_2 + PCl_3 \qquad (63)$$
$$\quad\ \ (79) \qquad\qquad (80)$$

$$2\,ClP(SeMe)_2 \rightleftharpoons P(SeMe)_3 + Cl_2PSeMe \qquad (64)$$
$$\qquad (80) \qquad\quad (78) \qquad\qquad (79)$$

$$(EtO)_2PCl \xrightarrow{\ \text{MeSeSiMe}_3\ } (EtO)_2PSeMe + EtO(Cl)PSeMe \qquad (65)$$
$$(81) \qquad\qquad\qquad (82)$$

The mixed species **83** was prepared by a more selective route[49]:

$$2\,PF_2I + Hg(SeCF_3)_2 \longrightarrow 2\,F_2PSeCF_3 + HgI_2 \qquad (66)$$
$$(83)$$

Similarly, the mixed species (**85**) or tris(trifluoromethylseleno)phosphane (**84**) were formed from the mercury compound with phosphorus tribromide[47]. Compound **84** was isolated as pure yellow liquid at $-30\,°C$. Interestingly, **84** is thermally unstable at room temperature, when a redox disproportionation leads to bis(trifluoromethyl) diselenide, but this decomposition remains uncomplete. After 24 h at $60\,°C$, diselenide formation is accompanied by precipitation of an orange–red insoluble solid that was suggested to have the approximate composition $(PSeCF_3)_x$[47]. Alkoxibis(butylseleno)phosphanes were prepared from the corresponding alkoxydichlorophosphanes with butylselenol in the presence of triethylamine in benzene solution[50].

$$2\,PBr_3 + 3\,Hg(SeCF_3)_2 \longrightarrow 2\,P(SeCF_3)_3 + 3\,HgBr_2 \qquad (67)$$
$$(84)$$

$$PBr_3 + Hg(SeCF_3)_2 \longrightarrow BrP(SeCF_3)_2 + HgBr_2 \qquad (68)$$
$$(85)$$

$$ROPCl_2 + 2\,BuSeH + 2\,NEt_3 \longrightarrow ROP(SeBu)_2 + 2\,HNEt_3Cl$$
$$(86)\ \ R = Et$$
$$(87)\ \ R = Pr \qquad (69)$$
$$(88)\ \ R = Bu$$

$$EtOP(SeBu)_2 + \tfrac{1}{2}O_2 \longrightarrow EtOP(=\!O)\,(SeBu)_2 \qquad (70)$$
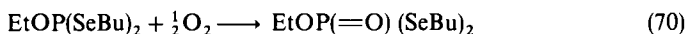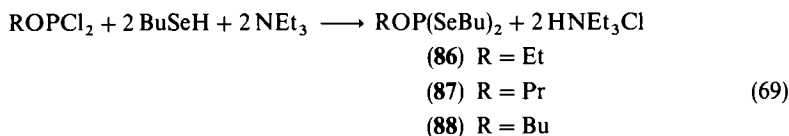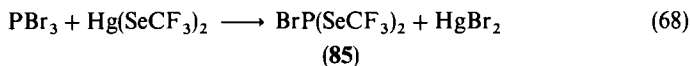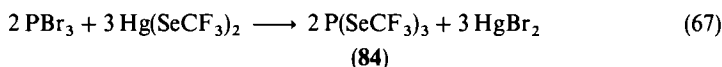
Compounds **86–88** are colourless, distillable liquids that are easily oxidized by oxygen or sulphur (see Section VI). The first derivatives of triselenophosphorous acid were tris(diselenoxanthogenato)phosphanes (orange–yellow solids) that were prepared straightforwardly from the potassium diselenoxanthogenates with PCl_3[51]. Reaction of a potassium diselenoxanthogenate with $POCl_3$ leads also to the tris(diselenoxanthogenato)phosphane and a diselenide [i-PropOC(Se)Se]$_2$ as oxidation product (equation 72)[52]. Separation of the products was achieved by crystallization of **90**, which is less soluble in diethyl ether[52].

$$PCl_3 + 3\ ROCSe_2K \longrightarrow P\left(SeC\underset{OR}{\overset{Se}{\lessgtr}}\right)_3 + 3\ KCl \qquad (71)$$

(89) R=Et
(90) R= i-Pr
(91) R= s-Bu

$$4\ POCl_3 + 15\ \ i\text{-}PrOC\underset{SeK}{\overset{Se}{\lessgtr}} \longrightarrow 9\ \textbf{90} + K_3PO_4 + 12\ KCl + 3\left[i\text{-}PrOC\underset{Se}{\overset{Se}{\lessgtr}}\right]_2 \qquad (72)$$
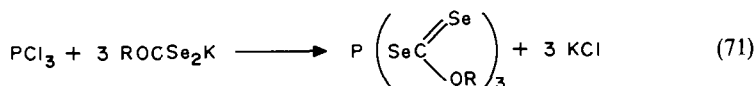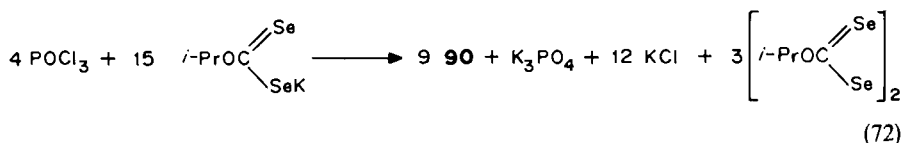
  b. *Tri(p-anisyltelluro)phosphane.* This compound has been prepared from finely divided white phosphorus with di-*p*-anisylditelluride in the presence of KOH[48]. At −50°C, the compound separated in moderate yield as rust-coloured crystals from the dark-red acetone solution. When dried under vacuum **92** gave satisfactory analytical data, but when an inert gas was admitted to the flask containing the compounds the crystals became beige–white and evolved white fumes. Under the mother liquor (acetone solution), crystalline **92** appears to be perfectly stable at −20 °C.

$$P_4 + 6\,p\text{-AnTeTeAn-}p \xrightarrow[\text{acetone}]{\text{(KOH)}} 4\ P(\text{TeAn-}p)_3 \qquad (73)$$

$$(\textbf{92})$$
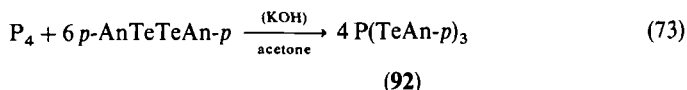
2. Arsenous acid esters, As(SeR)₃ [tri(organylseleno)arsanes]

  The preparation of these compounds is similar to that of the corresponding phosphorus compounds, i.e. arsenous halides were treated with trimethyl(methylseleno)silane[13], with bis(trifluoromethylseleno)mercury[47] and with potassium isopropyl diselenoxanthogenate[52].

$$AsCl_3 \xrightarrow[-\,3\,Me_3SiCl]{3\,MeSeSiMe_3} As(SeMe)_3 \qquad (74)$$

$$(\textbf{93})$$

$$AsCl_3 \xrightarrow[-\,2\,Me_3SiCl]{2\,MeSeSiMe_3} ClAs(SeMe)_2 \rightleftharpoons \tfrac{1}{2}Cl_2AsSeMe + \tfrac{1}{2}\textbf{93} \qquad (75)$$

$$\qquad\qquad\qquad\qquad (\textbf{94})\qquad\qquad (\textbf{95})$$

$$AsCl_3 \xrightarrow[-\,HgCl_2]{Hg(SeCF_3)_2} As(SeCF_3)_3 + ClAs(SeCF_3)_2 \qquad (76)$$

$$\qquad\qquad\qquad\quad (\textbf{96})\qquad\qquad (\textbf{97})$$

$$AsCl_3 \xrightarrow[-3\,KCl]{3\ i\text{-}PrOCSe_2K} As\left(SeC\underset{OPr-i}{\overset{Se}{\lessgtr}}\right)_3 \qquad (77)$$

$$(\textbf{98})$$
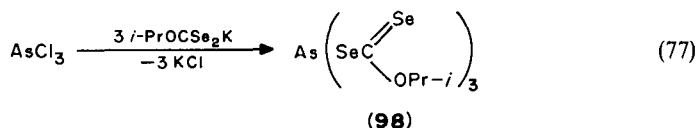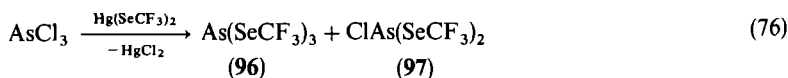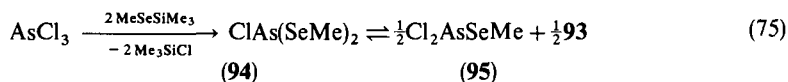
The physical properties of **93–98** seem to be similar to those of the corresponding phosphorous acid derivatives, but only **96** and **98** have been isolated in analytically pure states[47,52]*.

III. ORGANYL-SELENO- AND -TELLURO-DIPHOSPHANES

Only two compounds that contain an organyl-seleno or -telluro substituent bonded to a diphosphorus moiety have appeared in literature. Diphosphorus tetraiodide reacts with a large excess of bis(trifluoromethylseleno)mercury in CS_2 to give a mixture of tetrakis(trifluoromethylseleno)diphosphane **(99)** and tris(trifluoromethylseleno)phosphane **(84)**. Compound **99** was enriched by trap-to-trap distillation to 90–95% purity, but complete separation from the selenophosphane **(84)** was not achieved; **99** was characterized by ^{19}F and ^{31}P NMR and mass spectroscopy[47]. Thermal decomposition of the diphosphane leads to the trisselenophosphane **(84)** and a solid orange material which was not further characterized.

$$P_2I_4 + \xrightarrow{4\,Hg(SeCF_3)_2} (CF_3Se)_2PP(SeCF_3)_2 + P(SeCF_3)_3 + HgI_2 + CF_3SeHgI$$
$$\text{(99)} \qquad\qquad \text{(84)}$$

$$\tag{78}$$

$$(CF_3Se)_2PP(SeCF_3)_2 \xrightarrow{\Delta} P(SeCF_3)_3 + \text{orange solid} \tag{79}$$

$$\text{(99)} \qquad\qquad\qquad \text{(84)}$$
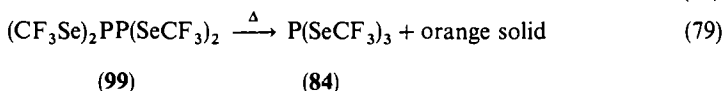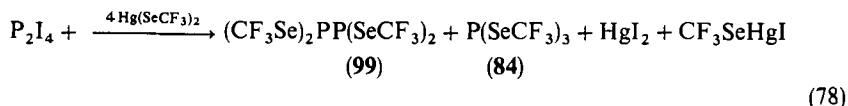
It should be recalled (Section II.C.1.a) that the monophosphane **84** itself undergoes partial thermal decomposition leading to bis(trifluoromethyl) diselenide and an orange solid that has the approximate composition of $(CF_3SeP)_x$[47].

This decomposition pathway resembles the reverse reaction of the degradation of P_4 or $(PhP)_5$[48,53] with dialkyl disulphides or dimethyl diselenide[48], which may be regarded as a sequence of P—P bond cleavages by $(2 + 2)$ dismutation with the dichalcogenide. The appearance of the diselenide and the (probably P—P-bond) polymers $(CF_3SeP)_x$ from **99** and **84**, respectively, could be explained by $(2 + 2)$ dismutation/retrodismutation
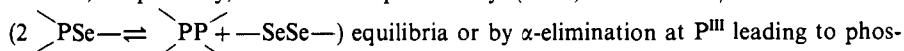
$(2 \diagup\!\!\!\!\diagdown\! PSe- \rightleftharpoons \diagup\!\!\!\!\diagdown\! PP\diagdown\!\!\!\!+ -SeSe-)$ equilibria or by α-elimination at P^{III} leading to phos-

phinidene (P^I) intermediates $(-\overset{..}{P}(SeR)_2 \rightarrow -\overset{..}{P} + R_2Se_2)$. In the case of Ph(I)PP(I)Ph, $Hg(SeCF_3)_2$ leads to complete oxidation of the diphosphane to give the fairly stable $PhP(SeCF_3)_2$ **(70)**. In the aryl-t-butyltellurium–phosphorus systems, the equilibrium of this redox [or $(2 + 2)$ dismutation] reaction seems to be more on the side of the P—P-bonded species. Tetra-t-butylcyclotetraphosphane does not react at all with di-p-tolyl ditelluride[54]. Strained tri-t-butylcyclotriphosphane does react with the diaryl ditelluride, but even with a large excess of the ditelluride only 1,2-di-t-butyl-1,2-di-p-tolylurodiphosphane **(73)** is formed, which does not react further with the ditelluride[30,31].

$$(t\text{-BuP})_4 + p\text{-TolTeTeTol-}p \nrightarrow \tag{80}$$

$$(t\text{-BuP})_3 + p\text{-TolTeTeTol-}p \longrightarrow \underset{p\text{-TolTe}}{\overset{t\text{-Bu}}{\diagdown}}P - P\underset{\text{TeTol-}p}{\overset{\text{Bu-}t}{\diagup}} + \tfrac{1}{4}(t\text{-BuP})_4 \tag{81}$$
$$\text{(73)}$$
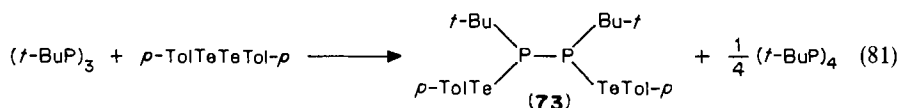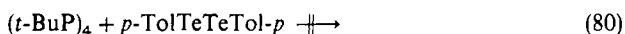
*For diselenophosphato complexes $M[Se_2P(OR)_2]_3$ (M = As, Sb, Bi), made by Zingaro's group, see Ref. 3 and references cited therein.

On the other hand, the attempted synthesis of *t*-butylbis(*p*-tolyltelluro)phosphane (**71**) (equation 57) led to the diphosphane (**73**) and di-*p*-tolyl ditelluride. Compound **71** appears to decompose by re-dismutation of one P—Te bond to give P—P-bonded **73** and the ditelluride. Compound **73** is thermally stable at room temperature. In the melt, irreversible decomposition leads to di-*p*-tolyl ditelluride and tetra-*t*-butylcyclotetraphosphane (see equation 80)[30,31]. The fair thermal stability of the diphosphane **73** is obviously due to kinetic stabilization from bulky *t*-butyl groups. A high-yield synthesis of **73** is the reaction of 1, 2-di-*t*-butyl-1, 2-dichlorodiphosphane with *p*-tolylteluromagnesium bromide. The pure compound (yellow crystals from pentane) was obtained in 75% yield from this reaction[30,31].

$$t\text{-Bu(Cl)PP(Cl)Bu-}t + 2\,p\text{-TolTeMgBr} \xrightarrow[-2'\text{MgBrCl'}]{\text{(THF)}} (73) \qquad (82)$$
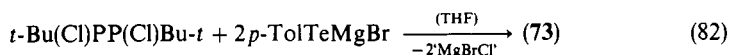
Surprisingly, **73** was also one of the main products when 1,2-di-*t*-butyl-1,2-dichlorodiphosphane was stirred with di-*p*-tolyl ditelluride at 50–55 °C in toluene for 24 h[30,54].

$$t\text{-BuP(Cl)P(Cl)Bu-}t + p\text{-TolTeTeTol-}p \xrightarrow[24\,\text{h}]{50-55\ ^\circ\text{C}} (p\text{-TolTe})(t\text{-Bu})\text{PP(Cl)Bu-}t + \mathbf{73}$$

$$\text{(100)}$$

$$\Big\downarrow{\scriptstyle 160\ ^\circ\text{C} \atop 24\,\text{h}} \qquad\qquad 160\ ^\circ\text{C} \Big| + t\text{-BuPCl}_2$$

$$(\text{PBu-}t)_4 + t\text{-BuPCl}_2$$

$$\tag{83}$$
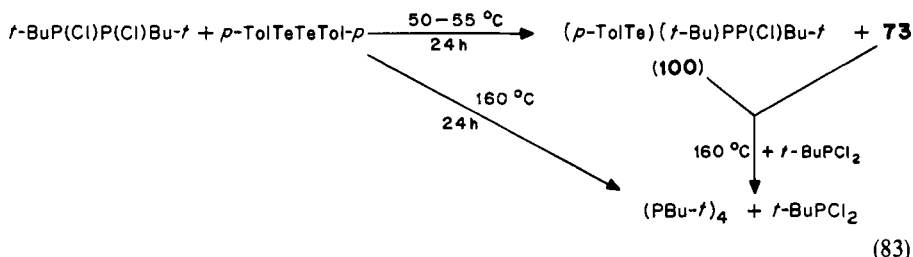
Compound **100** was detected by its AX-type ^{31}P NMR spectra [$\delta(P_A) + 124.8$ ppm, $\delta(P_X) + 34.3$ ppm; $J(AX) \pm 322.3$ Hz]; chiral discrimination leads obviously to the predominance of one isomer of **100**. At 160 °C, irreversible decomposition of both diphosphanes occurs and only (*t*-BuP)$_4$ and *t*-BuPCl$_2$ were detected by ^{31}P NMR after 24 h at this temperature. In solutions of **73**, two isomers are present that give ^{31}P NMR signals at $+ 39.6$ and $+ 29.2$ ppm. The isomer with ^{31}P NMR shift to higher field predominates (about 88%, probably *meso*-**73**). ^{31}P NMR 'tellurium satellites' and the [125]Te NMR spectrum of the predominant isomer are AA' and X parts of an AA'X spin system; analysis of the spectra led to $^1J(^{125}\text{Te}^{31}\text{P}) = -520$ Hz, $^2J(^{125}\text{Te}^{31}\text{P}) = -22.5$ Hz and $^1J(^{31}\text{P}^{31}\text{P}) = -319$ Hz. A diphosphanditelluride structure with P=Te bonds can therefore be ruled out[30,54].

IV. SELENO- OR TELLURO-BIS-PHOSPHANES, -ARSANES, -STIBANES AND -BISMUTHANES

A. Seleno- or Tellurophosphinous Anhydrides and Related Arsenic, Antimony and Bismuth Compounds

1. Preparation of seleno- and telluro-phosphinous anhydrides, R_2PEPR_2 (E = Se, Te)

a. Selenobisphosphanes. These compounds are very rare in the literature. The inorganic selenobisphosphane F_2PSePF_2 (**101**) was prepared from bromodifluorophosphane with disilylselane[14]. The NMR spectra of **101** are strongly temperature dependent: $^2J(PP)$ and

^4J(FF) increase by about 50% when the temperature of the sample is lowered from room temperature to 173 K. This should be due to conformational changes (changes in the thermal population of conformations) that lead to differences in lone pair–lone pair interactions which influence ^1J(PP) and long-range couplings[14].

Generally, chalcogenobisphosphanes are in equilibria with diphosphane chalcogenides. The latter may rearrange to give diphosphane dichalcogenides and diphosphanes:

SCHEME 1

A comprehensive study of this problem by Lutsenko and Foss[55] (with E = O, S) revealed that very bulky substituents generally favour the phosphinous anhydride isomer (A), so that $(t\text{-Bu}_2\text{P})_2\text{O}$ and $(t\text{-Bu}_2\text{P})_2\text{S}$[56] are thermally stable compounds, whereas $(i\text{-Pr}_2\text{P})_2\text{O}$ and $(i\text{-Pr}_2\text{P})_2\text{S}$ are in equilibria with the type B isomers (Scheme 1). On the other hand, thermodynamically less favoured isomers may be kinetically inert and can be isolated in the pure state in certain cases[55]. A further preparative problem is that chalcogenobisphosphanes (A) or diphosphanemonochalcogenides (B) can be further oxidized by elemental chalcogen.

Tetra-t-butyldiphosphane reacts with equimolar amounts of selenium to give two products, the selenobis(di-t-butylphosphane) (102) and the diseleno species (103) (NMR spectroscopic evidence). Compound 103 is the only product if the ratio of tetra-t-butyldiphosphane to selenium is 1:2. The diseleno species (103) was isolated in the pure state as colourless crystals from diethyl ether–pentane[57].

The NMR, IR and mass spectra of 103 are consistent with the P^{III}/P^V structure related to 'cacodyl disulphide', whose As^{III}/As^V structure was confirmed by crystallographic data[58]. With excess of selenium 103 is further oxidized to the selenophosphinic anhydride, $[(t\text{-Bu})_2\text{P}(=\text{Se})]_2\text{Se}$ (see Section VIII)[57].

$$2(t\text{-Bu})_2\text{PCl} + \text{Na}_2\text{Se} \longrightarrow 102 + 2\,\text{NaCl} \qquad (85)$$

From di-*t*-butylchlorophosphane with sodium selenide, **102** was obtained as thermally stable colourless needles from toluene–pentane[57].

b. Tellurobisphosphanes. Tellurobis(di-*t*-butylphosphane) (**30**) was first obtained in a pure state when di-*t*-butylchlorophosphane reacted with sodium telluride[28,31]; **30** is also formed in equilibria with di-*t*-butyl(trimethylsilyl-, -germyl- and -stannyl-telluro)phosphanes   (**27–29**)   (equation 28)   or   when   di-*t*-butyl-[tris(trimethylsilyl)methyltelluro]phosphane (**34**) decomposes to give the symmetrically substituted tellurium compounds[32]. A very straightforward preparation of **30** is tellurium insertion into the P—P bond of tetra-*t*-butyldiphosphane. Heating the diphosphane for 3 days with powdered tellurium in boiling toluene yields the tellurobisphosphane in quantitative crude yield; from pentane pure yellowish needles are obtained, which melt at 70–80 °C without decomposition[31,57].

$$2\,(t\text{-Bu})_2\text{PCl} + \text{Na}_2\text{Te} \longrightarrow (t\text{-Bu})_2\text{PTeP(Bu-}t)_2 + 2\,\text{NaCl} \tag{86}$$
$$\textbf{(30)}$$

$$(t\text{-Bu})_2\text{PP(Bu-}t)_2 + \text{Te} \xrightarrow[3\,\text{d}]{110\,°C} \textbf{30} \tag{87}$$
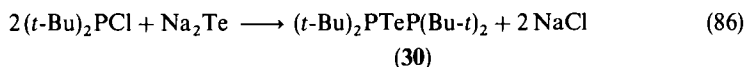
The latter preparation is much easier than the synthesis of the corresponding selenium compound **102** because neither further oxidation of **30** to give a species related to **103** nor significant di-insertion (to give a ditellurobisphosphane) occur with excess of tellurium. In contrast, reaction of sodium ditelluride with di-*t*-butylchlorophosphane leads to the formation of **30** with precipitation of elemental tellurium[30,54]. Photochemically, **30** decomposes[59] with extrusion of elemental tellurium (reverse reaction of the thermal synthesis from equation 87) and formation of tetra-*t*-butyldiphosphane. By-products are $(t\text{-Bu})_2\text{PH}$ [from $(t\text{-Bu})_2\text{P}$ radicals] and the tellurocyclophosphane $(t\text{-BuP})_3\text{Te}$ (from P—C cleavage; see Section IV.B).

$$(t\text{-Bu})_2\text{PTeP(Bu-}t)_2 \xrightarrow[\substack{\text{C}_6\text{H}_6/\text{C}_6\text{D}_6 \\ \text{(sealed tube)} \\ 30\,°C}]{h\nu\,(\text{UV})} (t\text{-Bu})_2\text{PP(Bu-}t)_2 + \text{Te}$$
$$\textbf{(30)}$$
$$[\,+ (t\text{-Bu})_2\text{PH} + (t\text{-BuP})_3\text{Te} + \text{H}_2\text{C} = \text{CMe}_2\,] \tag{88}$$
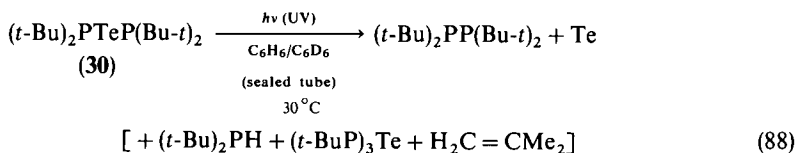
Tetraisopropyldiphosphane reacts with elemental tellurium under milder conditions than tetra-*t*-butyldiphosphane, but in this case tellurium insertion into the P—P bond is far from quantitative; equilibrium mixtures are obtained as yellow solutions that do not contain more than 60% of the tellurobisphosphane **104**[57]. Similar observations had been made when tri-*n*-alkylphosphanes were found to react 'incompletely' with elemental tellurium to give mixtures of phosphane tellurides and unreacted phosphane[60], but the formation of **104** according to equation 89 is the first case of an incomplete tellurium insertion.

$$(i\text{-Pr})_2\text{PP(Pr-}i)_2 + \text{Te} \rightleftharpoons (i\text{-Pr})_2\text{PTeP(Pr-}i)_2 \tag{89}$$
$$\textbf{(104)}$$
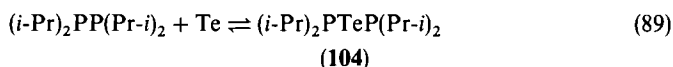
The sodium telluride–chlorophosphane reaction also does not lead to pure **104**, but some tellurium precipitation with formation of tetraisopropyldiphosphane again, occurs.

$$2\,(i\text{-Pr})_2\text{PCl} + \text{Na}_2\text{Te} \longrightarrow \textbf{104}\,[\,+ \text{Te} + (i\text{-Pr})_4\text{P}_2\,] \tag{90}$$
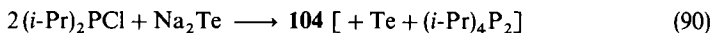
Crystallization from pentane afforded small amounts of yellow crystalline **104** that gave correct analytical data. In contrast to the *t*-butyl compound **30**, **104** is extremely sensitive

to air, moisture and thermal decomposition[31,57]. From equilibrium mixtures with tetraisopropyldiphosphane, **104** could be trapped by selective coordination with norbornadientetracarbonylchromium(0).

$$(i\text{-Pr})_4P_2 + Te \rightleftharpoons \mathbf{104} \xrightarrow[-\text{Nor}]{\text{NorCr(CO)}_4} (CO)_4Cr\overset{P(Pr\text{-}i)_2}{\underset{P(Pr\text{-}i)_2}{\diagup\diagdown}}Te \qquad (91)$$

(105)

$$\left(Nor = \right)$$
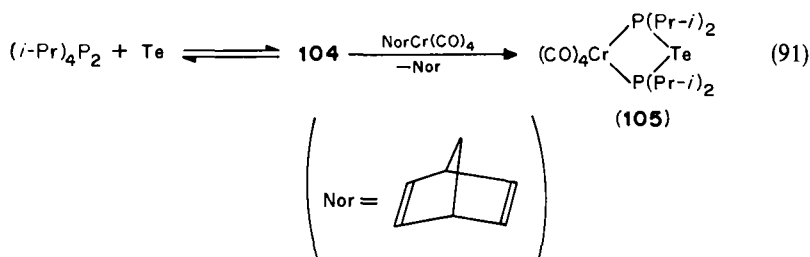
Compared with the ligand **104**, the four-membered chelate complex **105** is remarkably stable to thermal detelluration or hydrolytic decomposition. Pure red crystals of **105** were isolated after several recrystallizations from pentane–toluene[57]. Tetramethyldiphosphane reacts with elemental tellurium at room temperature to give a yellow solution, but ^{31}P NMR spectra reveal that again there is a large excess of the diphosphane present in solution. Attempts to isolate tellurobis(dimethylphosphane) (**106**) in a pure state (yellow crystals) are in progress. Reactions that should lead to tellurobis(diphenylphosphane) gave only tetraphenyldiphosphane and elemental tellurium[59].

$$Me_2PPMe_2 + Te \rightleftharpoons Me_2PTePMe_2 \qquad (92)$$

(106)

$$2\,Ph_2PSiMe_3 + Te \longrightarrow Ph_4P_2 + (Me_3Si)_2Te \qquad (93)$$
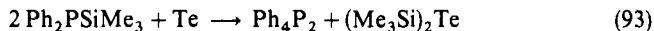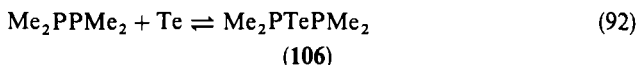
2. Synthesis and structures of μ-9,10-chalcogeno-9,10-diarsaanthracenes

The so-called 'arsanthrene oxide' (**107**) has been known since 1921; with hydrogen sulphide, selenide and telluride the corresponding μ-9,10-chalcogeno-9,10-diarsaanthracenes **108–110** are formed as stable crystalline compounds[61].

$$\qquad\qquad \xrightarrow[-H_2O]{H_2E\ (EtOH)} \qquad\qquad\qquad (94)$$

(107)

(108) E = S (colourless)
(109) E = Se (yellow)
(110) E = Te (red)
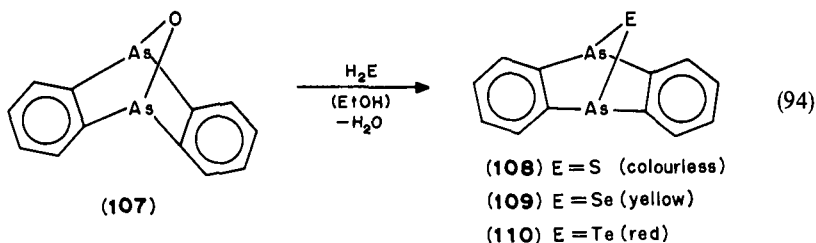
X-ray crystal structure analyses have been carried out on the chalcogenobisarsanes **107**–**110**[62]. All four compounds are in the 'butterfly' conformation about the plane of the As—X—As moiety and the molecules of all four compounds show non-crystallographic symmetry of 2mm (corresponding to molecular symmetry point group C_{2v}) about an axis bisecting the As—E—As bond angle. The As⋯As distances are determined by the increase in covalent radii from O to Te and by their preferred valency angles. In non-bridged 9,10-dihydro-9,10-dimethyl-9,10-diarsaanthracene, the As⋯As distance is 3.27 Å. The As⋯As distances in the selenium and tellurium compounds do not adapt sufficiently to allow the Se and Te atoms their preferred valency angle (Table 2).

TABLE 2. Comparison of structural features of μ-9,10-chalcogeno-9,10-diarsaanthracenes 107–110[62] with $C_2AsEAsC_2$ moieties

E	Compound	d(AsE)(Å)[a]	AsÊAs	d(As···As)(Å)	CÂsC
O	**107**	1.84	108.8	2.98	95.0
		1.82			
S	**108**	2.23	91.5	3.23	92.7
		2.26			
Se	**109**	2.39	86.2	3.28	93.4
		2.40			
Te	**110**	2.57	80.8	3.35	95.7

[a] Where two values are given, this is due to a slight distortion of the molecules in the crystals (deviation from ideal point group C_{2v}).

Compounds **108–110** are fairly inert towards electrophiles such as methyl iodide, but they are attacked by oxidizing agents and by nucleophiles such as methylmagnesium iodide[61].

3. Preparation of seleno- and telluro-bis(diorganylstibanes)

The first seleno- and telluro-bisstibanes, $R_2SbESbR_2$ (E = Se, Te), were prepared recently by Breunig and Jawad[39].

$$R_2SbSbR_2 + Se \longrightarrow R_2SbSeSbR_2 \qquad (95)$$
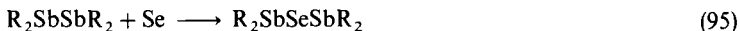
(111) R = Me (orange liquid)
(112) R = Et (yellow crystals)
(113) R = Ph (pale yellow crystals)

$$R_2SbSbR_2 + Te \longrightarrow R_2SbTeSbR_2 \qquad (96)$$
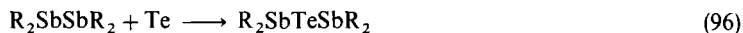
(114) R = Me (brown liquid)
(115) R = Et (red liquid)

Compounds **111–115** are formed under mild conditions by slightly exothermic reactions of the distibanes with elemental selenium or tellurium; the pure compounds have been isolated in high yields. Contrary to the reactions of non-strained diphosphanes, the distibanes are quantitatively mono-selenated and mono-tellurated. Compounds **111–115** are sufficiently thermally stable to be handled at room temperature in the pure state under inert gas and in inert solvents. A remarkable feature of the dimethylantimony selenium and tellurium derivatives **111** and **114** is their thermochromic behaviour. At 5 °C the orange–red liquid of **111** becomes a red crystalline solid, but below − 20 °C the colour of the solid is yellow. The properties of the tellurium compound **114** are even more striking: at room temperature **114** is a brown liquid and just below the melting point (8 °C) the crystals are blue–violet and look very much like solid iodine. The finding that only the methyl derivatives (and not the bulkier ethyl substituted compounds **112** and **115**) show this thermochromic behaviour led to the prediction that unusual short intermolecular contacts in the solids (a kind of secondary bonding) might be involved[39]. Such contacts have been confirmed to exist in solid tetramethyldistibane, which is also strongly thermochromic[63,64]. Spectroscopic investigations confirmed the chalcogenobisstibane

structure A for **111–115** and the distibane chalcogenide structure B could be ruled out.

$$R_2Sb\overset{\displaystyle E}{\diagdown\diagup}SbR_2 \qquad\qquad\qquad R_2Sb\overset{\displaystyle \overset{E}{\parallel}}{}SbR_2$$

A   B

4. Seleno- and telluro-bis(diorganylbismuthanes)

Recently, the formation of the first seleno- and telluro-bisbismuthanes was reported at a conference[65]. These compounds are also strongly coloured and they appear to be thermally less stable than the corresponding antimony compounds. The decomposition pathways seem to involve alkyl scrambling (compare Section II.A.4).

$$R_2BiBiR_2 + E \longrightarrow R_2BiEBiR_2 \qquad\qquad (97)$$

         (116) E = S, R = Me (Ref. 41)
         (117) E = Se, R = Pr (Ref. 65)
         (118) E = Se, R = Pr (Ref. 65)
         (119) E = Te, R = Pr (Ref. 65)

B. Cyclic Seleno- or Telluro-bisphosphanes and -bisarsanes

1. Chalcogenocyclophosphanes, $(RP)_nE_m$ $(E = Se, Te)$

a. Selenocyclophosphanes. Within the scope of their work on phosphorus ring systems, Baudler *et al.*[66] prepared the first selenadiphosphirane (**120**) by reaction of 1, 2-di-*t*-butyl-1, 2-dichlorodiphosphane with bis(trimethylstannyl)selenide.

$$(98)$$

Selenadiphosphirane **120** tends to give dimerization and subsequent elimination reactions leading to other cyclic compounds containing Se atoms and *t*-butylphosphosphandiyl groups as ring members which were detected by ^{31}P NMR spectroscopy. Typically, **120** shows an upfield ^{31}P shift and a small coupling constant $J(^{77}Se^{31}P)$.

                (122) $x = 3, y = 1$
                (123) $x = 3, y = 3$
                (124) $x = 4, y = 1$

$$(99)$$

The thiadiphosphirane corresponding to **120** was prepared similarly[66].

An alternative route to selenadiphosphiranes is the reaction of a diphosphene with elemental selenium. Formation of the selenadiphosphirane competes with di(seleno)metaphosphonate formation[67].

$$RP{=}PR \xrightarrow[\substack{NEt_3 \\ 70\ °C}]{Se} RP{-}\underset{\underset{\textstyle Se}{\diagdown\diagup}}{\quad}PR + RP\underset{\textstyle Se}{\overset{\textstyle Se}{\diagup\diagdown}} \qquad (100)$$

$$\begin{array}{ccc} & 17\% & 4\% \\ & \mathbf{(125)} & \mathbf{(126)} \end{array}$$

R = 2,4,6-tri-*t*-butylphenyl
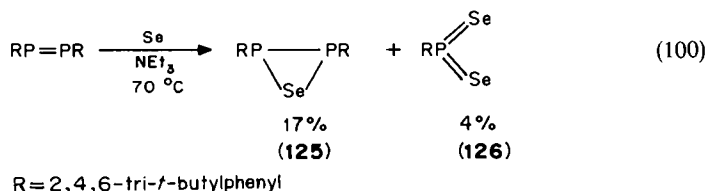
Reaction of the diphosphene with sulphur proceeds thermally with formation of a diphosphene sulphide (127), which can be rearranged photochemically to give the thiadiphosphirane that corresponds to 125[68].

$$RP{=}PR \xrightarrow{1/8\ S_8} \underset{R}{\overset{R}{\diagup}}P{=}P\underset{\textstyle S}{\overset{\textstyle R}{\diagup\diagdown}} \xrightarrow{h\nu\ or\ \Delta} RP\underset{\underset{\textstyle S}{\diagdown\diagup}}{\quad}PR \qquad (101)$$

$$\begin{array}{cc} \mathbf{(127)} & \mathbf{(128)} \end{array}$$

R = 2,4,6-tri-*t*-butylphenyl
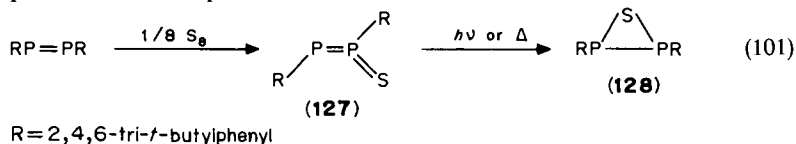
Much earlier, Maier found that phenylphosphane reacts with red selenium with evolution of hydrogen selenide and the formation of a material that had previously been assigned a tetraphenylcyclotetraphosphane–tetraselenide structure[69,70]. Similar arsenic compounds have also been reported[70a].

$$\begin{array}{c} PhPH_2 \xrightarrow[-H_2Se]{+2Se} \\ \\ 1/5\ (PhP)_5 + Se \end{array} \Bigg\} 1/x\ (PhPSe)_x \qquad (102)$$

$$\mathbf{(129)}$$
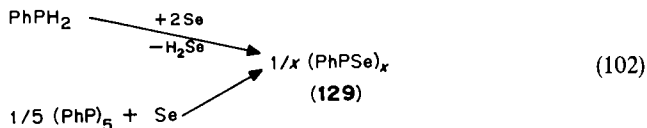
b. *Tellurocyclophosphanes*. Tellurocyclophosphanes are formed in a substitution and redox reaction between *t*-butyldichlorophosphane and sodium telluride. Essentially the same products are formed (in a different distribution) when the chlorophosphane reacts with bis(trimethylsilyl)telluride[30,54,59].

$$t\text{-}BuPCl_2 \xrightarrow[\text{or } (Me_3Si)_2Te,\ -2Me_3SiCl]{Na_2Te,\ -2NaCl} 1/x\ (t\text{-}BuP)_xTe + (1 - \tfrac{1}{x})Te \qquad (103)$$

$$\begin{array}{l} \mathbf{(130)}\ x = 2 \\ \mathbf{(131)}\ x = 3 \\ \mathbf{(132)}\ x = 4. \end{array}$$
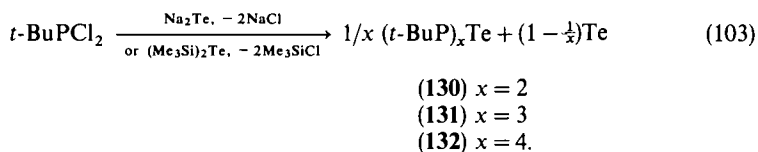
The main products of this reaction are the telluradiphosphirane 130 and the telluratriphosphetane 131, but several other species are also present in the red oil that was obtained as the pentane-soluble fraction of the reaction mixture. The telluradiphosphirane 130 is the only main product when sodium telluride is treated with *t*-butyl-dichlorophosphane in pentane solution. Application of a more polar solvent (such as diethyl ether) leads to dimerization of 130 to give the six-membered heterocycle 133, which decomposes further either with loss of a Te atom (to give 132) or with loss of a *t*-butylphosphandiyl unit to give the ditelluratriphospholan (t-BuP)$_3$Te$_2$ (134). Further extrusion of tellurium leads from 134 to 131 and from 132 to tetra-*t*-butylcyclotetraphosphane.

$$(104)$$

$$(105)$$

When the reaction according to equation 104 is carried out in pentane at 35–40 °C (5 h), evaporation of the solvent yields a yellow residue that contains mainly **130**(^{31}PNMR δ − 69 ppm). Pure **130** (26%) was isolated by distillation into a flask that was kept at 78 K. It condensed as a yellow solid which became a yellow oil at about − 40 °C. The telluratriphosphetane **131** was the only product containing P atoms when *t*-butyl-bis(trimethylsilyl)phosphane was stirred for 2 weeks with Te powder in the dark(without solvent)[59].

$$t\text{-BuP(SiMe}_3)_2 + 4/3\,\text{Te} \longrightarrow \tfrac{1}{3}\textbf{131} + (\text{Me}_3\text{Si})_2\text{Te} \tag{106}$$

Distillation of bis(trimethylsilyl)telluride into a 78 K trap within several days gave **131** as a red oil that gave correct analytical data. Compound **131** is thermally stable at room temperature. Evidence for the telluratriphosphetane structure is provided by EI and FI MS and by ^{31}P and ^{125}Te NMR data[30,54,59]. Selected data of the various tellurocyclophosphanes are compiled in Table 3. The ^{125}Te NMR shift of **131** given in Ref. 59 was incorrect owing to 'signal folding'.

TABLE 3. Properties of tellurocyclophosphanes[30,54,59] $(t\text{-BuP})_n\text{Te}_m$

Method	$n = 4, m = 2$ (133)	$n = 3, m = 2$ (134)	$n = 4, m = 1$ (132)	$n = 3, m = 1$ (131)	$n = 2, m = 1$ (130)
MS	—	520(M^+)	482(M^+)	394(M^+)	306(M^+)
	520(M^+	463(M^+	425(M^+	337(M^+	250(M^+
	− C$_4$H$_9$P)	− C$_4$H$_9$)	− C$_4$H$_9$)	− C$_4$H$_9$)	− C$_4$H$_8$)
^{31}NMR	+ 46.9(s)	+ 99.8(d)	+ 89.9	− 4.1(t)	− 70.0
		+ 153.7(t)	+ 94.8	− 60.5(d)	
		($J = \pm 26$ Hz)	(AA'BB')	($J = \pm 172.6$)	
^{125}NMR^a	δ − 33.7(m)	δ ca. + 160(m)	δ ca. + 50(m)	δ − 789(d, t)	δ − 1123.7(t)

^{a} ^{125}Te NMR: ditolyl ditelluride standard, Bruker WP80 instrument (25.27 MHz, ^{125}Te).

Mixtures containing some or all of the tellurocyclophosphanes **130–134** are formed from various reactions that lead to bond formation between Te and t-BuP groups[30,54].

$$t\text{-BuP(SiMe}_3)_2 + \text{Te} \xrightarrow{\text{Et}_2\text{O}/\Delta} \quad\quad\quad\quad (107)$$

$$(t\text{-Bu})_2\text{P}_2\text{Cl}_2 \xrightarrow{\text{(Me}_3\text{Si)}_2\text{Te}} (t\text{-BuP})_x\text{Te}_y \quad\quad (108)$$

$$(t\text{-Bu})_2\text{P}_2\text{Cl}_2 \xrightarrow[\text{100 °C}]{\text{Te}} \quad\quad\quad\quad\quad (109)$$

$$\xrightarrow[\Delta]{\text{Te}} (t\text{-BuP})_x\text{Te}_y \xrightarrow[\Delta]{-y\text{Te}} (t\text{-BuP})_4 \quad (110)$$

$$\xrightarrow{\text{Te}} \quad\quad\quad\quad\quad\quad (111)$$
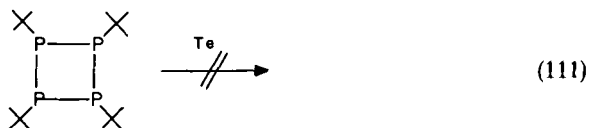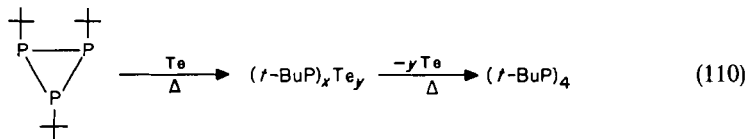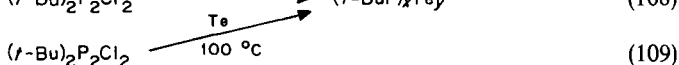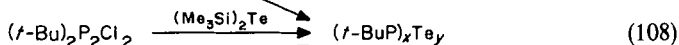
Tri-t-butylcyclotriphosphane reacts with elemental tellurium, but tetra-t-butylcyclotetraphosphane does not. Thermal decomposition reactions of tellurocyclophosphanes lead finally to tetra-t-butylcyclotetraphosphane (equation 110). Surprisingly, reactions under very mild conditions such as that of t-butyldichlorophosphane and bis(trimethylsilyl) telluride do not lead to 1,3-ditelluradiphosphetane but yield preferentially the three-membered telluradiphosphirane and products of its thermal decomposition (equation 103 and 107). The 1,2- or 1,3-ditelluradiphosphetane (A, B) are either unstable with respect to loss of tellurium with ring contraction, or the intermediate telluroxophosphane (t-BuP=Te), having a highly ylidic character, dimerizes not with (2 + 2) cycloaddition (to give a 1,3- or 1,2-ditelluradiphosphetane) but in a kind of (2 + 1) addition leading to the short-lived 'dimer' C, which undergoes spontaneous detelluration to give **130** (Scheme 2).
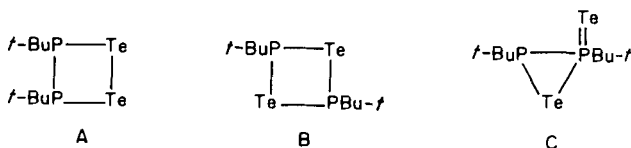
SCHEME 2.   Molecules that have *not* been detected in tellurocyclophosphane mixtures.

2. Selenocycloarsanes

The reaction of 1,1,1-tris(diiodoarsinomethyl)ethane with water or with hydrogen sulphide gives cage compounds of the adamantane type, but with sodium hydridoselenide a noradamantane compound (**135**) containing one As—As bond is formed. Sodium telluride leads to complete reduction and the cyclotriarsane (**136**) is formed[71-73].

$$E = O, S \qquad (112)$$

$$(113)$$

$$(135)$$

$$(114)$$

$$(136)$$
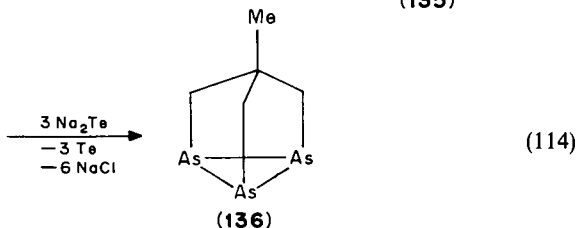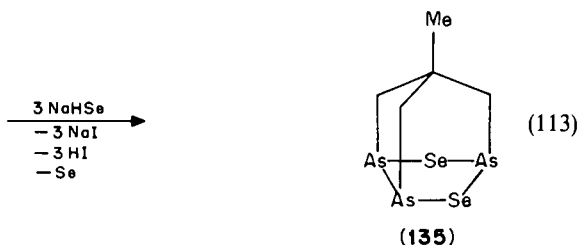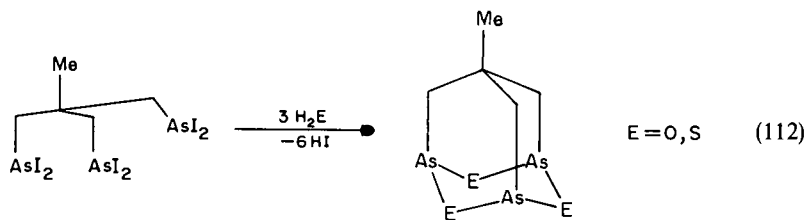
Reaction of the nortricyclene-type triarsane (136) with elemental selenium also led to the diseleno derivative 135 (sulphur reacts similarly); excess of sulphur or selenium did not lead to any further oxidation (i.e. S or Se insertion). With elemental tellurium, triarsane 136 did not react at all[71-73]. The structure of 135 was confirmed by an X-ray crystal structure analysis[71]. Compound 135 is less strained than a comparable compound containing $C(COOEt)_2$ groups in place of the selenium atoms. The As_3Se_2 fragment is a non-planar five-membered ring. The SeAsSe and AsSeAs angles (97–99°) are smaller than the AsAsSe angle (103°); the As—As bond is 0.05 Å longer than the sum of the arsenic covalent radii, the dihedral angle at the SeAsAsSe fragment being close to zero. The conformation of 135 is shown in Fig. 1.
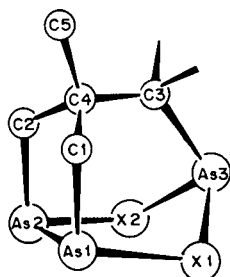
FIGURE 1. Conformation of $MeC(CH_2As)_3Se_2$ (135); X1, X2 = selenium atoms. Reproduced by permission of Verlag der Zeitschrift für Naturforschung from Reference 71

3. Selenocyclostibanes[74]

1,1,1-Tris(dichlorostibinomethyl)ethane reacts with NaSeH in THF to give the cage compounds **137** (60%) and **138** (20%).

$$\text{(115)}$$
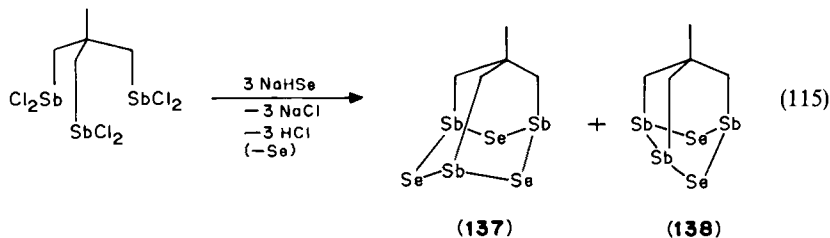
V. ORGANYL-SELENO- AND -TELLURO-PHOSPHONIUM IONS

A. Preparation of Selenophosphonium Ions

Alkoxyphosphonium ions are key intermediates in the course of the Arbuzov rearrangement. They can be stable when nucleophilic attack of the counter ion (generally leading to an alkyl halide and a P=O bond) is precluded by the use of bulky alkyl groups or/and by the use of non-nucleophilic anions. Thiophosphonium ions may react with nucleophiles not only at carbon (leading to a P=S bond) or at phosphorus (leading to substitution reactions at P), but also at the sulphur atom, leading to reduction to give the phosphane; this type of reaction can be used for the synthesis of certain chiral phosphanes[75]. Organylseleno- and organyltelluro-phosphonium salts are even more susceptible to nucleophilic attack at Se or Te, but at present very little is known about their chemistry. Three basic routes lead to organylselenophosphonium ions: (1) *P* alkylation of a selenophosphane; (2) *Se* alkylation of a selenophosphorane (phosphane selenide); (3) heteroatom (e.g. *O*) alkylation of an organylseleno-phosphinate, -phosphonate or -phosphate (se Section VI).

$$R_2{}^1PSeR^2 + R^3X \longrightarrow (R_2{}^1R^3PSeR^2)^+X^-$$

$$R_3{}^1P = Se + R^2X \longrightarrow (R_3{}^1PSeR^2)^+X^-$$
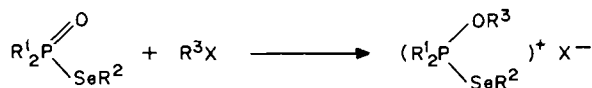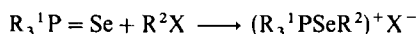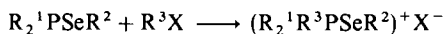
Little is known about the alkylation of selenophosphanes (route 1); alkylation of selenophosphoranes (which are generally more easily accessible than selenophosphanes) is the favourite method of preparation in all published studies dealing with selenophosphonium ions (route 2). A complete series of methoxy-, methylthio- and methylseleno-phosphonium ions have been prepared and studied with the aid of NMR and IR spectroscopy by Schmidpeter and Brecht[76].

Only the trimethoxy(methylseleno)phosphonium ion was too labile to be studied by NMR (instantaneous decomposition of $(MeO)_3P=Se$ and formation of the rearranged product $(MeO)_2(MeSe)P=O$ occurred). The alkylation of aminophosphaneselenides proceeds even with methyl iodide[77].

$$R^1R_2{}^2P{=}Se + Me_3O^+\,SbCl_6{}^- \xrightarrow{\ -Me_2O\ } R^1R_2{}^2PSeMe^+\,SbCl_6{}^- \qquad (115)$$

$$[or\ (MeO)_2SO_2/HSbCl_6]$$
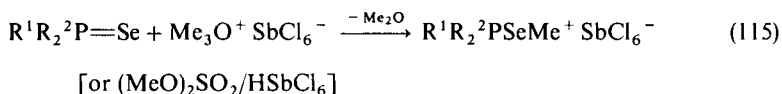
(139) $R^1 = R^2 = Ph$
(140) $R^1 = Ph, R^2 = OMe$
(141) $R^1 = OMe, R^2 = Ph$
(142) $R^1 = NMe_2, R^2 = Ph$
(143) $R^1 = Ph, R^2 = NMe_2$
(144) $R^1 = R^2 = NMe_2$
(145) $R^1 = R^2 = Bu$

$$R^1R_2{}^2P{=}Se + MeI \longrightarrow R^1R_2{}^2PSeMe^+I^- \qquad (116)$$
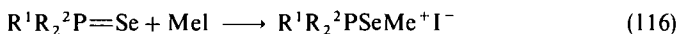
(144a) $R^1 = R^2 = NMe_2$
(146) $R^1 = R^2 = NEt_2$
(147) $R^1 = Et, R^2 = NMe_2$

Similarly, ethylation of triphenylphosphane selenide worked with triethyloxonium tetrafluoroborate, but with $(RO)_3P{=}Se$ loss of selenium or rearrangement to $(RO)_2(EtSe)P{=}O$ occurred[78].

$$Ph_3P{=}Se + (Et_3O)BF_4 \longrightarrow (Ph_3PSeEt)^+\,BF_4{}^- + Et_2O \qquad (117)$$
$$(148)$$
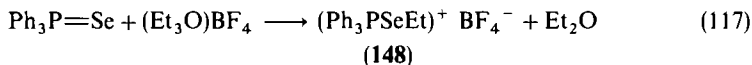
Methyl triflate is also a very efficient methylating agent for phosphane selenides or for the *O*-methylation of phosphinic acid *Se*-esters[79]. The methylselenium cation moiety can be transferred to more nucleophilic phosphanes (equation 118), or[80] removed with EtS^- or SH^- with retention of configuration at phosphorus[75], i.e. soft nucleophiles tend to attack selenophosphonium ions at the selenium atoms.

$$(Me_2N)_3P{\cdot}+ R^1R^2R^3P{*}SeMe^+CF_3SO_3{}^- \rightarrow R^1R^2R^3P{*} + (Me_2N)_3PSeMe^+CF_3SO_3{}^-$$
$$(149) \qquad\qquad (retention) \qquad (150)$$
$$(118)$$
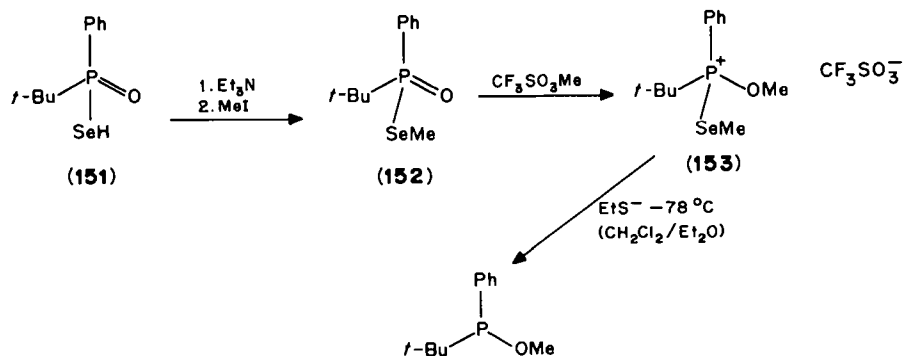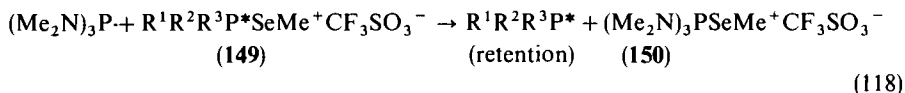
Arylselenenyl halides react with trivalent phosphorus compounds in redox reactions that might involve intermediate selenophosphonium ions[81].

$$Ph_3P + 2\,ArSeBr \longrightarrow ArSeSeAr + Ph_3PBr_2 \qquad (119)$$

$$(i\text{-PrO})_3P \ + \ 2 \, ArSeBr \ \longrightarrow \ ArSeSeAr \ + \ (i\text{-PrO})_2P{\overset{\displaystyle O}{\underset{Br}{<}}} \ + \ i\text{-PrBr}$$

$$Ar = 2,4\text{-}(NO_2)_2C_6H_3 \tag{120}$$
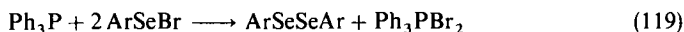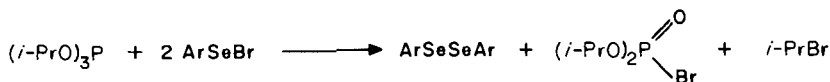
A kind of zwitterionic thio- and seleno-phosphonium aluminates are formed when thio-
of seleno-metaphosphates react with various aluminium compounds with organoalumin-
ation of a P=N bond. The four-membered heterocycles contain two-coordinated Se
bonded to four-coordinated P, but no Se—C bonds are present in the molecules[82].

$$R = alkyl, \ phenyl, \ Cl$$
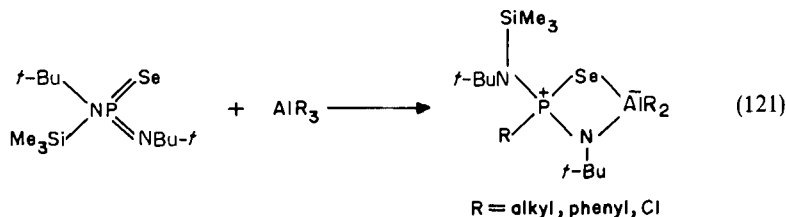
B. Preparation of Tellurophosphonium Ions

When triphenylphosphane reacted with 2-naphthyltellurenyl iodide (prepared *in situ*
from the ditelluride with iodine), a yellow intermediate was isolated, which might be an
aryltelluro(triphenyl)phosphonium iodide, but the structure of **154** is unknown[81].
Decomposition of the yellow adduct yielded dinaphthyl ditelluride and hydrolysis of the
P-containing product (probably Ph_3PI_2) gave triphenylphosphane oxide[81].

$$2\text{-NaphTeI} + Ph_3P \rightarrow (1{:}1 \text{ adduct}) \xrightarrow{\text{H}_2\text{O}} 2\text{-NaphTeTeNaph-2} + Ph_3P{=}O \tag{122}$$

$$(\mathbf{154})$$
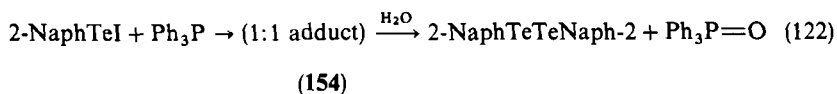
The first well characterized alkyl tellurophosphonium ions were prepared by Kuhn and
Schumann[83] by addition of methyl iodide to a series of tellurophosphoranes (phosphane
tellurides). The methyltellurophosphonium salts precipitate instantaneously from benzene
solution.

$$R_3P{=}Te + MeI \longrightarrow R_3PTeMe^+ \, I^- \tag{123}$$

$$(\mathbf{155}) \ R = Me$$
$$(\mathbf{156}) \ R = i\text{-Pr}$$
$$(\mathbf{157}) \ R = Bu$$
$$(\mathbf{158}) \ R = t\text{-Bu}$$
$$(\mathbf{159}) \ R = NMe_2$$
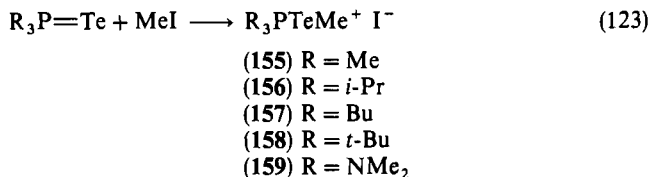
Compounds **156–159** are moderately soluble in nitromethane, allowing ^{31}P NMR
spectra to be run, but within 1 h in solution about 50% of the tellurophosphonium salts
decompose[83]. The reaction of dialkyl(*p*-tolyltelluro)phosphanes **25** and **26** with methyl
iodide proceeds with P-methylation, and ^{31}P NMR spectra provide evidence for the
formation of aryltellurophosphonium iodides, but subsequently nucleophilic attack at the
P—Te bond leads to redox reactions and a part of the tolyltelluro groups is lost as *p*-
tolylditelluride[84].
Cleavage of tellurophosphonium ions with nucleophiles leads preferentially to attack at
Te, i.e. they react like phosphane-stabilized tellurenyl cations. With methyllithium,

$$R_2PTeTol\text{-}p + MeI \longrightarrow \left[R_2P \begin{array}{c} {}^{Me} \\ \diagdown \\ TeTol\text{-}p \end{array} \right]^+ I^- + p\text{-}TolTeTeTol\text{-}p + R_2PMe_2^+ I^- + R_2PI$$

$$\textbf{(160)} \ R = i\text{-}Pr$$
$$\textbf{(161)} \ R = t\text{-}Bu \tag{124}$$
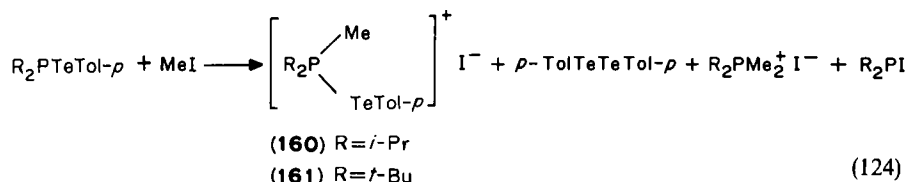
dimethyl telluride is formed from methyltellurophosphonium iodide with reduction leading back to the tertiary phosphanes[83]. Methylation of tellurotri-*tert*-butylphosphorane occurs even when it is coordinated as a ligand with the pentacarbonyltungsten acceptor, but complex **163** is *not* formed from **158** and $(CO)_5W$–THF[85].

$$(CO)_5W\text{--}\ddot{\underset{\displaystyle ..}{Te}} \diagdown_{P(Bu\text{-}t)_3} + MeI \longrightarrow \left[(CO)_5W\text{--}\ddot{Te} \diagup^{Me} \diagdown_{P(Bu\text{-}t)_3} \right]^+ I^- \tag{125}$$

$$\textbf{(162)} \hspace{6cm} \textbf{(163)}$$
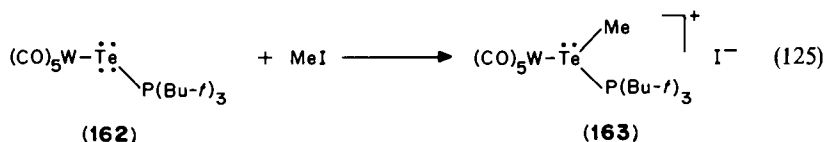
Protonation of seleno- or telluro-phosphoranes with strong acids leads to species of the type R_3PEH^+ ($E = Se, Te$), which have been the topic of NMR spectroscopic studies (see Section IX), but none of these cations has been isolated in the pure state[78]. Similarly, complexes such as **162**, which may be regarded as zwitterions containing a chalcogeno-phosphonium centre, are not included in this section.

VI. ORGANYL-SELENO- AND -TELLURO-PHOSPHINATES, -PHOSPHONATES AND -PHOSPHATES

Numerous organoselenium derivatives of pentavalent phosphorus have been described, but very few corresponding tellurium compounds are known. Organo-selenium and -tellurium derivatives of pentavalent arsenic, antimony and bismuth are in general very rare.

A. Organylseleno Derivatives of Pentavalent Phosphorus

1. Selenophosphinic acid Se-organyl esters, $R_2'P(\!=\!E)SeR^2$ ($E = O, S, Se$)

The attempted synthesis of diphenyl(phenylseleno)phosphane (**3**) with work-up in the presence of air led to diphenylselenophosphinic acid *Se*-phenyl ester (**4**); **4** is also obtained when tetraphenyldiphosphane dioxide reacts with phenylselenenyl bromide or when diphenylphosphinic chloride reacts with phenylselenomagnesium bromide[11]. Compound **4** is stable in water and the colourless compound melts at 78–80 °C.

$$\underset{Ph_2P\!-\!PPh_2}{\overset{O\ O}{\overset{\|\ \|}{}}} + PhSeBr \xrightarrow{-Ph_2P(=O)Br} Ph_2P \overset{\diagup\!\!O}{\underset{\diagdown\!\!SePh}{}} \tag{126}$$

$$\textbf{(4)}$$

$$Ph_2P \overset{\diagup\!\!O}{\underset{\diagdown\!\!Cl}{}} + PhSeMgBr \xrightarrow{-'MgBrCl'} \textbf{4} \tag{127}$$
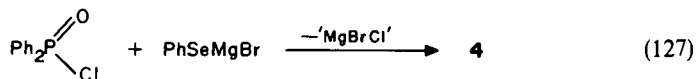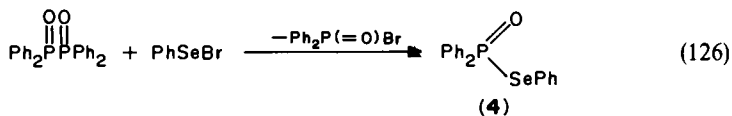
Seleno(thio)- and diseleno-phosphinic acid derivatives have been prepared by Kuchen and Knop[86].

$$Et_2PCl \xrightarrow{\text{Se}} Et_2P(=Se)Cl \xrightarrow[-NaCl, \\ -H_2Se]{2\ NaHSe} Et_2P\!\!\begin{array}{c}\nearrow Se \\ \diagdown Se\end{array}^{-} \quad Na^+ \qquad (128)$$

$$(164)$$

$$164\ +\ RBr \longrightarrow Et_2P\!\!\begin{array}{c}\nearrow Se \\ \diagdown SeR\end{array} \ +\ NaBr \qquad (129)$$

$$(165)R=Et$$
$$(166)R=Pr$$

$$Et_2P\!\!\begin{array}{c}\nearrow S \\ \diagdown Se\end{array}^{-} \ Na^+\ +\ EtBr \longrightarrow Et_2P\!\!\begin{array}{c}\nearrow S \\ \diagdown SeEt\end{array} \ +\ NaBr \qquad (130)$$

$$(167) \hspace{7cm} (168)$$
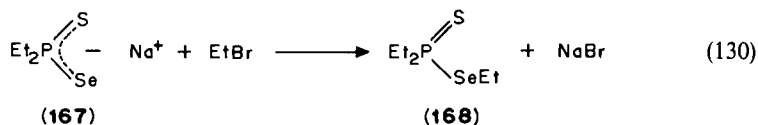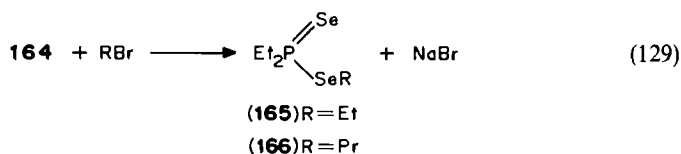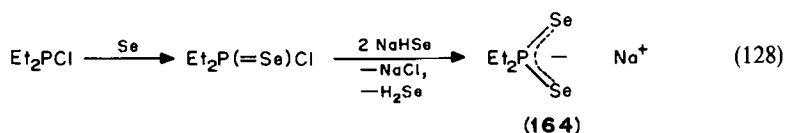
Compounds **165, 166** and **168** are colourless liquids that can be distilled under reduced pressure. *Se*-alkylation of **167** is preferred to *S*-alkylation; bromination of diethylseleno-thiophosphinic acid *Se*-ethyl ester (**168**) leads to diethylthiophosphinic bromide by P—Se bond cleavage[86]. *Se*-alkylation is preferred to *O*-alkylation when *tert*-butyl(phenyl)selenophosphinic acid (**151**) reacts with methyl iodide[75,87] (see Section V.A).
Selenophosphinic acid *O*-alkyl esters give the rearranged *Se*-esters by a thermal reaction[88]; the *Se*-esters are also formed in the course of transesterification reactions from P=Se bonded compounds with alkyl bromides (see also Section V)[89].

$$R^1_2P\!\!\begin{array}{c}\nearrow Se \\ \diagdown OCH_2CH=CHR^2\end{array} \xrightarrow{100\ °C} R^1_2P\!\!\begin{array}{c}\nearrow SeCH_2CH=CHR^2 \\ \diagdown O\end{array} \qquad (131)$$

$$(169) \hspace{5cm} (170)$$
$$R^1=Et$$
$$R^2=Me$$
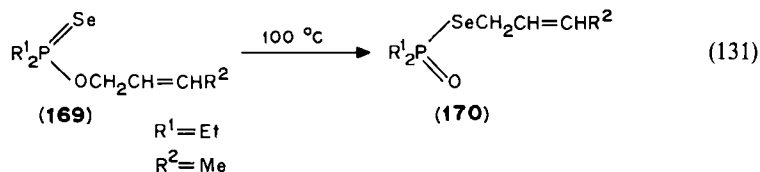
A decision between *Se*- and *O*-ester structures is easily made by ^{31}PNMR[88,89].

$$Et_2P\!\!\begin{array}{c}\nearrow Se \\ \diagdown OMe\end{array} \ +\ BuBr \longrightarrow Et_2P\!\!\begin{array}{c}\nearrow SeBu \\ \diagdown O\end{array} \ +\ MeBr \qquad (132)$$

$$(171) \hspace{5cm} (172)$$
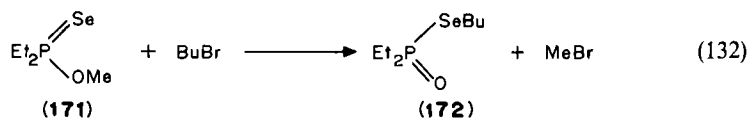
2. Selenophosphonic acid Se-esters, $R^1P(=E)$ (XR^2) (SeR^3)

Ethyl(seleno)phosphonic acid *O*-ethyl ester reacts with octyl iodide with *Se*-alkylation[90] (equation 133). The selenophosphonate **175** reacts with 2-diethylaminoethyl chloride with *Se*-alkylation to give highly toxic **176**[91], and ethyl(seleno)phosphonic acid *O,O*-diethyl ester (**177**) reacts with butyl bromide to the rearranged product **178**[89].

$$
\underset{\substack{\text{Se}\\ \|\\ \text{Et}\overset{|}{\underset{|}{\text{P}}}\text{OH}\\ \text{OEt}\\ (\textbf{173})}}{}
\quad\xrightarrow[\substack{\text{—H}_2\text{NEt}_2\text{I}}]{\substack{\text{1.HNEt}_2\\ \text{2.C}_8\text{H}_{17}\text{I,}}}\quad
\underset{\substack{\text{O}\\ \|\\ \text{Et}\overset{|}{\underset{|}{\text{P}}}\text{SeC}_8\text{H}_{17}\\ \text{OEt}\\ (\textbf{174})}}{}
\qquad (133)
$$

$$
\underset{\substack{\text{Se}\\ \|\\ \text{Et}\overset{|}{\underset{|}{\text{P}}}\text{O}^-\;\text{Na}^+\\ \text{OEt}\\ (\textbf{175})}}{}
\quad\xrightarrow[\substack{\text{—NaCl}}]{\substack{\text{ClCH}_2\text{CH}_2\text{NEt}_2}}\quad
\underset{\substack{\text{O}\\ \|\\ \text{Et}\overset{|}{\underset{|}{\text{P}}}\text{SeCH}_2\text{CH}_2\text{NEt}_2\\ \text{OEt}\\ (\textbf{176})}}{}
\qquad 134)
$$

$$
\underset{\substack{\text{Se}\\ \|\\ \text{Et}\overset{|}{\underset{|}{\text{P}}}\text{OEt}\\ \text{OEt}\\ (\textbf{177})}}{}
\quad\xrightarrow[\substack{\text{—EtBr}}]{\substack{\text{BuBr}}}\quad
\underset{\substack{\text{O}\\ \|\\ \text{Et}\overset{|}{\underset{|}{\text{P}}}\text{SeBu}\\ \text{OEt}\\ (\textbf{178})}}{}
\qquad (135)
$$
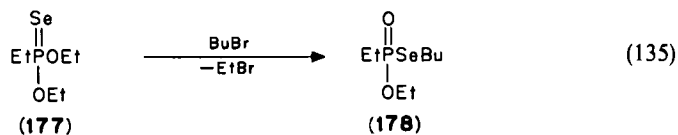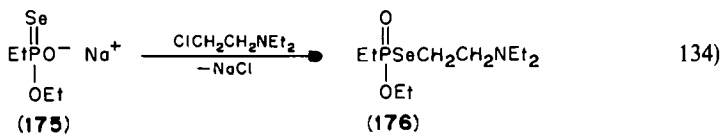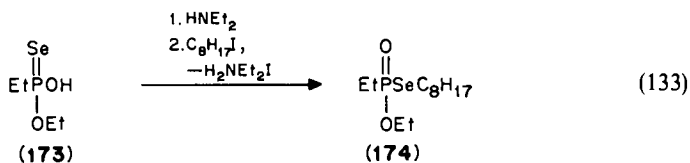
Ethylphosphonous acid ethyl ester reacts with dialkyl diselenides to give the seleno-phosphonic acid *Se*-esters **179** and **180** in high yield. Other preparations of selenophosphonic acid *O, Se*-diesters are the chloroselenation of alkenes with EtP(=O)(OEt)SeCl[92] or the reaction of ethyldi(ethoxy)phosphane with phenylselenenyl chloride or bromide[93].

$$
\underset{\substack{\text{O}\\ \|\\ \text{Et}\overset{|}{\underset{|}{\text{P}}}\text{H}\\ \text{OEt}}}{}
\quad\xrightarrow[\substack{\text{—RSeH}}]{\substack{\text{RSeSeR}}}\quad
\underset{\substack{\text{O}\\ \|\\ \text{Et}\overset{|}{\underset{|}{\text{P}}}\text{SeR}\\ \text{OEt}}}{}
\qquad (136)
$$

(**179**) R = Me   (Ref. 94)

(**180**) R = Et   (Ref. 94)

$$
\underset{\substack{\text{O}\\ \|\\ \text{Et}\overset{|}{\underset{|}{\text{P}}}\text{SeCl}\\ \text{OEt}\\ (\textbf{181})}}{}
\;+\;
\quad\longrightarrow\quad
\underset{(\textbf{182})}{}
\qquad (137)
$$

$$
\textbf{181}\quad\xrightarrow{}\quad
\underset{\substack{\text{O}\\ \|\\ \text{Et}\overset{|}{\underset{|}{\text{P}}}\text{SeCH}_2\text{CH(Cl)OEt}\\ \text{OEt}\\ (\textbf{183})}}{}
\qquad (138)
$$

$$
\text{EtP(OEt)}_2\quad\xrightarrow[\substack{\text{—EtX}}]{\substack{\text{PhSeX}}}\quad
\underset{\substack{\text{O}\\ \|\\ \text{Et}\overset{|}{\underset{|}{\text{P}}}\text{SePh}\\ \text{OEt}\\ (\textbf{184})}}{}
\qquad (139)
$$

X = Cl or Br
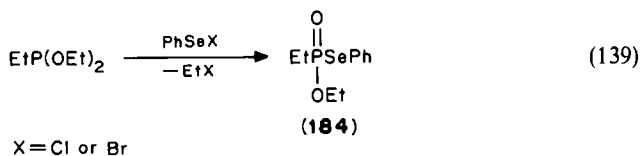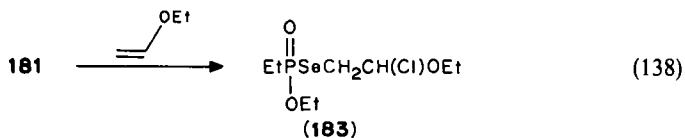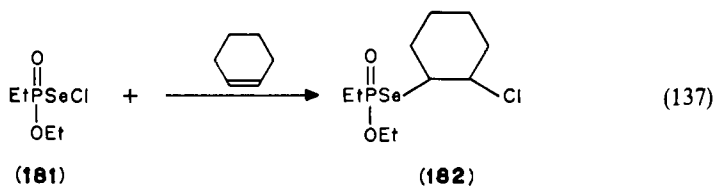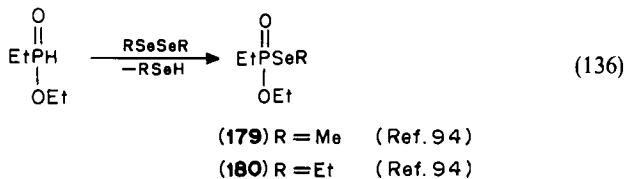
Selenophosphonic acid O,Se-diesters in most cases are thermally stable colourless liquids that can be distilled *in vacuo*. UV spectra of these compounds show a bathochromic shift and a significant decrease in the extinctions of λ_{max} compared with the isomeric O,O-diesters containing P=Se chromophores[95].

3. Selenophosphoric acid Se-esters

An excellent review covering (also) selenophosphoric acid Se-esters up to 1980 appeared in Houben-Weyl[2]. Here only basic types of the formation of P—Se bonds leading to this class of compounds will be considered.

a. Oxidation of phosphites with arylselenenyl halides or with diselenides[96]. See Table 4.

TABLE 4. Oxidation of phosphorous acid derivatives with arylselenenyl halides or with organic diselenides[2]. In most cases R^1 is Me or Et and R^2 is aryl or CF_3

$$(R^1O)_3P + R^2SeX \longrightarrow (R^1O)_2P(=O)SeR^2 + R^1X$$

$$R^1 = Me, Et, Pr, i\text{-}Pr, Bu$$
$$R^2 = Ph, 2\text{-}O_2NC_6H_4, 4\text{-}O_2NC_6H_4$$

$$(R^1O)_2P(=X)H + R^2SeX \longrightarrow (R^1O)_2P(=X)SeR^2 + HX$$

$$(R^1O)_2PCl + R^2SeX \xrightarrow{-R^1X} (R^1O)P(=O)(Cl)SeR^2 \xrightarrow[-HCl]{BuSH} R^1OP(=O)(SBu)SeR$$

$$R^1OPCl_2 + CF_3SeCl \xrightarrow[\text{or } BCl_3]{(SbCl_5)} Cl_2P(=O)SeCF_3 + R^1Cl \quad \text{(ref. 97)}$$

$$(R^1O)_3P + R^2SeSeR^2 \longrightarrow (R^1O)_2P(=O)SeR^2 + R^1SeR^2 \quad \text{(ref. 98)}$$

$$(R^1O)_2P(=S)H + R^2SeSeR^2 \longrightarrow (R^1O)_2P(=S)SeR^2 + R^2SeH$$
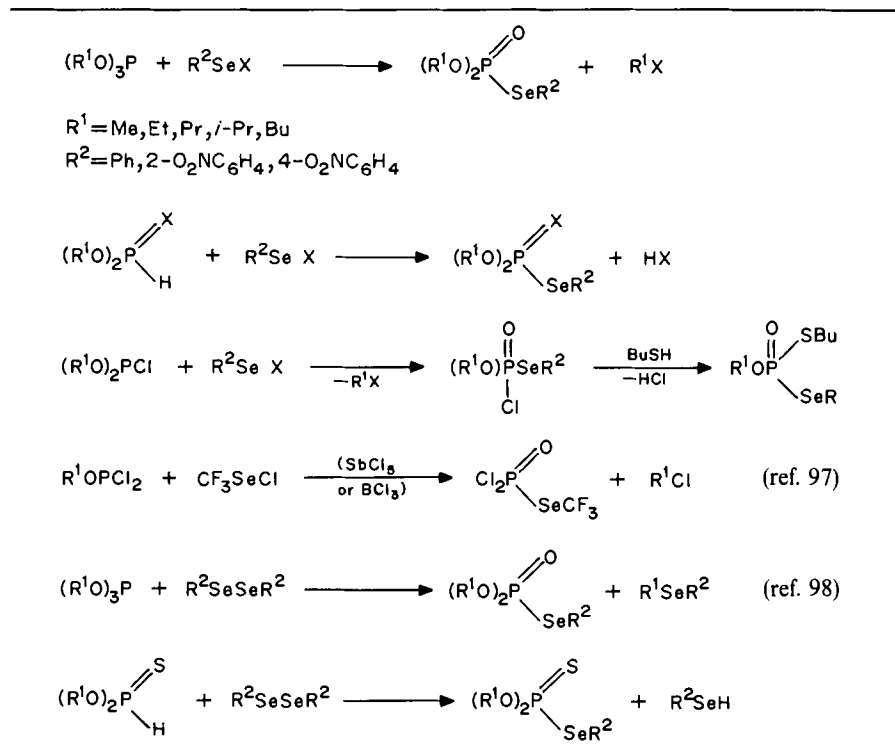
b. Oxidation of selenophosphites with oxygen or sulphur[11,48]

$$(SePh)_3P + Y \longrightarrow (PhSe)_3P=Y \qquad (140)$$
$$Y = 1/2\ O_2,\ 1/8\ S_8$$
$$\textbf{(77)}\ Y = O$$
$$\textbf{(185)}\ Y = S$$

$$ROP(SeBu)_2 + Y \longrightarrow RO(BuSe)_2P{=}Y \quad \text{(ref. 50)} \tag{141}$$

(86–88)

$$Y = 1/2\ O_2,\ 1/8\ S_8$$

(186) R = Et, Y = O
(187) R = Et, Y = S
(188) R = Pr, Y = O
(189) R = Pr, Y = S
(190) R = Bu, Y = O
(191) R = Bu, Y = S
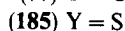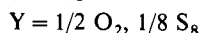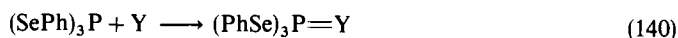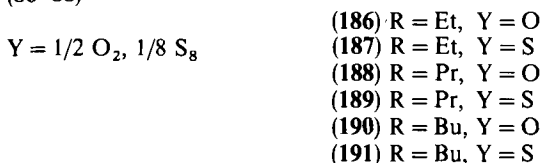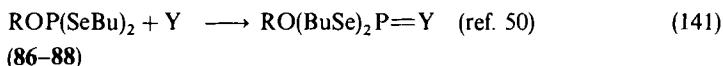
For comparison, the ethoxy derivatives **186** and **187** were also prepared from EtOP $({=}Y)Cl_2$ $(Y = O, S)$ with butylselenol in the presence or triethylamine[50] (see Section VI.A.3.e).

  c. Rearrangement of selenophosphoric acid O-esters containing at least one n-alkyl or 2-alkenyl group R^2[2,3]. These rearrangements are catalysed by Lewis acids such as BF_3 and many other metal or metalloid halides, but there are cases known where Lewis acids are unnecessary for the 1,3-alkyl shift (R^2 = allyl[88]). For instance, oxidation of the diazaphosphole **192** with elemental selenium in the presence of methanol gave the selenide **193**, which rearranged thermally to give the *Se*-methyl ester **194**[99].

$$\tag{142}$$

(192)   (193)   (194)

R = Me

$$\tag{143}$$
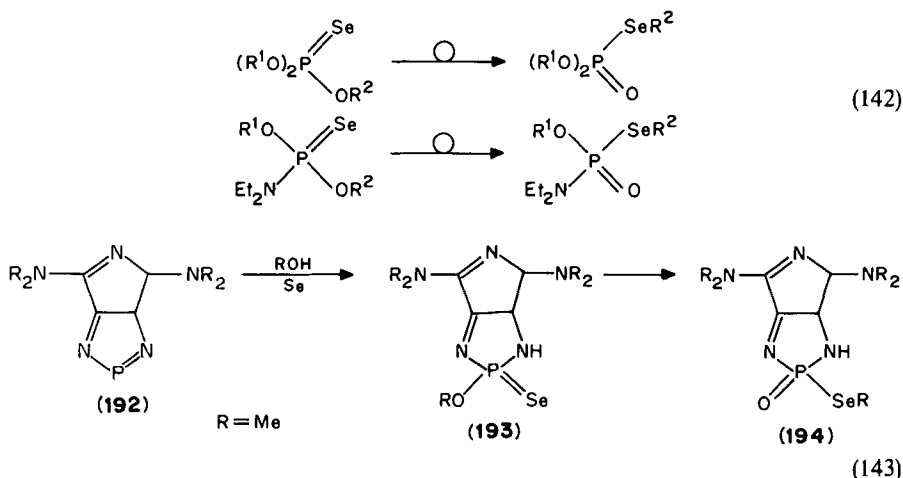
  d. Alkylation and acylation of anionic selenophosphates. This type of reaction leads mainly to *Se*-alkylation; with acyl halides, *Se*-acylation is in competition with *O*-acylation.
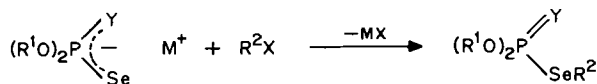
R^1 is Et, *i*-Pr or Ph in most cases, Y may be O, S or Se and various alkyl and 2-alkenyl halides were found to give this reaction. In a similar manner, aziridine is cleaved to give the highly toxic ester **196**[91].

$$\tag{144}$$

(195)   (196)
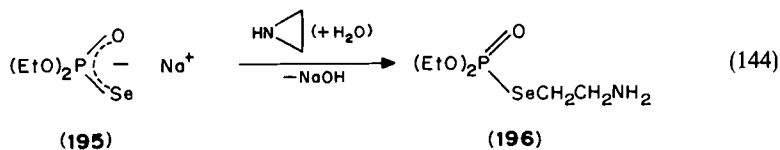
The anionic selenophosphates may be prepared *in situ*[100]. Acylation of seleno(thio)phosphoric acid *O,O*-diethyl and -diphenyl esters led to a series of 'mixed anhydrides'[101].

$$(R^1O)_2P \overset{S}{\underset{Se}{<}} \;\; K^+ \; + \; R^2C \overset{O}{\underset{Br}{<}} \;\; \xrightarrow{-KBr} \;\; (R^1O)_2P \overset{S}{\underset{SeC}{<}} \overset{O}{\underset{R^2}{<}} \qquad (145)$$

(197) R^1=Et, R^2= Me

(198) R^1=Et, R^2= Et

(199) R^1=Et, R^2= Pr

(200) R^1=Et, R^2= Ph

(201) R^1=Et, R^2= *i*-Pr

(202) R^1=Et, R^2= OEt

(203) R^1=Ph, R^2= Me

(204) R^1=Ph, R^2= Et

(205) R^1=Ph, R^2= Ph

(206) R^1=Ph, R^2= OEt
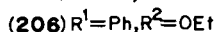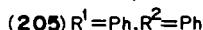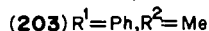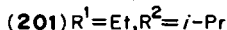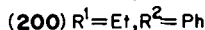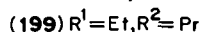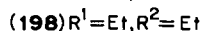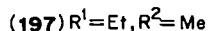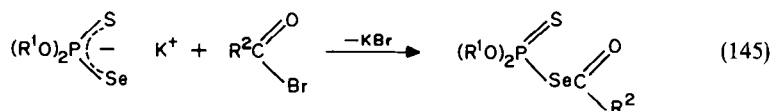
Se-acylation was predominant, but some *S*-acylation also occurred, as shown by thin-layer chromatography[101]. The reaction of Na[SeOP(OPr-*i*)$_2$] with various main group halides was followed by NMR and IR spectroscopy. *Se*-alkylation and *O*-acylation occurred[78], with organotin halides both types of reactions were observed (see equation 146).

$$(i\text{-PrO})_2P \overset{Se}{\underset{O}{<}} \;\; Na^+ \; + \; RX \;\; \xrightarrow{-NaX} \;\; (i\text{-PrO})_2P \overset{Se}{\underset{OR}{<}} \;\; or \;\; (i\text{-PrO})_2P \overset{O}{\underset{SeR}{<}}$$

(207)   A   B

(208) R = COPh   (213) R = Et

(209) R = SnMe$_3$ (214) R = SiMe$_3$

(210) R = 1/2 SnPh$_2$ (215) R = GePh$_3$

(211) R = 1/3 SnPh   (216) R = SO$_2$Ph

(212) R = 1/3 P   (217) R = 1/3 As
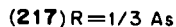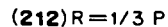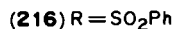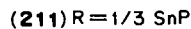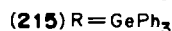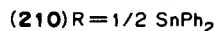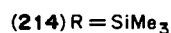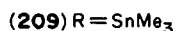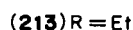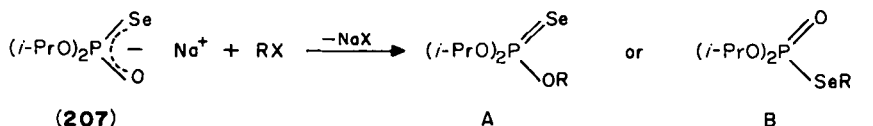
(146)

e. Hydrogen chloride elimination from phosphoric acid chlorides with phenyl- or butyl-selenols in the presence of triethylamine[2,50].

$$\underset{Cl}{\overset{O}{\underset{|}{EtOPCl}}} \;\; \xrightarrow[-2\,HNEt_3Cl]{2\,BuSeH,\,2\,NEt_3} \;\; \underset{SeBu}{\overset{X}{\underset{|}{EtOPSeBu}}} \qquad (147)$$

(218) X = O

(219) X = Se

$$P(=X)Cl_3 \xrightarrow[\substack{-3\ HNEt_3Cl}]{\substack{3\ PhSeH,\\3\ NEt_3}} (PhSe)_3 P=X \qquad (148)$$

$$(77)\ X = O$$
$$(185)\ X = S$$
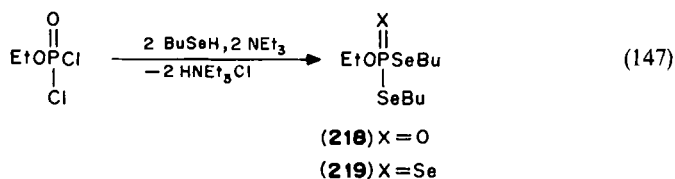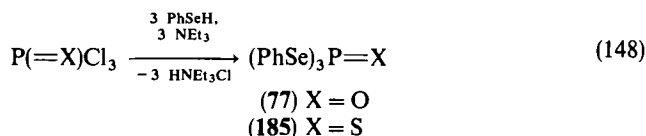
f. Chloroselenation reactions. Se-chloroselenophosphoric acid O, O-diethyl ester reacts with N, N-dialkylanilines by aromatic substitution to give the corresponding Se-aryl esters[102].

$$(EtO)_2P\underset{SeCl}{\overset{O}{\diagup}} + C_6H_5NR_2 \xrightarrow[-HCl]{toluene,\ -15\ °C} (EtO)_2P\underset{SeC_6H_4NR_2\text{-}p}{\overset{O}{\diagup}} \qquad (149)$$

(220)

(221) R = Me
(222) R = Et
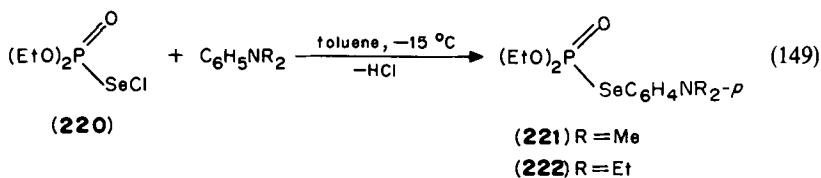
Compound **220** adds also to cyclohexane and to ethyl vinyl ether by chloroselenation [**220** is prepared *in situ* from $(EtO)_3P=Se$ with SO_2Cl_2 [92,93,102]].

$$\textbf{220} \longrightarrow (EtO)_2P\underset{Se}{\overset{O}{\diagup}}\cdots Cl \qquad (150)$$

(223)

$$\textbf{220} \xrightarrow{\overset{OEt}{\diagup\diagdown}} (EtO)_2P\underset{SeCH_2CH(Cl)OEt}{\overset{O}{\diagup}} \longrightarrow (EtO)_2P\underset{SeCH_2CH(OEt)_2}{\overset{O}{\diagup}}$$

(224)   **(225)**

$$(151)$$
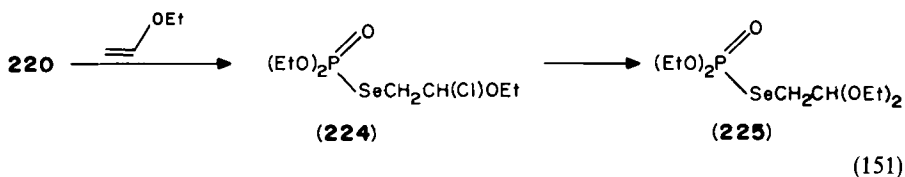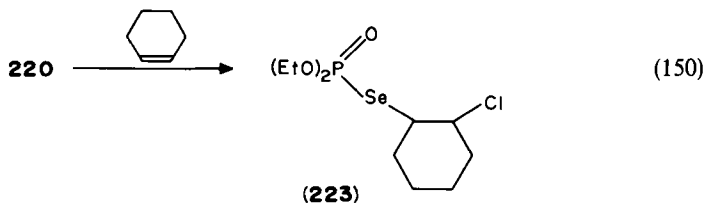
B. Organyltelluro Derivatives of Pentavalent Phosphorus

Sodium or potassium diethyl phosphite react with elemental tellurium in ethanol to give colourless crystalline tellurophosphates which are sensitive to air and moisture[103] (corresponding selenophosphates were formed in a similar manner[104]). With methyl iodide, methylation occurs at tellurium[105] (equation 152). Tellurophosphoric acid O, O-diethyl-*Te*-methyl ester **227** has been characterized in solution by ^{1}H and ^{31}P NMR. *Te*-alkylation has been proposed as the key step of the oxirane deoxygenation with **226** (equation 153).

$$(EtO)_2P\underset{Te}{\overset{O}{\diagup}}^{-}\ Na^+ \xrightarrow[-NaI]{MeI} (EtO)_2P\underset{TeMe}{\overset{O}{\diagup}} \qquad (152)$$

(226)   **(227)**

$$(153)$$
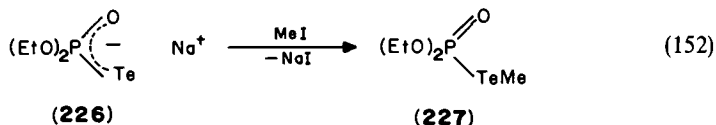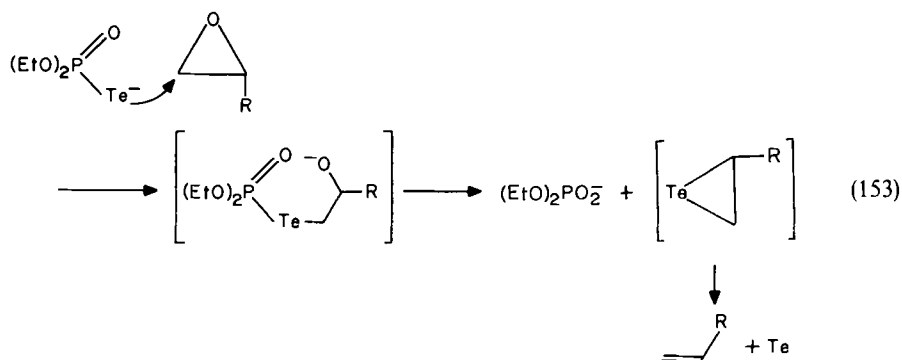
The first tellurocarbohydrates were prepared by *Te*-alkylation of a tellurophosphoric acid O,O-diester anion with $2,3,4,6$-tetra-O-acetyl-α-D-glucopyranosyl bromide[106]. The reaction proceeds with inversion at the anomeric carbon atom. Spectroscopic evidence for *Te*-alkylation comes from the magnitude of the NMR coupling constant, $^1J(^{125}Te^{31}P) = 1245\,Hz$[106]. Oxidation of β-D-glucosyl tellurophosphate (**229**) led to novel di(β-D-glucosyl) ditelluride.

$$(154)$$
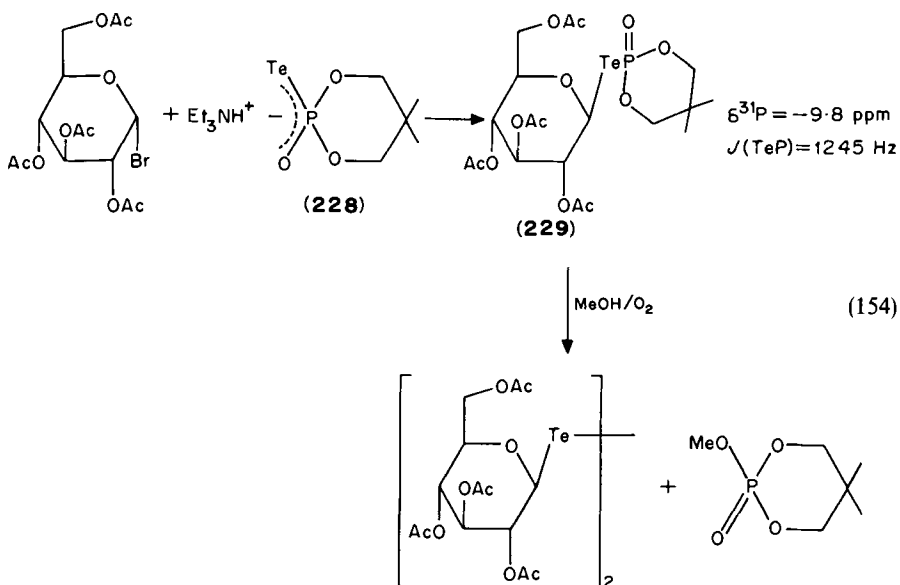
VII. PENTAVALENT THREE-COORDINATE PHOSPHORUS COMPOUNDS WITH P=Se DOUBLE BONDS

A. Methylene(selenoxo)phosphoranes, R¹P(=R²) (=Se)

$2,4,6$-Tri-*tert*-butylphenyl[bis(trimethylsilyl)methylene]phosphanes reacts with ozone $(-78\,^\circ C)$, sulphur[107] or selenium to give the alkylidene(oxo, thioxo or

selenoxo)phosphoranes **230–232**, which were obtained in pure state by crystallization from acetonitrile–toluene[108]. Compounds **230–232** are stable to air; with tris(dimethylamino)phosphane, **231** and **232** can be desulphurated and deselenated, respectively[108]. ^{31}P NMR spectra show typically a large coupling constant, $^1J(^{77}Se^{31}P)$ ($\pm$ 846 Hz for **232**), and downfield shifts in the range + 160 to + 205 ppm[108]. The related phosphaalkene $RC\equiv CP=CR_2$ (R = SiMe$_3$) adds sulphur or selenium to form the thio- and seleno-phosphiranes **19** and **20**[25] (see Section II.A.1.a).

(155)
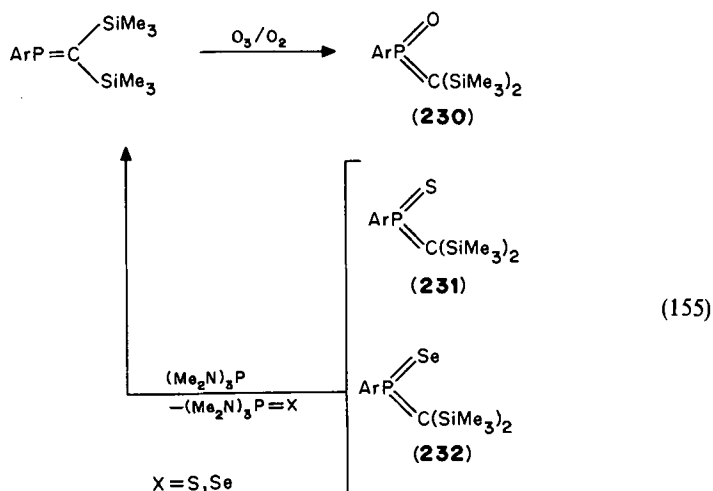
Ar = 2,4,6-tri-*tert*-butylphenyl

2,4,6-Trimethylphenyl(diphenylmethylene)phosphane reacts with oxygen, sulphur and selenium to give the alkylidene (oxo, thioxo or selenoxo)phosphoranes **233–235**. These compounds are unstable: **233** was never isolated, **234** could be observed spectroscopically and the selenium compound **235** was isolable but decomposed with reversal of its formation reaction. Tellurium did not react at all with the phosphaalkene. Compounds **233—235** could be intercepted by the addition of ethanol to furnish **236–238**[109].

(156)

(**233**) E = O   (**236**) E = O
(**234**) E = S   (**237**) E = S
(**235**) E = Se   (**238**) E = Se
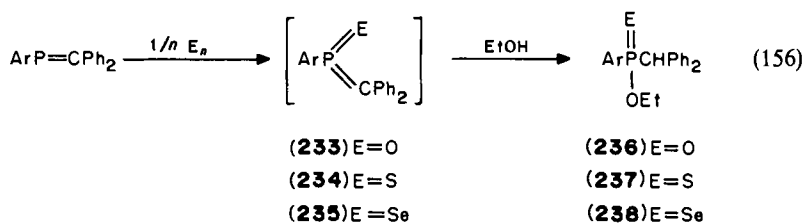
Ar = 2,4,6-trimethylphenyl

Bis(trimethylsilyl)amino(trimethylsilylmethylene)phosphane reacts with sulphur or selenium to give the corresponding thioxo- and selenoxo-phosphoranes **239** and **240**. The latter was not isolated in the pure state, but NMR data [δ(P) = 172.4 ppm, $J(^{77}Se^{31}P)$ 882.5 Hz] confirm that the alternative selenaphosphirane structure can be ruled out[110].

$$(Me_3Si)_2NP=CHSiMe_3 + 1/n\ E_n \longrightarrow (Me_3Si)_2NP\overset{E}{\underset{CHSiMe_3}{\lesseqgtr}} \tag{157}$$

$$(239)\ E = S$$
$$(240)\ E = Se$$
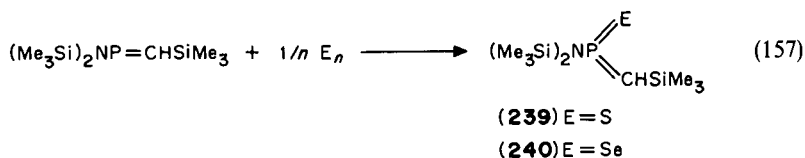
B. Metaselenophosphonates, R'P(=E) (=Se)

Yoshifuji showed that bis(2, 4, 6-tri-*tert*-butylphenyl)diphosphene gives various types of oxidation products with sulphur and selenium[67,68]. With sulphur, isomers **127** and **128** have been characterized; with selenium, a thermal reaction in the presence of triethylamine afforded the selenadiphosphirane (**125**) and a true metadiselenophosphonate (**126**). The metaselenophosphonate structure was confirmed by NMR data.

$$ArP=PAr \xrightarrow{Se,\ NEt_3 \atop 70\ °C} ArP\overset{Se}{\triangle}PAr + ArP\overset{Se}{\underset{Se}{\lesseqgtr}} \tag{158}$$

$$17\% \qquad 4\%$$
$$(125) \qquad (126)$$
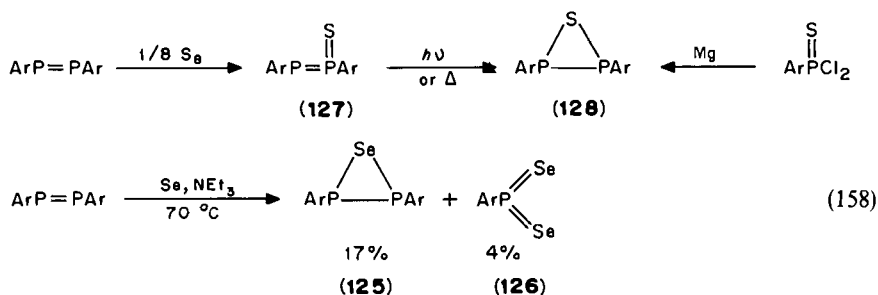
Ar = 2,4,6-tri-*tert*-butylphenyl

C. Metaselenophosphates, R'R²NP(=NR') (=Se)

Monomeric amino(imino)phosphanes ['phospha(III)azenes'] with bulky substituents are oxidized by selenium to metaselenophosphoric acid derivatives[111,112].

$$R^1R^2NP= NBu-t + Se \longrightarrow R^1R^2NP\overset{Se}{\underset{NBu-t}{\lesseqgtr}} \tag{159}$$

$$(243)\ R^1 = t\text{-Bu},\ R^2 = Me_3Si\ [111]$$
$$(244)\ R^1 = R^2 = Me_3Si\ [112]$$
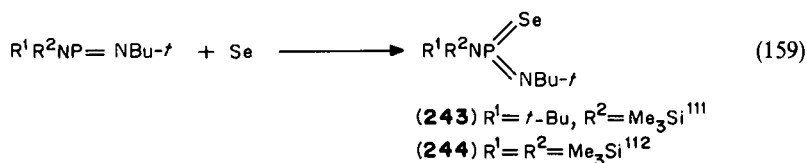
Compounds **243** and **244** are thermally stable; they are soluble in inert solvents, but sensitive to protic and oxidizing agents (as are the corresponding metathiophosphates); **243** is an orange and **244** a greenish yellow liquid. With ethylenebis-(triphenylphosphane)platinum(0), the metaselenophosphate **243** reacts with η_2-coordination of the P=Se bond with the bis(triphenylphosphane)platinum acceptor moiety[113].

$$(245) \tag{160}$$
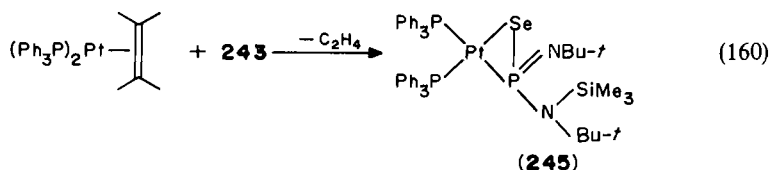
The coordinated phosphorus atom of the metaselenophosphate ligand is a centre of chirality, but rapid scrambling of the trimethylsilyl groups between both nitrogen atoms occurs at room temperature leading to a single ^{1}H NMR signal for both *tert*-butyl groups bonded to nitrogen. There is no 1,3-silyl scrambling in non-coordinate **243** under comparable conditions. With aluminium triorganyls and trichloride and related Lewis acids, 1,2-addition at the P—N bond of **243** takes place and four membered heterocycles such as **246** and **247** are formed. The corresponding metathiophosphate behaves similarly[82].

$$\text{(161)}$$

(**246**) R=Me

(**247**) R=Ph
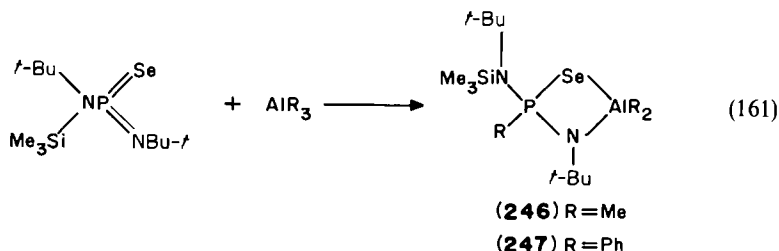
VIII. FOUR-COORDINATE P^V, As^V AND Sb^V COMPOUNDS WITH DOUBLE BONDS TO SELENIUM OR TELLURIUM

Most tertiary phosphanes, phosphinites, phosphonites and phosphites react with sulphur or selenium (or sulphur or selenium sources), as do tertiary arsanes and stibanes. Only strongly basic P^{III} compounds add tellurium to form P=Te bonds; compounds with As=Te or Sb=Te and any compounds with Bi=X (X = S, Se, Te) bonds are unknown.

A. Four-coordinate Phosphorus Compounds with P=Se or P=Te Bonds

1. Chalcogenophosphoranes, $R^1P_2{}^2P$=E (E = Se, Te; R^1, R^2 = alkyl, aryl or H) (Phosphane chalcogenides)

a. Phosphane selenides. Trialkyl- and triaryl-phosphanes react with selenium or selenium sources in a similar manner to their reactions with sulphur. Electron-donating substituents at phosphorus favour oxidation, sulphuration and selenation reactions; di- and tri-arylphosphanes need more severe conditions to react with selenium; the selenocyanate ion may be used as a source of selenium[1-3,5].

Secondary phosphanes react with selenium to give secondary phosphane selenides (selenophosphinous acids), R_2P(=Se)H; primary PhPH$_2$ gave evolution of H$_2$Se and a cyclic oligomer of (PhPSe) was formed (Section IV). Bis(diphenylphosphino)methane gives a mono- and a di-selenide[114]. Mixing the 'diselenide' **248** with the diphosphane leads to immediate selenium transfer to give the 'monoselenide' **249**.

$$\text{(162)}$$

$$\text{(163)}$$
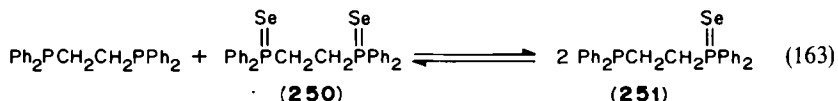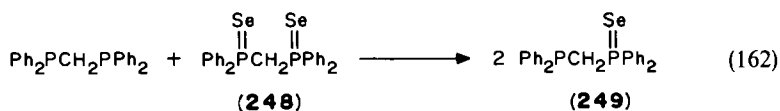
With 1,2-bisdiphenylphosphinoethane a statistical distribution of selenium take place (equation 163) and pure 'monoselenide' **251** is not obtained[114]. Compound **248** is less favoured in the equilibrium because the electron-deficient P^V atom deactivates the close P^{III} atom in the molecule, so that monoselenide **249** is formed according to equation 162. Temperature-dependent NMR spectra have shown that coalescence temperatures for the above and various related systems are in the range 90–160°C in most cases; their concentration dependence indicates that even with chelating phosphanes, selenium transfer is at least partly intermolecular.

b. Phosphane tellurides. Early work by Zingaro and coworkers showed that trialkylphosphanes tend to react incompletely with elemental tellurium. Pure phosphane tellurides could be obtained by crystallization of the compounds from mother liquors that contained an excess of unreacted phosphane[60,115]. Aryl substituents at phosphorus lead to unfavourable equilibria and triphenylphosphane does not react with elemental tellurium. Telluration of triphenylphosphane was achieved with tetraphenylarsonium tellurocyanate in the presence of lithium perchlorate. Under these conditions, a remarkable compound of composition $(Ph_3P)_2Te$ separated as yellow crystals from acetone solution that contained a large excess of triphenylphosphane. X-ray diffraction analysis of a disordered crystal led to the conclusion that a linear $P=Te...P$ arrangement with very different $P—Te$ bond distances is present in the crystal $(P=Te\ 2.27–2.42\ \text{Å};\ P...Te\ 3.37–3.95\ \text{Å})^{116}$.

$$R_3P + 1/x\ Te_x \rightleftharpoons R_3P = Te \tag{164}$$

$$2\ Ph_3P\ +\ Ph_4As^+\ TeCN^-\ \xrightarrow[\text{acetone}]{\text{(LiClO}_4)}\ Ph_3PTe\cdots PPh_3\ +\ Ph_4As^+\ CN^- \tag{165}$$
$$\textbf{(252)}$$
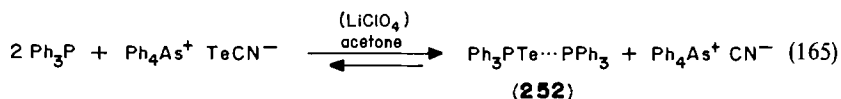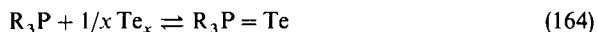
^1H, ^{31}P and ^{125}Te NMR spectra of phosphane telluride–phosphane mixtures revealed that rapid transfer of tellurium atoms occurs at room temperature in solutions in all known cases[117–121]. Transition states related to **252** have been proposed, i.e. nucleophilic attack of phosphane at coordinated tellurium leads to the tellurium transfer reaction (S_N-type of associative reaction).

$$R_3P\ —\ \ddot{T}e\ :PR_3$$
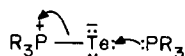
The course of the reaction of a trialkylphosphane with tellurium is sensitive to branching at the α-C atom. With tributylphosphane, 1:1 mixtures of phosphane and phosphane telluride are formed in toluene solution, but with tri-*tert*-butylphosphane telluration proceeds quantitatively. Tributylphosphane telluride (**253**) suffers from decomposition by loss of tellurium, but tri-*tert*-butylphosphane telluride (**254**) is remarkably thermally stable in the pure state and in inert solvents[117].

$$Bu_3P + Te \rightleftharpoons Bu_3P = Te \tag{166}$$
$$\textbf{(253)}$$

$$t\text{-}Bu_3P + Te \rightarrow t\text{-}Bu_3P = Te \tag{167}$$
$$\textbf{(254)}$$
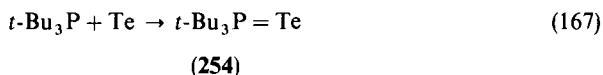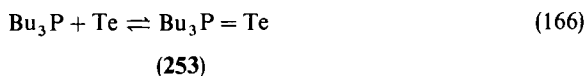
2. *Chalcogenophosphinic esters and amides,* $R_2{}^1(R_n{}^2X)P{=}E$ $(E = Se,\ Te)$

a. *Phosphinic acid derivatives with P=Se bonds.* Oxidation of secondary phosphane selenides (selenophosphinous acids) in the presence of triethylamine leads to the corresponding selenophosphinic acid, e.g. equation 168[87].

$$\text{(168)}$$
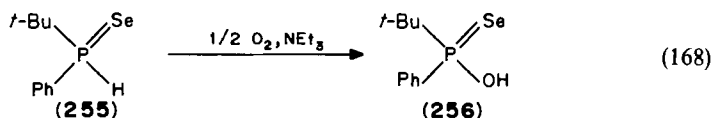
Dialkyl(chloro)phosphanes are easily selenated[1,2]. Selenation in the presence of alcohols and triethylamine leads to selenophosphinic acid *O*-esters (equation 169) (For reactions leading to the corresponding *Se*-esters, see Section VI).

$$R^1{}_2PCl\ +\ Se\ +\ NEt_3\ +\ R^2OH\ \longrightarrow\ R^1{}_2P{\overset{Se}{\underset{OR^2}{\big\langle}}}\ +\ HNEt_3Cl\qquad\text{(169)}$$

Selenophosphinic acid amides are generally obtained by selenation of the parent aminophosphanes. Seleno(thio)phosphinic acid *S*-esters are correspondingly prepared by selenation of organylthiophosphanes or from $R_2P({=}Se)Cl$ with a thiol in the presence of triethylamine. Diselenophosphinates and corresponding esters were prepared according to equations 128, 129 and 169)[86].

$$\text{(257)}\qquad\xrightarrow[\substack{-NaCl,\\-H_2Se}]{2\ NaHSe}\qquad\text{(164)}\ Na^+\qquad\xrightarrow[-NaBr]{RBr}\qquad\text{(165) R = Et}$$
$$\text{(166) R = Pr}$$
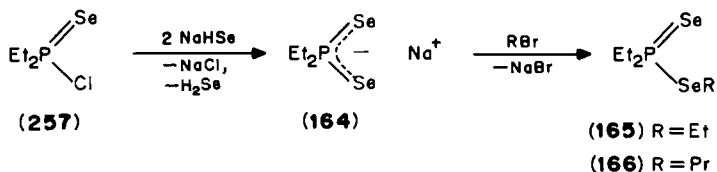
Dithio-, seleno(thio)- and diseleno-phosphinates are soft ligands that can act as bidentate chelating or bridging ligands with many metal acceptors. Protonation of **164** leads to bis(selenophosphinyl)-selenide, -diselenide and -triselenide[86].

$$\textbf{164}\ \xrightarrow[\text{dioxane}]{HCl}\ (Et_2\overset{Se}{\overset{\|}{P}})_2Se_n$$
$$\text{(258)}\ n = 1$$
$$\text{(259)}\ n = 2\ \text{(unstable)}\qquad\qquad\text{(170)}$$
$$\text{(260)}\ n = 3$$

$$\textbf{164}\ \xrightarrow[H_2O]{KI_3}\ \textbf{258}\ +\ \textbf{260}\ +\ \text{other products}\qquad\text{(171)}$$
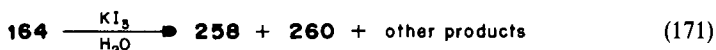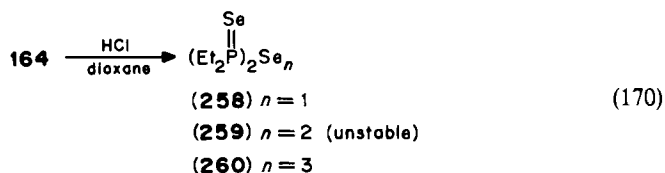
Oxidation or protonation of sodium diethylseleno(thio)phosphinate leads to Se—Se bond formation as in **259–261**; the P=S bonds remain in terminal positions [X-ray crystallographic evidence on $Et_2P({=}S)SeSeP({=}S)Et_2$[122]].

$$\textbf{164 + 257}\ \longrightarrow\ Et_2\overset{Se}{\overset{\|}{P}}SePEt_2\ +\ NaCl\qquad\text{(172)}$$
$$\text{(258)}$$

$$\text{2 Ph}_2\text{PSiMe}_3 \;+\; \text{4 Se} \quad\longrightarrow\quad \overset{\text{Se}}{\overset{\|}{\text{Ph}_2\text{P}}}\overset{\text{Se}}{\overset{\|}{\text{SePPh}_2}} \;+\; (\text{Me}_3\text{Si})_2\text{Se} \qquad (173)$$

$$(\mathbf{261})$$
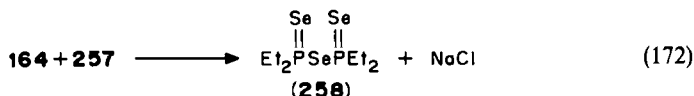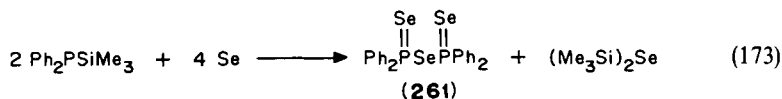
Bis(selenophosphinyl) selenide (**258**) was formed according to equation 170 or 172. A bis(selenophosphinyl)selenide (**261**) related to **258** was formed when diphenyl(trimethylsilyl)phosphane reacted with elemental selenium[123].

With sulphur, the silylphosphane gave diphenyldithiophosphinic acid trimethylsilyl ester (**262**)[123]. In contrast, di-*tert*-butyl(trimethylsilyl)phosphane reacts with excess of sulphur or selenium to give di-*tert*-butyldichalcogenophosphinic acid silyl esters in both cases[29].

$$\text{R}_2\text{PSiMe}_3 \;+\; \text{2 E} \quad\longrightarrow\quad \text{R}_2\text{P}\overset{\diagup\!\!E}{\underset{\diagdown\!\!\text{E SiMe}_3}{}} \qquad (174)$$

(**262**) R = Ph, E = S

(**263**) R = *t*-Bu, E = S

(**264**) R = *t*-Bu, E = Se
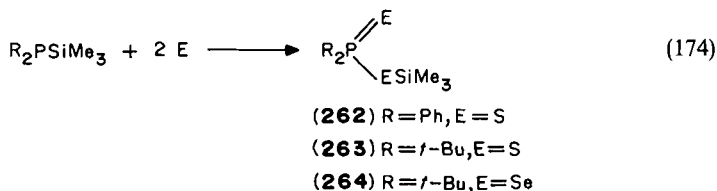
b. Tellurophosphinic acid esters. A compound of this type was prepared by telluration of the corresponding phosphinous acid ester with elemental tellurium[124].

3. Chalcogenophosphonic esters and amides $R^1(R_n{}^2X)_2P{=}E$ (E = Se, Te)

a. Selenophosphonic acid derivatives with P=Se bonds. These compounds are generally prepared by methods related to those described for selenophosphinic halides, esters and amides[1-3,5].

$$\text{RP}\overset{\diagup\!\!X^1}{\underset{\diagdown\!\!X^2}{}} \;+\; \text{Se} \quad\longrightarrow\quad \overset{\text{Se}}{\overset{\|}{\text{RPX}}}\underset{\|}{\underset{X}{}}$$

$$\overset{\text{Se}}{\overset{\|}{\text{RPCl}_2}} \quad\xrightarrow[-2\,\text{Cl}^-]{2\,\text{X}^-}\quad \overset{\text{Se}}{\overset{\|}{\text{RPX}_2}}$$

$$X = F^-, EtO^-, R^2CO_2^-, R^2S^-, R_2^2N^-$$
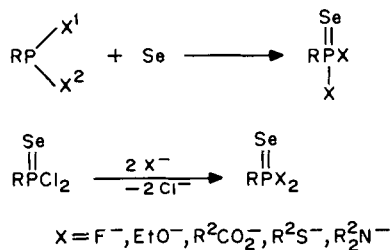
Alkylphosphonous dihalides do not react very straightforwardly with elemental selenium; red selenium and catalytic amounts of aluminium trichloride enhance the selenation. Electron-donating substituents such as dialkylamino groups favour the tendency of phosphonites to react with selenium (as with other oxidizing agents). Cl/F exchange occurs with SbF_3 and catalytic amounts of $SbCl_5$[125]; monofluoridation [to give $RP(=Se)$ (Cl)F] has also been achieved. Selenophosphonic acid O-monoesters, $R^1P(Se)$ $(OR^2)OH$, may be split into their optical antipodes with help from chiral bases[126]. For O-ester to Se-ester rearrangements of selenophosphonates, see Section VI.A.2.

Selenophosphonates are also formed when amino(imino)phosphanes (**243**) react with triorganylaluminium compounds with organoalumination of the P=N double bond (leading, finally, to **246** and **247**)[82].

Reaction of *tert*-butylbis(trimethylsilyl)phosphane with excess of selenium to give bis(trimethylsilyl)telluride and a high yield of dimeric diselenometaphosphonic anhydride $[t\text{-BuPSe}_2]_2$ containing a diselenadiphosphetane structure[57] (compare equation 106).

  b. Tellurophosphonic acid derivatives with P=Te bonds. Ethylphosphonous acid diethyl ester (ethyldiethoxyphosphane) was reported to react with elemental tellurium to give a red solution, but the tellurophosphonate (265) decomposed on attempted purification[126].

$$RP(OEt)_2 \ + \ Te \ \xrightarrow[\text{(NEt}_3)]{\text{C}_6\text{H}_6} \ \overset{\overset{\displaystyle Te}{\|}}{RP}(OEt)_2 \qquad (175)$$

$$(265)\ R = Et$$
$$(266)\ R = CH_2CH=CH_2$$
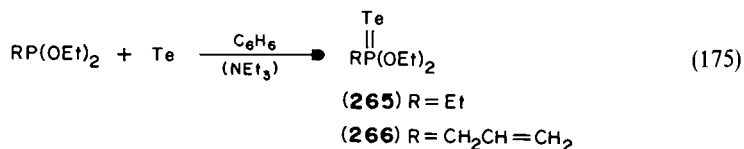
Measurement of density and refraction index confirmed that the reaction had occurred. Decomposition led to 'tellurium mirrors'[127]. The corresponding alkyl tellurophosphonate (266) was reported to be a distillable liquid[128]. Ethyl and phenyl tellurophosphonic diamides were similarly isolated as pure solids[129]. Tellurides of bidentate bis(diamino)phosphanes such as 270 are stable compounds[130].

$$R^1P(NR^2{}_2)_2 \ + \ Te \ \longrightarrow \ \overset{\overset{\displaystyle Te}{\|}}{R^1P}(NR^2{}_2)_2 \qquad (176)$$

$$(267)\ R^1 = Et, R^2 = Me \ (ref.129)$$
$$(268)\ R^1 = Ph, R^2 = Me \ (ref.129)$$
$$(269)\ R^1 = Me, R^2 = Et \ (ref.130)$$

$$(Et_2N)_2P(CH_2)_4P(NEt_2)_2 \ + \ 2\ Te \ \longrightarrow \ (Et_2N)_2P \overset{\diagup Te}{\underset{\diagdown CH_2CH_2CH_2CH_2}{}} \overset{Te\diagdown}{\underset{\diagup}{P}}(NEt_2)_2$$

$$(270)$$

$$(177)$$
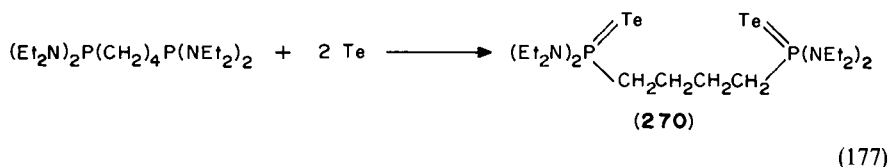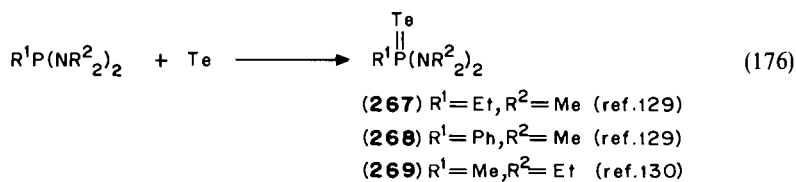
  N-, P-Alkyldiazadiphosphetidines react with sulphur, selenium and tellurium. The thermal stability of the oxidation products decreases with increasing atomic number of the chalcogen[131]. Compound 271 is mixture of *cis* and *trans* isomers; the Cl-substituted phosphorus atom is not tellurated. Compound 272 appears to be only one isomer.

$$(271) \qquad (178)$$

$$(272) \qquad (179)$$
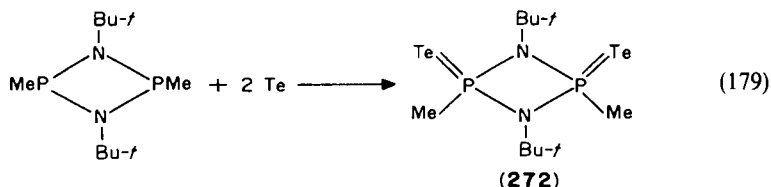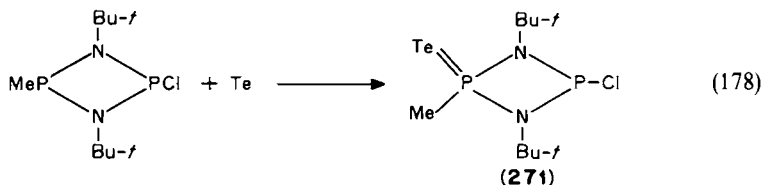
The yellow crystalline compounds are stable in the pure state, but **271** suffers from loss of tellurium in solution[131]. Reaction of a *cis*-1,3,2λ^3,4λ^3-diazadiphosphetidine (equation 180) with an approximately equimolar amount of tellurium leads to a monotelluride (**273**), which undergoes rapid tellurium transfer in solution[120].

(180)
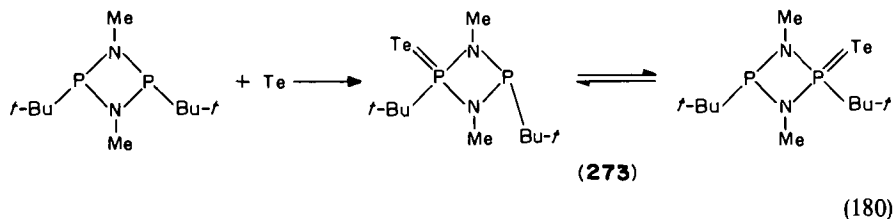
The concentration dependence of the temperature of coalescence indicates that tellurium transfer is not strictly intramolecular. At $-60\,^\circ$C, separate signals for λ^3-P [δ(P) $+200.4$ ppm] and λ^5-P [δ(P) $+119.5$ ppm] and also ^2J(PP) (18.0 Hz) are well resolved[120]. An X-ray crystal structure analysis confirmed that Te is tightly bonded to *one* P atom, and there is no indication of any type of secondary bonding between Te and λ^3-P. The deviation from planarity of the P_2N_2 ring of **273** is about 30% larger than that in the related ditelluride or disulphide[132,133]. Stronger folding of the P_2N_2 ring favours an intramolecular tellurium atom transfer. The *trans*-diazadiphosphetidine ditelluride contains a planar P_2N_2 core[133].

4. Phosphoric acid derivatives with P═Se or P═Te bonds

a. Selenophosphoric acid esters, amides and other derivatives. Synthetic aspects of this well studied class of compounds are covered up to 1980 in Houben-Weyl[2]. Selenophosphates with various substitution patterns are preparatively fairly readily available (see also Section VI.A.3.a). The main synthetic pathways are the direct selenation of P^{III} compounds or substitution reactions at P—Cl bonds, for instance with alcohols or thiols in the presence of triethylamine or with excess of a secondary amine. Diselenophosphates can be obtained from diphosphorus pentaselenide with various alcohols[2,3]. Transesterification reactions are also known. Oxidation of diselenophosphoric acid O,O-diesters leads to di(selenophosphoryl) selenides and diselenides[134,135].

(181)

(182)
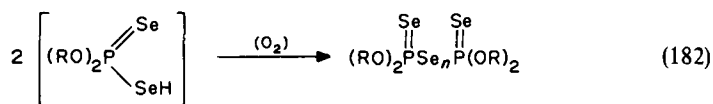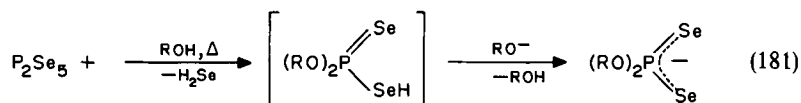
b. Tellurophosphoric acid amides and esters. The first tellurophosphoric acid triamides [tris(dialkylamino)phosphanetellurides] were prepared independently by two different groups[129,136]. The reaction of the aminophosphanes was reported to proceed 'with difficulty' compared with addition of sulphur or selenium to amides of trivalent phosphorus, but the reaction is much closer to being quantitative than the reaction of most

trialkylphosphanes with elemental tellurium[129] (Section VIII.A.1.b). A careful study of the 'tellurium basicity' of trivalent phosphorus species revealed an exceptional tellurophilicity of tri(pyrrolidino)phosphane, the only phosphane being superior to the cyanide ion (see Table 5)[137].

$$R_3{}^1P + TeCN^- \rightleftharpoons R_3{}^1P = Te + CN^- \qquad (183)$$
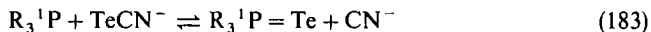
For phosphites, $P(OR)_3$ (R = alkyl), K was in the range 10^{-3}. The exceptional donor properties of tris(pyrrolidino)phosphane are presumably due to the fact that the nitrogen atoms are highly flexible and adapt easily to planar coordination geometry of the PNC_2 moiety[137]. Like other compounds with an (at least formal) P=Te double bond, tellurophosphoric acid amides behave like labile phosphane complexes and zerovalent tellurium; in the presence of non-coordinated p^{III} compounds, tellurium atom transfer takes place as a reaction that is fast on the ^1H or ^{31}P NMR time-scales[114,117-120,138,139].

$$(t\text{-Bu})_3PTe + (Me_2N)_3P \rightleftharpoons (t\text{-Bu})_3P + (Me_2N)_3PTe \qquad (184)$$
$$\quad\textbf{(254)} \qquad\qquad\qquad\qquad\qquad\qquad \textbf{(274)}$$

$$274 + (Me_3N)_3P^* \rightleftharpoons (Me_2N)_3P + (Me_2N)_3P^*Te \qquad (185)$$

$$(186)$$

(275)
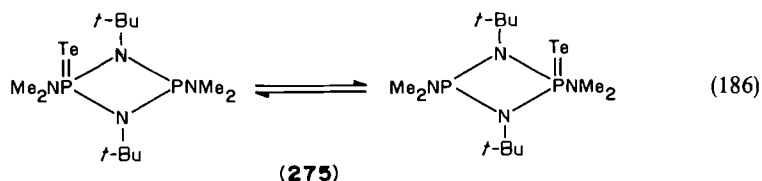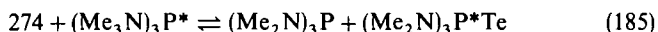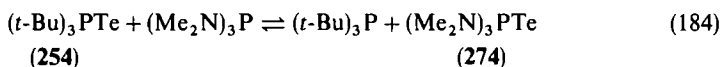
In 1950, Foss[103] showed that potassium diethylphosphite reacts with tellurium to give telluro-O,O-diethylphosphate **(226)** (Section VI.B) as colourless hygroscopic needles. Recently, this compound has been used for the deoxygenation of expoxides[105]. In contrast to tellurophosphoric acid O,O-diester anions, the neutral species (like tellurophosphoric acid trialkyl esters) appear to be unstable. Interestingly, tellurophosphorous acid bis(trimethylsilyl) ester, $(Me_3SiO)_2P(H)Te$ **(276)**, was reported to be a distillable liquid[140].

TABLE 5. Equilibrium constants for the reactions between some phosphanes and the tellurocyanate ion[137]

$R_3{}^1P^a$	K
$(Pyrr)_3P$	80
CN^-	1 (by definition)
$(Pip)_3P$	0.6
$(Me_2N)_3P$	0.54
$(Et_2N)_3P$	0.27
$(n\text{-Bu})_3P$	0.17
$(Mor)_3P$	0.09
$[(n\text{-Pr})_2N]_3P$	0.048
Ph_3P	0

*Pyrr = pyrrolidino; Pip = piperidino; Mor = morpholino.

B. Arsenic Compounds with As=Se or As=Te Double Bonds

1. Tertiary arsane selenides (selenoarsoranes)

Trialkylarsane selenides are easily prepared by heating tertiary arsanes with a solvent and powdered grey selenium[141]. Triphenylarsane selenide can be prepared from dichlorotriphenylarsorane with ammonium selenide[142]; the thermolabile compound decomposes readily with precipitation of selenium. Two infrared absorptions in the range 330–360 cm^{-1} were assigned to the As=Se stretching vibration[143]. Ditertiary arsanes give diselenides that are in equilibrium with the monoselenides and elemental selenium[144,145]. Formation of the monoselenide **277** is favoured in the methylenebis(dimethylarsane)/selenium system. The reason for this behaviour should be deactivation of As^{III} by a neighbouring electron-withdrawing selenoarsinyl group (as in the case of phosphane selenides **248** and **249**)[114]. Additionally, monoselenide **277** gives a low temperature of coalescence (60 °C) in ^{1}H NMR, which is due to rapid selenium transfer.

$$\text{Me}_2\text{As} \underset{\text{CH}_2}{\overset{\text{Se}}{\diagup}} \text{AsMe}_2 \quad \rightleftharpoons \quad \text{Me}_2\text{As} \underset{\text{CH}_2}{\overset{\text{Se}}{\diagdown}} \text{AsMe}_2 \qquad (187)$$

(277)
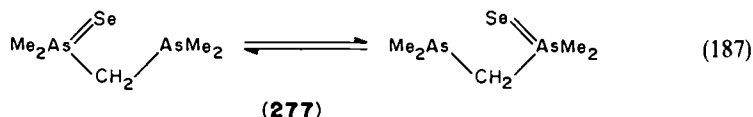
In contrast to ^{1}H NMR line broadening of the Me$_2$As proton resonances of **277** in solution, ditertiary arsane (mono)selenides, in which the As atoms were separated by three or four methylene groups, gave sharp separated signals for Me$_2$As and Me$_2$As (=Se) groups[145]. Line broadening due to selenium transfer was also observed in the ^{13}C NMR spectra of tri-*tert*-butylarsane selenide/tri-*tert*-butylarsane mixtures in inert solvents[117,118].

$$(t\text{-Bu})_3\text{As} = \text{Se} + (t\text{-Bu})_3\text{As}^* \rightleftharpoons (t\text{-Bu})_3\text{As} + (t\text{-Bu})_3\text{As}^* = \text{Se} \qquad (188)$$

(278)
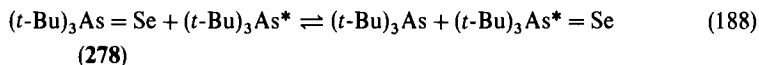
Tetra-tertiary diphenylarsinomethanes such as C(CH$_2$AsPh$_2$)$_4$ are reluctant to react with sulphur or selenium, but the dimethylarsinomethanes are easily oxidized to give selenides such as C[CH$_2$As(= Se)Me$_2$]$_4$[146]. A tertiary arsane telluride has not yet been isolated. Even tri-*tert*-butylarsane (first ionization potential only 7.8 eV[147]) is not able to coordinate significantly with tellurium. Spectroscopic evidence for $(t\text{-Bu})_3\text{As} \rightarrow \text{Te}$ coordination was recently provided by the NMR spectra of the (kinetically) labile tri-*tert*-butylphosphane telluride in presence of a three-fold excess of tri-*tert*-butylarsane.

$$(t\text{-Bu})_3\text{PTe} \quad + \quad (t\text{-Bu})_3\text{As} \quad \underset{}{\overset{(K \approx 10^{-3})}{\rightleftharpoons}} \quad (t\text{-Bu})_3\text{P} \quad + \quad (t\text{-Bu})_3\text{AsTe} \qquad (189)$$

(254)   **(279)**
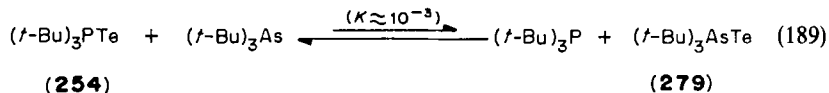
Tri-*tert*-butylphosphane telluride and (de-tellurated) tri-*tert*-butylphosphane give a single ^{1}H NMR doublet signal; the magnitude of the averaged $^3J(^{31}\text{P}^1\text{H})$ of the reaction mixture is smaller than that of pure **254**[117,118].

2. Selenoarsinic acid derivatives containing a terminal As—Se bond

The formation of sodium dimethyldiselenoarsinate (**281**) is very similar to that of the corresponding sulphur compound **280**[148].

Addition of water to an ethanolic solution of **280** or **281** leads to crystallization as colourless dihydrates [Me$_2$As(E)ENa.2H$_2$O]. Metal complexes based on **281** were much less stable than those with the dithioarsinate as anionic ligand[148].

$$Me_2As \overset{O}{\underset{O}{\diagdown}} - Na^+ \xrightarrow[-H_2O]{H_2E} Me_2As \overset{O}{\underset{E}{\diagdown}} - Na^+ \xrightarrow[-H_2O]{H_2E} Me_2As \overset{E}{\underset{E}{\diagdown}} - Na^+ \quad (190)$$

<div align="right">

(**280**) E = S

(**281**) E = Se

</div>
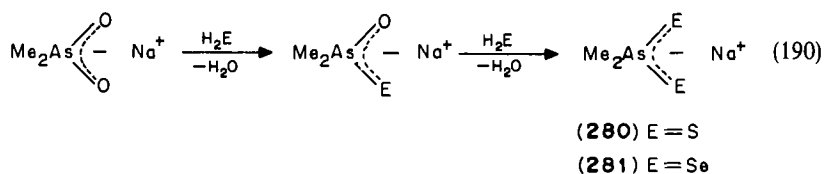
C. Stibane Selenides

Trialkylstibanes react with powdered selenium to yield stable trialkylstibane selenides[149]. Only with trimethylstibane is a labile compound of the composition Me_3SbSe_2 formed[150]. Acyclic dimer structure was proposed for this stibane diselenide; attempts to trap the compound by coordination with cyclopentadienyl(dicarbonyl)iron(I) as a two-electron acceptor led to loss of selenium and formation of the stibane selenide complex **284**[151]. Among all $Me_3M{=}E$ molecules (M = P, E = S, Se, Te, M = As, E = S, Se; M = Sb, E = S, Se), only $Me_3P{=}Te$ showed a larger donor/acceptor ratio than $Me_3Sb{=}Se$ (**283**) towards the iron(I) acceptor [v(CO) infrared and $\delta^{13}C({=}O)$ NMR evidence][151].

$$Me_3Sb + 2 Se \longrightarrow \tfrac{1}{2}(Me_3SbSe_2)_2 \qquad (191)$$
$$(\mathbf{282})$$

(192)
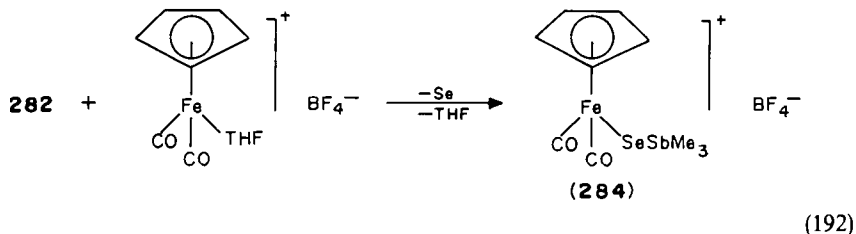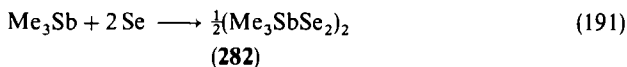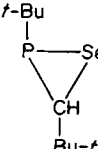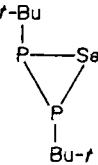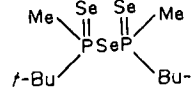
IX. STRUCTURE, BONDING AND REACTIONS OF ORGANIC SELENIUM AND TELLURIUM COMPOUNDS WITH BONDS BETWEEN Se OR Te AND P, As, Sb OR Bi

A. ^{31}P, ^{77}Se and ^{125}Te NMR Spectra

Owing to the occurrence of satellite spectra from $J(^{77}Se^{31}P)$ and $J(^{125}Te^{31}P)$, ^{31}P NMR is a very useful tool for the assignment of structures when P—Se or P—Te bonds are involved. $\delta(P)$ follows empirically known trends as far as typical substituent effects, steric crowding influence, small ring effects or coordination shifts are concerned. More specific information comes from one-bonded coupling constants $^1J(SeP)$ and $^1J(TeP)$. The magnitude of these coupling constants is large in all cases of terminal $P^{III}{=}Se$, $P^V{=}Se$ and $P^V{=}Te$ bonds. Electron-withdrawing substituents such as halogen atoms or CF_3 groups lead to increased $^1J(SeP)$, and $^1J(SeP)$ steric effects are also of some importance. The influence of conformational effects on $^1J(SeP)$ was demonstrated by the different P—Se couplings in the enantiomers of **285** (see Table 6). $J(TeP)$ generally follows the trends of $J(SeP)$, but its magnitude is larger in all comparable cases. An excellent review appeared a few years ago[152]; some typical data are compiled in Table 6.
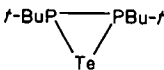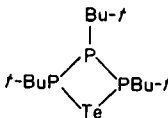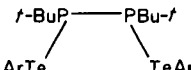
TABLE 6. NMR data for PSe compounds: ^{31}P and ^{77}Se NMR[a]

Compound	δ^{31}P (ppm)	$J(^{77}Se^{31}P)$ (Hz)	$\delta^{77}Se$(ppm)	Ref.
$(MeO)_3P = Se$	+ 77.5	− 963	− 396	153
$(Me_2N)_3P = Se$	+ 81.8	− 805	− 366	153
$Me_3P = Se$	+ 8	− 648	− 235	153
$(t\text{-}Bu)_3P = Se$	+ 92.5	± 711	− 428	85, 117, 118
$Ph_3P = Se$	+ 34	− 736	− 275	78, 154
$(p\text{-}Tol)_3P = Se$	+ 32	− 726		154
$(o\text{-}Tol)_3P = Se$	+ 26	− 708		154
Me_2PSeMe	+ 0.8	− 218	+ 58	15, 155, 156
$Me_2P(= S)SeMe$		− 341	+ 196	156
$Me_2(MeSe)PW(CO)_5$	− 16.4	± 309		155
$(CF_3)_2PSeMe^2$	+ 27.9	± 294		15, 155
$(CF_3)_2(MeSe)PW(CO)_5$	+ 45.1	± 432		155
$(CF_3)_2PSeP(CF_3)_2$	+ 246.9		+ 700.8	14

(structure)	− 62	± 53.7		23
$ArP(Se) = C(SiMe_3)_2$	+ 195.2	± 846		108
(structure)	− 76.9	± 135.2		66
(285)	+ 79.7	− 346.2, − 760.4		157
	+ 78.0	− 390.6, − 751.1		

[a]^{31}P shifts to low field from 85% H_3PO_4; ^{77}Se shifts to low field from Me_2Se.[152]

Coordination of seleno- or telluro-phosphanes leads in most cases (non-chelating P ligands) to an increase in ^1J(SeP) or ^1J(TeP). Coordination of phosphane selenides or phosphane tellurides leads to decreased (in some cases fairly constant)[158,85] Se–P or Te–P coupling constants[78]. Three-membered heterocycles containing phosphorus and selenium or tellurium give very small magnitudes of J(SeP) or J(TeP) and upfield ^{31}P shifts. However, the isomeric selenoxophosphoranes containing P^V with coordination number three have deshielded ^{31}P nuclei that couple strongly with ^{77}Se. Several early papers on the preparation of phosphane tellurides reported that the compounds were so unstable in solution that ^{31}P NMR spectroscopic data could not be collected. In fact, difficulties arise from rapid tellurium transfer reactions, especially in the presence of larger amounts of P^{III} compounds (when the reaction with elemental tellurium was not complete). Concentration-dependent line broadening up to complete coalescence occurs in many cases at temperatures close to 25 °C. To resolve ^{125}Te satellites, samples have to be very pure and/or cooling to temperatures below 0 °C is helpful. Similarly, ^{125}Te NMR signals of phosphane tellurides appear as singlets due to tellurium transfer when a non-coordinated phosphane is present in solution. ^{77}Se and ^{125}Te shifts of phosphane selenides

TABLE 7. Hetero-NMR data for tellurophosphanes

Structures:

(130): t-BuP——PBu-t with Te bridging below (telluradiphosphirane)

(131): Bu-t at top on P, t-BuP / PBu-t with Te bridging

(73): t-BuP——PBu-t with ArTe and TeAr

	(130)	(131)	(73)
$\delta^{31}P$ (ppm)	− 70.9^a	−4.1–60.5 (J = ± 172.6 Hz)	+ 29 (88%) + 39 (12%)
$\delta^{125}Te$ (ppm)^b	− 1123.7^b (t)	− 789.2 (d,t)	− 23 (X-part of ABX) (main isomer)
J(TeP) (Hz)	± 226.4^c	± 84 (^2J) ± 10.7 (^1J,^3J)	^1J = − 519.9 ^2J = − 22.5

^{a}At − 30 °C.
^{b}δ relative to di-p-tolyl ditelluride[152].
^{c}at − 30 °C J − 235.4 Hz.

and tellurides are at the upfield edge of ^{77}Se or ^{125}Te shift scales, which would be consistent with a predominance of an ylidic type of bonding (described by the phosphoniochalcogenate structure $R_3\overset{+}{P}$—$\overset{-}{E}$ (E = Se, Te), but apparently certain seleno- or telluro-phosphanes $R_2^1PER^2$ are in a similar ^{77}Se and ^{125}Te shift range (Table 7). The ^{125}Te shifts of the first tellurostibanes are upfield from comparable tellurophosphanes, and the ^{125}Te NMR signal of tellurobismuthane (64)[46] appears even further upfield. Telluradiphosphirane (130) appears in ^{125}Te NMR far upfield of larger Te—P heterocycles and from acyclic tellurodiphosphanes such as 73 (Table 7)[30,31,54].

B. Vibrational, UV–Visible and He(I)–PE Spectra

Normal coordinate analyses have been carried out on basic molecules with P–Se and P=Se (and related main Group 5/main Group 6) (group 15/group 16) subunits. In the case of trimethylphosphane chalcogenides, P=E stretching force constants were determined to decrease in the following order (all values $\times 10^2$N/m)[159,160]:

Ref.	Me$_3$PO	Me$_3$PS	Me$_3$PSe	Me$_3$PTe
159	7.04	3.73	2.84	2.20
160	8.03	3.37	2.35	

The assignment of strong infrared absorptions (and corresponding Raman emissions) in the region of 500 cm^{-1} to the P=Te stretching vibration led to the calculation of force constants that were significantly larger than f(P=S)[136]. This would suggest unusually strong P=Te bonds, but crystallographic bond length determinations do not support this idea. Possibly, strong coupling of v(P=E) with symmetric stretching modes (like vs (PC$_3$) in tri-$tert$-butylphosphane chalcogenides)[117] leads to sets of IR and Raman bands that cannot be unequivocally assigned to v(P = Se), v(P = Te) or v(PC$_3$) vibrations. Similarly, intensity criteria were not sufficient for the assignment of P—Se and As—Se stretching vibrations in methylthio- and methylseleno-bis(trifluoromethyl)-phosphanes and -arsanes (10, 49 and related sulphur compounds)[161]. Owing to the mass of the CF$_3$ groups, v_s(PC$_2$)

is close to ν(PSe), and coupling of the vibrational modes leads to difficulties in determining precise force constants in these cases. Nevertheless, ν(PSe) may be used empirically for the determination of the abundance of conformational isomers[162] or for the decision between P($=$Se)OR and P($=$O)SeR type structural isomers and related problems.

In UV–visible spectroscopy, differences in the absorption between P$=$Se- and P—Se-bonded isomers can also be used for the prediction of structures. As in the case of compounds with P$=$S bonds, substituents lead to bathochromic shifts of λ_{max} of the P$=$Se chromophore in the order OEt $<$ NEt$_2$ $<$ Et $<$ Cl $\approx$ SEt (210–260 nm)[95]. Most phosphane tellurides are yellow owing to an absorption in the region of 280 cm^{-1} that stretches into the visible region.

The dipolar character of P$=$X bonds increases in the order P$=$S $<$ P$=$Se $<$ P$=$Te; arsane chalcogenides are more polar than the corresponding phosphane chalcogenides[163]. Electron-withdrawing substituents in phosphane or arsane chalcogenides lower the polarity of the compounds.

The first ionization potential (IP$_1$) of phosphane oxides, sulphides and selenides is assigned to orbitals exhibiting predominant lone pair character on O, S or Se. IP$_1$ may be correlated with the sum of substituent electronegativities and 'coordination' of a phosphane with O, S or Se is paralleled by an overall stabilization of the corresponding phosphane energies. As the atomic ionization potentials decrease from O to Se, a related decrease of IP$_1$ was observed on going from phosphane oxides to phosphane selenides[164].

The first two He(I)—PE bands of dimethyl(methylthio and seleno)-phosphanes and -arsanes, Me$_2$MEMe (M = P, As; E = S, Se), are due to orbitals that arise from linear combinations of the lone pairs at P or As and S or Se. The large splitting between the two linear combinations of the lone pair-type orbitals indicates gauche conformations in these molecules (torsion angle $\tau \neq 0°$, $\neq 180°$)[165].

C. Bond Lengths and Angles

Most structure determinations that have been carried out on organic selenium and tellurium compounds with bonds to P, As, Sb or Bi are from phosphane selenides and tellurides, R$_3$P$=$E (E = Se, Te). P$=$Se bond lengths are in the region of 210 ± 2 pm in most tertiary phosphane selenides and related dialkylamino- and alkoxy-phosphane selenides (seleno-phosphinic, -phosphonic and -phosphoric esters and amides), compared with about 207 pm estimated from P and Se 'double bond radii'[166]. P$=$Te bond lengths determined in tellurophosphonic and tellurophosphoric amides range from 231 to 235 pm; these values are significantly longer than the sum of the predicted double bond radii[167]. The deviation of determined P$=$Se and P$=$Te bond lengths from the estimated double bond distances was interpreted as evidence for increasing ylidic character of the P$=$Se and P$=$Te bonds compared with P$=$O or P$=$S bonds[168].

$$\begin{array}{ccc} \diagdown \\ \diagup P = \ddot{E} & \qquad & \diagdown \overset{+}{\diagup} P - \ddot{\ddot{E}}: \\ \diagup & & \diagup \\ \mathbf{A} & & \mathbf{B} \end{array}$$

Increased participation of the mesomeric structure B would also explain the high polarity of phosphane selenides and tellurides and their strong nucleophilic character. In a series of papers on studies of the P—N bond, Rϕmming and coworkers compared the structures of tris(dialkylamino)phosphanes with those of the corresponding phosphane selenides and tellurides[137,168–171]. The structures of the pentacovalent phosphorus compounds (R$_2$N)$_3$P$=$E (R = dimethylamino, morpholino, piperidino or pyrrolidino)

were found to be closely related to the structures of the parent aminophosphanes. In all cases, the molecular skeleton $P(NC_2)_3$ does not possess C_3 symmetry (in the solid). At least two different nitrogen atoms (essentially sp^3 hybridized/pyramidal and sp^2 hybridized/planar, respectively) with different P—N bond distances are present in the molecules. Two nitrogen lone pairs are nearly orthogonal to the phosphorus lone pair or to the P=Se bond and the lone pair of the third nitrogen atom is close to being antiparallel to the phosphorus lone pair or to the P=Se or P=Te bond, respectively. In these conformations the sum of the repulsive lone pair–lone pair interactions is obviously a minimum. P=Se or P=Te bonds seem to exert the same conformational influence as the phosphorus lone pair. Compared with the aminophosphanes, the sums of NPN angles are 11–12° larger in the phosphane selenides and tellurides (average about 4° per NPN angle), the individual angles varying from 102° to 114°. Hence phosphorus is far from having a regular tetrahedral coordination geometry in compounds with the N_3P=E (E = Se, Te) skeleton. Correspondingly, the Se=P—C angles in tertiary phosphane selenides (like the Se=P—N angles in aminophosphane selenides) are in the range 112–114°.

Coordination of phosphane selenides with Lewis acids weakens the P=Se bonds. Complex formation of triphenylphosphane selenide $[d(PSe) = 210.6 \text{ pm}]$[172] with $HgCl_2$ leads to elongation of the PSe bond $(Ph_3PSeHgCl_2)_2 : d(PSe = 217 \text{ pm})$[173] half the way to P^V—Se single bond distances $[d(PSe) = 224–228 \text{ pm}]$[122,166,174]. Similarly, $d(PSe)$ of the complexes **286** and **287** is close to 216 pm[175].
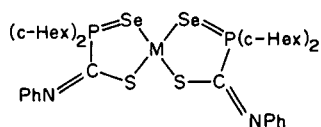
(286) M = Zn, d(P—Se) = 215.9 pm
      ∠ZnSeP = 96°

(287) M = Cd, d(P—Se) = 215.6 pm
      ∠CdSeP = 89.2°
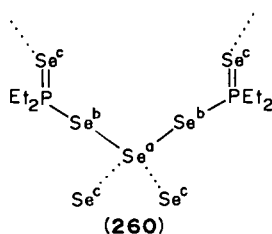
(260)

d(P=Se) = 209.5 pm, d(Se—Se) = 235.2 pm

d(P—Se) = 223.9 pm, d(Se···Se) = 367.9 pm

∠Se^{b}Se^{a}Se^b = 103.9°

∠Se^{c}Se^{a}Se^c = 89.9°

(intermolecular)

Weak intermolecular secondary bonding (Se···Se 367.9 pm) between double-bonded selenium atoms and the central Se atom of the triselenium chain of **260** was confirmed by an X-ray crystal structure analysis[166]. In $(CO)_5WTeP(Bu-t)_3$ (**162**), d(TeP) (243.9 pm) is close to a Te—P single bond length[85].

Coordination of tellurobis(di-*tert*-butylphosphane) (**30**) with tetracarbonylchromium led to a chelate complex, $(CO)_4Cr(\mu-PBu-t_2)_2Te$. In **288**, the X-ray crystal structure determination gave 248 pm for the P—Te bond distance, fitting well the value expected for a single bond[176]. The P—Te—P bond angle is only 78°; tellurium seems to be the softest atom of the CrP_2Te heterocycle as far as the ability to adapt to small bond angles is concerned. The small P—Te—P bond angle in the four-membered chelate is paralleled by μ-9, 10-telluro-9, 10-diarsaanthracene (**110**), where the As—Te—As angle (80.8°) adapts to the preferred geometry of the 9, 10-diarsaanthracene system, which demands As···As distances of about 330 pm[62]. The small angles at tellurium do not lead to any special reactivity which could be expected if significant ring strain were present in both compounds.
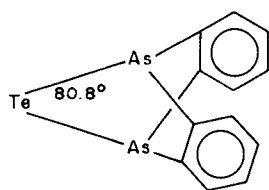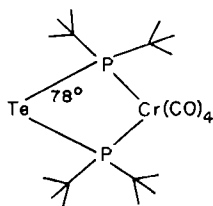
(110)   (288)

1. Selected Reactions Involving Bonds between Se or Te and P, As, Sb or Bi

1. Reactions of seleno- and telluro-phosphanes and -arsanes with cationic and anionic hydrides. As highly polar compounds, phosphane oxides, selenides and tellurides can give hydrogen bonds with protic agents such as phenol or carboxylic acids[78,177]. In contrast, seleno- and telluro-phosphanes are of very low polarity and fairly inert to water and methanol. Owing to the small differences in the electronegativities of P, As, Se and Te, electron-withdrawing substituents might lead to 'umpolung' of the P—Se, P—Te or As—Te bond polarity[28,178]. With hydrogen iodide, $Me_2AsSeCF_3$ is cleaved to give CF_3SeH as a protic reaction product, but $(CF_3)_2PSeMe$ and $(CF_3)_2TeMe$ lead to $(CF_3)_2PH$[178]. Cleavage of the same educts with trimethyltin hydride leads in all cases to Me_2AsH or $(CF_3)_2PH$ and organotin-selenium or -tellurium compounds. Bond polarity is obviously not sufficient to explain the nature of these reaction products. Primary products (according to P—Se or As—Se bond polarity) can rearrange to give the observed final product[177].

$$Me_2AsSeCF_3 \quad \overset{HI}{\nearrow} \quad CF_3SeH \\ \text{(48)} \quad \underset{Me_3SnH}{\searrow} \quad Me_2AsH \tag{193}$$

$$(CF_3)_2PSeMe \quad \overset{HI}{\nearrow} \quad (CF_3)_2PH \\ \text{(10)} \quad \underset{Me_3SnH}{\searrow} \quad (CF_3)_2PH \tag{194}$$
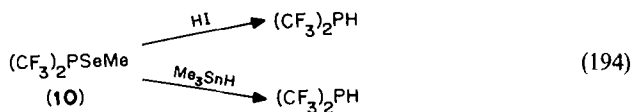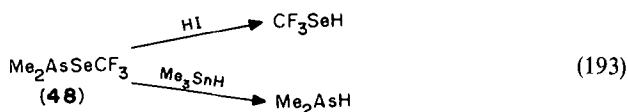
A careful study of the cleavage of **10** with trimethyltin hydride revealed that at − 40 °C, 20 min after mixing the educts significant amounts of $(CF_3)_2PSnMe_3$ are present, and in a separate experiment it was shown that $(CF_3)_2PSnMe_3$ is rapidly cleaved by MeSeH to give the final products of equation 194, $(CF_3)_2PH$ and $Me_3SnSeMe$ (i.e. P appears to be negatively charged and Se should be positively charged in **10**)[178]. Similarly, $(CF_3)_2AsSeMe$ **(49)** reacts stepwise with cyclopentadienyltricarbonyl-chromium, -molybdenum and -tungsten hydride[179].

Cleavage of the tellurophosphane $(t\text{-Bu})_2PTeTol\text{-}p$ **(26)** with gaseous HCl leads to di-p-tolyl ditelluride and products that are related to products of the cleavage of tetra-*tert*-butyldiphosphane with HCl[29].

(195)
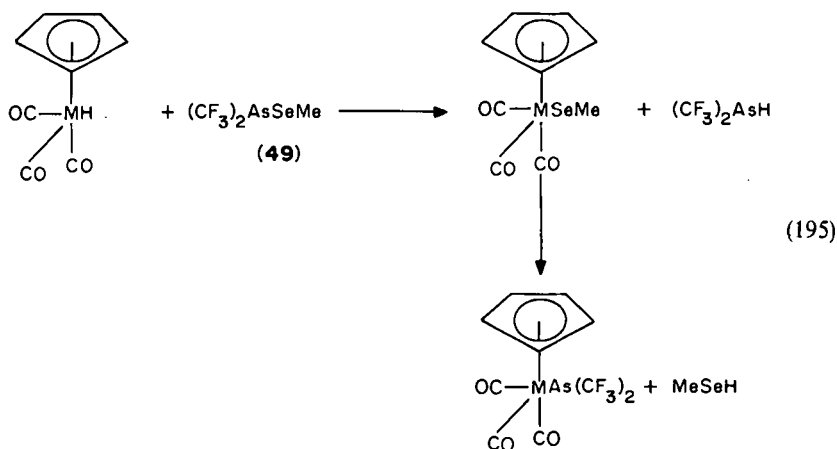
2. Types of coordination of ligands with bonds between Se or Te and P, As, Sb or Bi

a. P^{III} and As^{III} ligands. Thio-, seleno- and telluro-phosphanes coordinate with transition metal acceptors preferentially via the lone pair at phosphorus and the corresponding arsanes via As. With monodentate (P) ligands, mono- and di-substituted complexes have been characterized; bidentate $[(t\text{-}Bu)_2P]_2Te$ gives four-membered chelate complexes with metal carbonyls and platinum or palladium dichloride.

$$(CO)_5MTHF + R_2{}^1PER^2 \xrightarrow{-THF} (CO)_5MPR_2{}^1ER^2 \quad \text{(refs. 20, 155, 180, 181, 183)} \quad (196)$$

$$(CO)_4M(\eta^4\text{-}C_7H_8) + 2R_2{}^1PER^2 \xrightarrow{-C_7H_8} (CO)_4M(PR_2{}^1ER^2)_2 \quad \text{(ref. 182)} \quad (197)$$

$$(cis \longrightarrow trans \text{ rearrangement})$$

(198)

(199)

$$\text{Pd(COD)Cl}_2 \;+\; [(\textit{t}\text{-Bu})_2\text{P}]_2\text{Te} \;\xrightarrow{\;-\,\text{COD}\;}\; \text{Cl}_2\text{Pd}\underset{(\text{Bu-}\textit{t})_2}{\overset{(\text{Bu-}\textit{t})_2}{\diamond}}\text{Te} \qquad (\text{ref. 29})$$

(200)

b. η^2-*P-, Se-coordination.* The metaselenophosphate **243** (Section VII.C) coordinates with the bis(triphenylphosphane)platinum(0) acceptor by η^2-orientation of the P=Se double bond to platinum[185].

Addition of sulphur or selenium to W≡P double bonds leads to three-membered ring systems (compare Section II.A.1.a) that contain $(\textit{t}\text{-Bu})_2\text{PS}$ or $(\textit{t}\text{-Bu})_2\text{PSe}$ moieties as η^2-coordinated three-electron ligands[186].

$$\xrightarrow{\;1/8\ E_8\;}$$

(201)

(289) E = S
(290) E = Se

In solid **290**, the P—Se bond length determined to be 217.1 pm [$d(\text{WP}) = 243.1\,\text{pm}$, $d(\text{WSe}) = 268.9\,\text{pm}$] (compare Section IX.C).

Alternatively, cyclopentadienyltricarbonyl(diphenylphosphino)tungsten reacts with sulphur or red selenium to give the corresponding diphenyl-thio- or -seleno-phosphinyl complexes (**291**, **292**) that are decarbonylated to give the π^2-diphenyl-chalcogenophosphinite complexes (**293**, **294**)[187].

$$\xrightarrow{\;\tfrac{1}{8}E_8\;}$$

(291) E = S
(292) E = Se

$$\xrightarrow[\Delta,\,h\nu]{\;-\text{CO}\;}$$

(202)

(293) E = S
(294) E = Se

In ^{77}Se NMR, **294** appears at $\delta = -911$ ppm (compared with $\delta = +166$ ppm for **292**[186]). Thermal decomposition of **292** (3 months at room temperature) leads to the η^1-diselenophosphinate complex $Cp(CO)_3WSeP(=Se)Ph_2$, which was detected by ^{31}P and ^{77}Se NMR. With methyl iodide, complexes related to **291** have been methylated to give metallo-substituted thio- or seleno-phosphonium salts[186]. The R_2PSe moiety can also act as a bridging bidentate ligand in dinuclear complexes[188,189].

c. Se- or Te-coordination. Tertiary phosphane selenides give complexes with many main group and transition metal acceptors[3]. Examples of coordination compounds with R_3PTe, R_3AsSe and R_3SbSe ligands are comparatively rare[151]. Triphenylphosphane sulphide is a better donor than triphenylphosphane selenide towards boron trichloride and boron tribromide as shown by ligand exchange reactions[190]. The geometry of phosphane selenide complexes is strongly related to that of phosphane sulphide complexes (angular M—Se—P arrangements due to stereochemically active lone pairs of electrons at Se)[3,173].

Diselenophosphinates often act as bidentate ligands with metal acceptors; chelating coordination is predominant, but not exclusive. Phosphane selenides and selenophosphinates are softer ligands than the corresponding S ligands[3], as expected from the rules for hard and soft acids and bases.

In diethylthioselenophosphinatothallium(I) (**295**), sulphur and selenium are bridging two thallium atoms to give dimeric units, thallium being at the tops of distorted square pyramids. The Tl—Se distances within the dimer are long (342.4 pm), but there are further intermolecular contacts between selenium and the thallium atoms of two different dimers. These intermolecular Tl—Se bonds link the dimeric units together to give a two-dimensional polymeric layer structure[191]. The relatively strong P—S and P—Se bonds in **295** are consistent with findings from IR spectroscopy[192].

$$
\begin{aligned}
&\text{pm}\\
d(P—S) &= 204.2\\
d(P—Se) &= 211.5\\
d(Tl—S) &= 323.7\\
d(Tl—Se) &= 342.4 \text{ (intramolecular)}\\
d(Tl—Se) &= 359.4 \text{ (intermolecular)}
\end{aligned}
$$

(295)
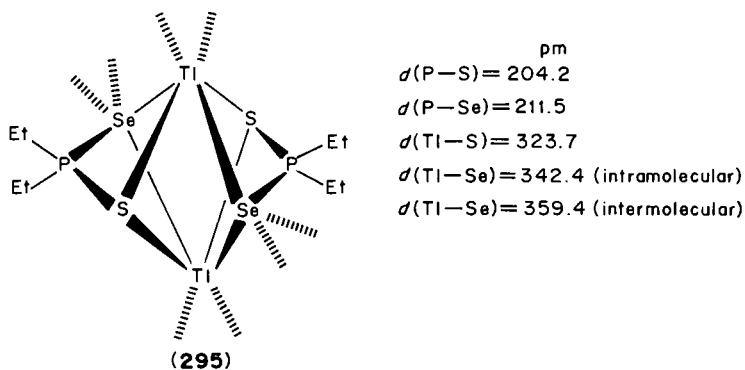
The large TlS and TlSe distances in **295** are probably partly due to a high degree of polar bond character, they also reflect the bridging nature of the $[\eta^2\text{-}]$sulphur and $[\eta^4\text{-}]$selenium atoms.

3. Alkylation, oxidation, deoxygenation and other reactions

Charge-transfer adducts of phosphane chalcogenides with iodine have been investigated using UV–visible spectroscopy[193]. The equilibrium constants increased from E = O to E = Se in each series of compounds[193,194].

$$R_3P{=}E + I_2 \rightleftharpoons R_3P{=}E\cdots I_2$$
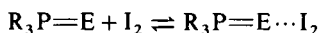
Structural evidence is not yet available. Protonation of phosphane selenides occurs with strong acids and may be followed by ^{31}PNMR[78]. Similarly, strong solvation of phosphane selenides by liquid SO_2 is indicated by significant downfield shifts in ^{77}SeNMR and by decreasing coupling constants $^1J(^{77}Se^{31}P)$ in SO_2 solution[195]. Tris(dimethylamino)phosphane telluride, $(Me_2N)_3P=Te$ (**274**), gives a deep red adduct with liquid SO_2; an upfield shift in ^{31}P and lowering of $^1J(^{125}Te^{31}P)$ is also observed[195]. With methyl iodide, seleno- and telluro-phosphanes are primarily subject to P-alkylation (subsequently P—Se or P—Te bond breaking occurs, Section V); phosphane selenides need strong alkylating agents such as dimethyl sulphate or trialkyloxonium salts, but compounds that are activated by electron-donating dialkylamino groups can even react with methyl iodide (for rearrangements under the action of alkylating halides, see Section VI).

Recent experiments have shown that phosphane tellurides are also methylated with methyl iodide under mild conditions[83].

Triphenylphosphane selenide gives a reaction related to the Wittig alkene synthesis with hexafluoroacetone or bis(trisfluoromethyl)ketene to give 1,3-diselenetanes[196]. The latter synthesis is less successful than the reaction of triphenylphosphane sulphide with bis(trifluoromethyl)ketene, which gives the 1,3-dithietane in 60% yield.

$$2Ph_3P=Se \ + \ 2(CF_3)_2CO \ \longrightarrow \ 2Ph_3P=O \ + \ (CF_3)_2C\overset{\displaystyle Se}{\underset{\displaystyle Se}{\diamond}}C(CF_3)_2$$

73% yield

(203)

$$2Ph_3P=Se \ + \ 2(CF_3)_2C=C=O \ \longrightarrow \ 2Ph_3P=O \ + \ (CF_3)_2C=C\overset{\displaystyle Se}{\underset{\displaystyle Se}{\diamond}}C=C(CF_3)_2$$

16% yield

(204)
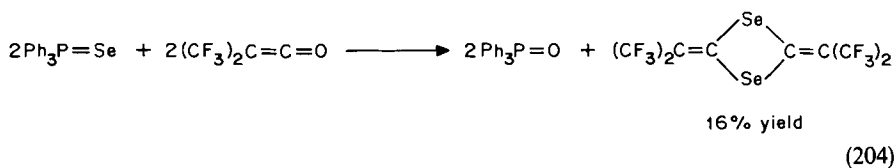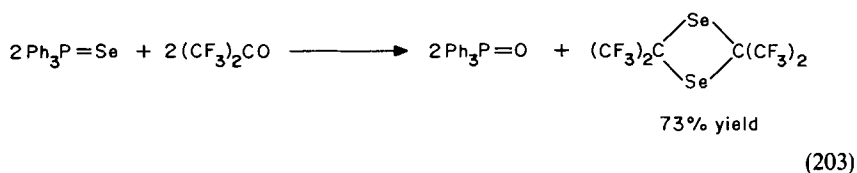
Reactions of epoxides with tertiary phosphane selenides in the presence of trifluoroacetic acid lead to deoxygenation of the epoxide and to precipitation of elemental selenium. In the $Ph_3P=S$–epoxide reaction, episulphides are formed under mild conditions, but episelenides (seleniranes), being less stable, suffer spontaneous deselenation, leading stereospecifically to alkenes[197,198].

$$R\overset{\displaystyle O}{\triangle}R \ \xrightarrow[(H^+),\,-Ph_3PO]{Ph_3PSe} \ R\overset{\displaystyle Se}{\triangle}R \ \longrightarrow \ \underset{R}{\overset{}{>}}C=C\underset{R}{\overset{}{<}} \ + \ Se$$

(205)
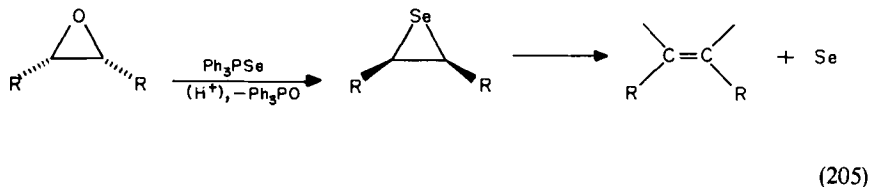
Sodium tellurodiethyl phosphate leads in a similar manner to deoxygenation of epoxides, possibly via extremely labile telluriranes[105]. The reaction may even be carried out starting from sodium diethyl phosphite with catalytic amounts of elemental tellurium[105]. The reducing properties of selenodiethyl phosphate have been used for the

deoxygenation of various sulphoxides[199]. Selenophosphonic and selenophosphoric acid
Se-esters can act as phosphorylating cholinesterase inhibitors; some of them are extremely
toxic[91]. Appropriate care should be taken in handling these compounds.

X. ACKNOWLEDGEMENT

XI. REFERENCES

1. K. Sasse, 'Organische Phosphorverbindungen', in *Houben-Weyl, Methoden der Organischen
   Chemie*, 4. Aufl., Vols. XII/1 and XII/2, Georg Thieme, Stuttgart, 1963.
2. M. Regitz (Ed.), 'Organische Phosphorverbindungen', in *Houben-Weyl, Methoden der Organis-
   chen Chemie*, Vols. E1 and E2, Georg Thieme, Stuttgart, 1982.
3. R. A. Zingaro and W. C. Cooper (Eds.), *Selenium*, Van Nostrand Reinhold, New York, 1974.
4. K. J. Irgolic, *The Organic Chemistry of Tellurium*, Gordon and Breach, New York, 1974.
5. G. M. Kosolapoff and L. Maier, *Organic Phosphorus Compounds*, Vol. 1, Wiley–Interscience,
   New York, 1972.
6. H. J. Gysling, *Coord. Chem. Rev.*, **42**, 133 (1982).
7. H. Goldwhite, *Introduction to Phosphorus Chemistry*, Cambridge University Press, Cambridge,
   1981.
8. A. F. Wells, *Structural Inorganic Chemistry*, 5th ed., Clarendon Press, Oxford, 1984.
9. H. J. Emeleus, K. J. Parker and N. Weleman, *J. Chem. Soc.*, 2529 (1962).
10. A. Darmadi, A. Haas and B. Koch, *Z. Naturforsch., Teil B*, **35**, 526 (1980).
11. N. Petragnani, V. G. Toscano and M. de Moura Campos *Chem. Ber.*, **101**, 3070 (1968).
12. R. A. N. McLean, *Inorg. Nucl. Chem. Lett.*, **5**, 745 (1969).
13. J. W. Anderson, J. E. Drake, R. T. Hemmings and D. L. Nelson, *Inorg. Nucl. Chem. Lett.*, **11**, 233
    (1975).
14. D. E. J. Arnold, J. S. Dryburgh, E. A. V. Ebsworth and D. W. H. Rankin, *J. Chem. Soc., Dalton.
    Trans.*, 2518 (1972).
15. P. Dehnert, J. Grobe, W. Hildebrandt and Duc le Van, *Z. Naturforsch., Teil B*, **34**, 1646 (1979).
16. Yu. N. Shlyk, G. M. Bogolyubov and A. A. Petrov, *Zh. Obshch. Khim.*, **38**, 193 (1968).
17. W. R. Cullen, D. S. Dhaliwal and W. B. Fox, *Inorg. Chem.*, **3**, 1332 (1964).
18. W. R. Cullen and D. S. Dhaliwal, *Can. J. Chem.*, **45**, 379 (1967).
19. I. B. Mishra and A. B. Burg, *Inorg. Chem.*, **11**, 664 (1972).
20. J. Grobe and Duc le Van, *Z. Naturforsch., Teil B*, **35**, 694 (1980).
21. J. Grobe and D. le Van, *J. Fluor. Chem.*, **19**, 279 (1982).
22. J. Grobe, D. le Van, J. Nientiedt, *Z. Naturforsch., Teil B*, **41**, 149 (1986).
23. E. Niecke and E. Symalla, *Chimia*, **39**, 320 (1985).
24. W. W. Schoeller and E. Niecke, unpublished work, presented at the Colloque Nationale sur la
    Chimie du Phosphore, La Tour Carol, France, 1985.
25. R. Appel and C. Casser, *Chem. Ber.*, **118**, 3419 (1985).
26. W.-W. du Mont, S. Kubiniok and T. Severengiz, *Z. Anorg. Allg. Chem.*, **521**, 21 (1985).
27. S. Kubiniok, *Diplomarbeit*, Universität Oldenburg, 1984.
28. W.-W. du Mont, *Angew. Chem.*, **92**, 562 (1980); *Angew. Chem., Int. Ed. Engl.*, **19**, 554 (1980).
29. W.-W. du Mont and R. Hensel, unpublished results.
30. T. Severengiz, *PhD Thesis*, Oldenburg, 1985.
31. W.-W. du Mont, R. Hensel and T. Severengiz, *Phosphorus Sulfur*, **18**, 73 (1983).
32. F. Sladky, B. Bildstein and D. Obendorf, *J. Organomet. Chem.*, **295**, C1 (1985).
33. L. Lange and W.-W. du Mont, unpublished results.
34. L. S. Sagan, R. A. Zingaro and K. J. Irgolic, *J. Organomet. Chem.*, **39**, 301 (1972).
35. G. C. Chen, J. R. Daniel and R. A. Zingaro, *Carbohydr. Res.*, **50**, 53 (1976).
36. G. C. Chen, R. A. Zingaro and C. R. Thompson, *Carbohydr. Res.*, **39**, 61 (1975).
37. R. A. Pyles, K. J. Irgolic and G. C. Pappalardo, unpublished work, 1983.

38. W.-W. du Mont, T. Severengiz and H. J. Breunig, *Z. Naturforsch., Teil B*, **38**, 1306 (1983).
39. H. J. Breunig and H. Jawad, *J. Organomet. Chem.*, **277**, 257 (1984).
40. H. J. Breunig and S. Gülec, *Z. Naturforsch., Teil B*, in press.
41. M. Wieber and I. Sauer, *Z. Naturforsch., Teil B*, **39**, 887 (1984).
42. H. J. Breunig and D. Müller, *Angew. Chem.*, **94**, 448 (1982); *Angew. Chem., Int. Ed. Engl.*, **21**, 439 (1982).
43. G. Becker and M. Rössler, *Z. Naturforsch., Teil B*, **37**, 91 (1982).
44. A. J. Ashe, III, E. G. Ludwig and J. Oleksyszyn, *Organometallics*, **2**, 1859 (1983).
45. M. Wieber and I. Sauer, *Z. Naturforsch., Teil B*, **39**, 1668 (1984).
46. W.-W. du Mont, T. Severengiz, H. J. Breunig and D. Müller, *Z. Naturforsch., Teil B*, **40**, 848 (1985).
47. A. Darmadi, A. Haas and M. Kaschani-Motlagh, *Z. Anorg. Allg. Chem.*, **448**, 35 (1979); see also A. G. Osborne, R. E. Hollands, R. F. Bryan and S. Lockhart, *J. Organomet. Chem.*, **288**, 207 (1985).
48. L. Maier, *Helv. Chim. Acta*, **59**, 252 (1976).
49. C. J. Marsden, *J. Fluor. Chem.*, **5**, 423 (1975).
50. Ya. I. Kolodii, Ya. I. Mel'nik, V. V. Turkevich and A. P. Vas'kiv, *Zh. Obshch. Khim.*, **48**, 331 (1978).
51. A. Rosenbaum, H. Kirchberg and E. Leibnitz, *J. Prakt. Chem.*, **19**, 1 (1963).
52. A. Rosenbaum, *J. Prakt. Chem.*, **37**, 200 (1968).
53. M. Schmidt, I. Boie, C. Osterroth, R. Schröer and H. F. Grützmacher, *Chem. Ber.*, **101**, 1381 (1968).
54. W.-W. du Mont, S. Kubiniok and T. Severengiz, 4th International Symposium on Inorganic Ring Systems, Orsay, France, 1985, Abstract 37.
55. I. F. Lutsenko and V. L. Foss, *Pure Appl. Chem.*, **52**, 917 (1980).
56. K. Issleib and M. Hoffmann, *Chem. Ber.*, **99**, 1320 (1966).
57. R. Hensel, *PhD Thesis*, Universität Oldenburg (FRG), 1987; W.-W. du Mont, R. Hensel, S. Kubiniok, L. Lange and T. Severengiz, *X Int. Conf. on Phosphorus Chemistry, Bonn, 1986*, Abstract B 42.
58. N. Camerman and J. Trotter, *J. Chem. Soc.*, 219 (1964).
59. W.-W. du Mont, T. Severengiz and B. Meyer, *Angew. Chem.*, **95**, 1025 (1983); *Angew. Chem., Int. Ed. Engl.*, **22**, 983 (1983).
60. R. A. Zingaro, B. H. Steeves and K. Irgolic, *J. Organomet. Chem.*, **4**, 320 (1965).
61. D. W. Allen, J. C. Coppola, O. Kennard, F. G. Mann, W. D. S. Motherwell and D. G. Watson, *J. Chem. Soc. C*, 810 (1970).
62. O. Kennard, D. L. Wampler, J. C. Coppola, W. D. S. Motherwell, F. G. Mann, D. G. Watson, C. H. MacGillavry, C. H. Stam and P. Benci, *J. Chem. Soc. C*, 1511 (1971).
63. O. Mundt, M. Riffel, G. Becker and A. Simon, *Z. Naturforsch., Teil B*, **39**, 317 (1984).
64. A.-J. Ashe, III, E. G. Ludwig, J. Oleksyszyn and J. C. Huffmann, *Organometallics*, **3**, 337 (1984).
65. H. J. Breunig and D. Müller, VI FECHEM Conference on Organometallic Chemistry, Riga/Yurmala, USSR, 1985, Abstract 136; H. J. Breunig and D. Müller, *Z. Naturforsch., Teil B*, **41**, (1986).
66. M. Baudler, H. Suchomel, G. Fürstenberg and U.Schings, *Angew. Chem.*, **93**, 1087 (1981); *Angew. Chem., Int. Ed. Engl.*, **20**, 1044 (1981).
67. M. Yoshifuji, K. Shibayama and N. Inamoto, *Chem. Lett.*, 6036 (1984).
68. M. Yoshifuji, K. Shibayama, K. Ando and M. Inamoto, *Heterocycles*, **21**, 475 (1984).
69. H. L. Krauss and H. Jung, *Z. Naturforsch., Teil B*, **15**, 545 (1960).
70. L. Maier, *Helv. Chim. Acta*, **48**, 1190 (1965).
70a.D. Herrmann, *Z. Anorg. Allg. Chem.*, **416**, 50 (1975).
71. G. Thiele, H. W. Rotter and M. Lietz and J. Ellermann, *Z. Naturforsch., Teil B*, **39**, 1344 (1984).
72. J. Ellermann and L. Brehm, *Chem. Ber.*, **117**, 2675 (1984).
73. J. Ellermann and M. Lietz, *Z. Naturforsch., Teil B*, **35**, 1514 (1980).
74. J. Ellermann and A. Veit, *Z. Naturforsch., Teil B*, **40**, 948 (1985).
75. M. Mikolajczyk, *Pure Appl. Chem.*, **52**, 959 (1980).
76. A. Schmidpeter and H. Brecht, *Z. Naturforsch., Teil B*, **24**, 179 (1969).
77. I. A. Nuretdinov, N. A. Buina and N. P. Grechkin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 169 (1969) (Engl. transl., 163).
78. C. Glidewell and E. J. Leslie, *J. Chem. Soc., Dalton Trans.*, 527 (1977).

79. J. Omelańczyk, W. Perliskowa and M. Mikoloajczyk, *Phosphorus Sulfur*, **18**, 444 (1983).
80. J. Omelańczyk and M. Mikolajczyk, *Tetrahedron Lett.*, **25**, 2493 (1984).
81. N. Petragnani and M. de Moura Campos, *Tetrahedron*, **21**, 13 (1965).
82. V. D. Romanenko, V. F. Shulgin, V. V. Skopenko, A. N. Chernega, M. Yu. Antipin, Yu. T. Struchkov, I. E. Boldeskul and L. N. Markovski, *Zh. Obshch. Khim.*, **55**, 282 (1985).
83. N. Kuhn and H. Schumann, *Phosphorus Sulfur*, **26**, 199 (1986).
84. S. Kubiniok and W.-W. du Mont, unpublished results.
85. N. Kuhn, H. Schumann and G. Wolmershäuser, *J. Chem. Soc., Chem. Commun.*, 1595 (1985); N. Kuhn, unpublished work.
86. W. Kuchen and B. Knop, *Angew. Chem.*, **77**, 259 (1965); *Chem. Ber.*, **99**, 1663 (1966).
87. B. Krawiecka, Z. Skrzypczynski and J. Michalski, *Phosphorus*, **3**, 177 (1973).
88. I. A. Nuretdinov, N. A. Buina and E. V. Bayandika, *Zh. Obshch. Khim.*, **48**, 1073 (1978) (Engl. transl., 977).
89. E. V. Bayandina, I. A. Nuretdinov and E. I. Loginova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1627 (1976) (Engl. transl. 1543).
90. I. A. Nuretdinov, E. V. Bayandina and D. N. Sadkova, *Dokl. Akad. Nauk SSSR*, **239**, 1110(1978) (Engl. transl., 142).
91. S. Akerfeldt and L. Fagerlind, *J. Med. Chem.*, **10**, 115 (1967).
92. A. Markovska, *Bull. Acad. Pol. Sci., Ser. Sci. Chem.*, **15**, 153 (1967); *Chem. Abstr.*, **67**, 90891B (1967).
93. E. G. Kataev, T. G. Mannafov and G. I. Kostina, *Zh. Obshch. Khim.*, **38**, 363 (1968).
94. I. A. Nuretdinov, D. N. Sadkova and E. V. Bayandina, *Izv. Akad. Nauk SSSR. Ser. Khim.*, 2635 (1977) (Engl. transl., 2441).
95. R. R. Shagidullin, A. V. Chernova, I. A. Nuretdinov, G. M. Doroshkina and E. V. Bayandina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1**, 184 (1976) (Engl. transl. 174).
96. W. Lorenz and B. Schrader, to Bayer AG, *US Pat.*, 3 082 240 (1960/63); *Chem. Abstr.*, **59**, 5077 (1963).
97. A. Haas and J. Mikolajczak, *Chem. Ber.*, **114**, 829 (1981).
98. A. Haas and A. Lopusiński, *Chem. Ber.*, **114**, 3176 (1981).
99. A. Schmidpeter, personal communication, 1985.
100. W. J. Stec, A. Okrusecek, K. Lesiak, B. Uznanski and J. Michalski, *J. Org. Chem.*, **41**, 227 (1976).
101. N. I. Zemlyanski, N. M. Chernaya and V. V. Turkevich, *Zh. Obshch. Khim.*, **37**, 495 (1967) (Engl. transl., 464).
102. A. Markowska and W. Buchowiecki, *Bull. Acad. Pol. Sci, Ser. Sci. Chim.*, **21**, 455 (1973).
103. O. Foss, *Acta Chem. Scand.*, **4**, 1241 (1950).
104. O. Foss, *Acta Chem. Scand.*, **1**, 8 (1947).
105. D. L. J. Clive and S. M. Menchen, *J. Chem. Soc. Chem. Commun.*, 658 (1977).
106. J. Czyzewska-Chlebny and M. Michalska, *J. Chem. Soc., Chem. Commun.*, 693 (1985).
107. M. Caira, R. H. Neilson, W. H. Watson, P. Wisian-Neilson and Z.-M. Xie, *J. Chem. Soc., Chem. Commun.*, 698 (1984).
108. R. Appel and C. Casser, *Tetrahedron Lett.*, **25**, 4109 (1984).
109. T. A. van der Knaap and F. Bickelhaupt, *Phosphorus Sulfur*, **18**, 47 (1983).
110. E. Niecke and D.-A. Wildbredt, *J. Chem. Soc., Chem. Commun.*, 72 (1981).
111. O. J. Scherer and N. Kuhn, *J. Organomet. Chem.*, **78**, C17 (1974).
112. O. J. Scherer and N. Kuhn, *J. Organomet. Chem.*, **82**, C3 (1974).
113. G. J. Scherer, H. Jungmann, C. Krüger and G. Wolmershäuser, *Chem. Ber.*, **117**, 2382 (1984).
114. D. H. Brown, R. J. Cross and R. Keat, *J. Chem. Soc., Dalton Trans.*, 871 (1980).
115. R. A. Zingaro, *J. Organomet. Chem.*, **1**, 200 (1963).
116. T. Austad, T. Rød, K. Åse, J. Songstad and A. H. Norbury, *Acta Chem. Scand.*, **27**, 1939 (1973).
117. W.-W. du Mont and H.-J. Kroth, *J. Organomet. Chem.*, **113**, C35 (1976).
118. W.-W. du Mont, *Z. Naturforsch., Teil B*, **40**, 1453 (1985).
119. W.-W. du Mont and H.-J. Kroth, *Z. Naturforsch., Teil B*, **36**, 332 (1981) [the δ^{125}Te values in this paper have been withdrawn (see ref. 26)].
120. O. J. Scherer and G. Schnabl, *Angew. Chem.*, **89**, 500 (1977).
121. W.-W. du Mont, paper presented at the DFG Symposium and EUCHEM Conference on 'Shortlived Species in Inorganic Chemistry, Their Reactivity and Their Stabilization', Burghausen, F.R.G., 1984.
122. S. Husebye, *Acta Chem. Scand.*, **20**, 51 (1966).

123. H.-G. Horn and H.-G. Lindner, *Chem. Ztg.*, **109**, 77 (1985).
124. I. A. Nuretdinov and E. I. Loginova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2827 (1973).
125. H. W. Roesky and W. Kloker, *Z. Naturforsch., Teil B*, **28**, 697 (1973).
126. I. A. Nuretdinov, N. A. Buina, E. V. Bayandina and E. G. Sibgatulind, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 483 (1974).
127. E. Gryszkiewicz-Trochimowski, J. Quinchon and O. Gryszkiewicz-Trochimowski, *Mém. Présentés Soc. Chim.*, **299**, 1794 (1960).
128. A. I. Razumov, B. G. Liovbev, M. B. Gazizov and Z. M. Khammatova, *Zh. Obshch. Khim.*, **34**, 1851 (1964).
129. N. P. Grechkin, I. A. Nuretdinov and N. A. Buina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1, 168 (1969).
130. K. Diemert, W. Kuchen and J. Kutter, *Phosphorus Sulfur*, **15**, 155 (1983).
131. O. J. Scherer and G. Schnabl, *Chem. Ber.*, **109**, 2996 (1976).
132. S. Pohl, *Z. Naturforsch., Teil B*, **33**, 610 (1978).
133. S. Pohl, *Z. Naturforsch., Teil B*, **34**, 256 (1979).
134. N. I. Zemlyanskii and R. D. Gorak, *Zh. Obshch. Khim.*, **41**, 2446 (1971).
135. R. D. Gorak and N. I. Zemlyanskii, *Zh. Obshch. Khim.*, **41**, 1994 (1971).
136. F. Räuchle, W. Pohl, B. Blaich and J. Boubean, *Ber. Bunsenges. Phys. Chem.*, **75**, 66 (1971).
137. C. Rǿmming, A. J. Iversen and J. Songstad, *Acta Chem. Scand., Ser. A*, **34**, 333 (1980).
138. D. H. Brown, R. J. Cross and D. Millington, *J. Organomet. Chem.*, **125**, 219 (1977).
139. R. Keat and D. G. Thompson, *J. Organomet. Chem.*, **141**, C13 (1977).
140. K. Issleib, W. Mögelin and A. Balszuweit, *Z. Anorg. Allg. Chem.*, **530**, 16 (1986).
141. R. A. Zingaro and A. Merijanian, *Inorg. Chem.*, **3**, 580 (1964).
142. K. A. Jensen and P. H. Nielsen, *Acta Chem. Scand.*, **17**, 1875 (1963).
143. F. L. Kolar, R. A. Zingaro and J. Laane, *J. Mol. Struct.*, **18**, 319 (1973).
144. P. B. Chi and F. Kober, *Z. Anorg. Allg. Chem.*, **466**, 183 (1980).
145. F. Kober and P. B. Chi, *Z. Anorg. Allg. Chem.*, **454**, 24 (1979).
146. F. Kober and P. B. Chi, *Z. Anorg. Allg. Chem.*, **477**, 139 (1981).
147. H. Schumann, U. Franck, W.-W. du Mont and F. Marschner, *J. Organomet. Chem.*, **222**, 217 (1981).
148. W. Kuchen, M. Förster, H. Hertel and B. Höhn, *Chem. Ber.*, **105**, 3310 (1972).
149. G. O. Doak and L. D. Freedman, *Organometallic Compounds of Arsenic, Antimony and Bismuth*, Wiley–Interscience, New York, London, Sydney, Toronto, 1970.
150. R. A. Zingaro and A. Merijanian, *J. Organomet. Chem.*, **1**, 369 (1964).
151. N. Kuhn and H. Schumann, *J. Organomet. Chem.*, **288**, C51 (1985); *J. Organomet. Chem.*, **304**, 181 (1986).
152. C. Rodger, N. Sheppard, C. McFarlane and W. McFarlane, in *NMR and the Periodic Table* (Eds. R. K. Harris and B. E. Mann), Academic Press, New York, 1978, p. 402.
153. W. McFarlane and D. S. Rycroft, *J. Chem. Soc., Chem. Commun.*, 902 (1972); *J. Chem. Soc., Dalton Trans.*, 2162 (1973).
154. R. P. Pinell, C. A. Megerle, S. L. Manatt and P. A. Kroon, *J. Am. Chem. Soc.*, **95**, 977 (1973).
155. J. Grobe and D. le Van, *J. Fluor. Chem.*, **24**, 25 (1984).
156. W. McFarlane and J. A. Nash, *J. Chem. Soc., Chem. Commun.*, 913 (1969).
157. I. J. Colquhoun, H. C. E. McFarlane, W. McFarlane, J. A. Nash, R. Keat, D. S. Rycroft and D. G. Thompson, *Org. Magn. Reson.*, **12**, 473 (1979).
158. I. J. Colquhoun and W. McFarlane, *J. Chem. Soc., Dalton Trans.*, 658 (1981).
159. F. Watari, *Inorg. Chem.*, **20**, 1776 (1981).
160. E. J. Jacob and S. Samdal, *J. Am. Chem. Soc.*, **99**, 5656 (1977).
161. P. Dehnert, R. Demuth and J. Grobe, *Spectrochim. Acta Part A*, **36**, 3 (1979).
162. I. I. Vandyukova, R. R. Shagidullin and I. A. Nuretdinov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1390 (1976).
163. R. R. Carlson and D. W. Meek, *Inorg. Chem.*, **13**, 1741 (1974).
164. S. Elbel and H. tom Dieck, *J. Chem. Soc., Dalton Trans.*, 1762 (1976).
165. M. C. Böhm, M. Eckert-Maksić, R. Gleiter, J. Grobe and D. le Van, *Chem. Ber.*, **114**, 2300 (1981).
166. S. Husebye and G. Helland-Madsen, *Acta Chem. Scand.*, **23**, 1398 (1969).
167. A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).
168. C. Rǿmming and J. Songstad, *Acta Chem. Scand., Ser. A*, **32**, 689 (1979).
169. C. Rǿmming, K. Maartmann-Moe and J. Songstad, *Acta Chem. Scand., Ser. A*, **38**, 349 (1984).

170. C. Rømming and J. Songstad, *Acta Chem. Scand., Ser. A*, **33**, 187 (1979).
171. C. Rømming and J. Songstad, *Acta Chem. Scand.. Ser. A*, **32**, 689 (1978).
172. P. W. Codding and K. A. Kerr, *Acta Crystallogr., Sect. B*, **35**, 1261 (1979).
173. L. S. Dent Glasser, L. Ingram, M. G. King and G. P. McQuillan, *J. Chem. Soc. A*, 2501 (1969).
174. S. Husebye, *Acta Chem. Scand.*, **23**, 1389 (1969).
175. R. Kramolowsky, J. Sawluk, unpublished work; J. Sawluk, *PhD Thesis*, Universität Hamburg, 1985.
176. R. Hensel, W.-W. du Mont, R. Boese, D. Wewers and L. Weber, *Chem. Ber.*, **118**, 1580 (1985).
177. R. R. Shagidullin, I. P. Lipatova, I. A. Nuretdinov and S. A. Samartseva, *Dokl. Akad. Nauk SSSR*, **211**, 1363 (1973).
178. P. Dehnert, J. Grobe and D. le Van, *Z. Naturforsch., Teil B*, **36**, 48 (1981).
179. J. Grobe and R. Haubold, *Z. Anorg. Allg. Chem.*, **522**, 159 (1985).
180. J. Grobe and D. le Van, *Z. Naturforsch., Teil B*, **34**, 1653 (1979).
181. J. Grobe and D. le Van, *Z. Allg. Anorg. Chem.*, **518**, 36 (1984).
182. J. Grobe, M. Köhne-Wächter and D. le Van, *Z. Anorg. Allg. Chem.*, **519**, 67 (1984).
183. W.-W. du Mont, S. Kubiniok, T. Severengiz, W. Saak and S. Ponl, unpublished results (X-ray crystal structure analysis).
184. R. Hensel and W.-W. du Mont, *Chem. Ber.*, **118**, 5016 (1985).
185. O. J. Scherer, H. Jungmann, C. Krüger and G. Wolmershäuser, *Chem. Ber.*, **117**, 2382 (1984).
186. W. Malisch, unpublished work (1985).
187. W. Malisch, R. Maisch, I. J. Colquhoun and W. McFarlane, *J. Organomet. Chem.*, **220**, C1 (1981).
188. B. Walther, B. Messbauer and H. Meyer, *Inorg. Chim. Acta*, **37**, L525 (1979).
189. J. Grobe, J. Vetter and D. Rehder, *Z. Naturforsch., Teils B*, **40**, 975 (1985).
190. M. Schmidt and H. D. Block, *Chem. Ber.*, **103**, 3705 (1970).
191. S. Esperås and S. Husebye, *Acta Chem. Scand.*, **27**, 3355 (1973).
192. W. Kuchen and H. Hertel, *Angew. Chem.*, **81**, 127 (1969); *Angew. Chem. Int. Ed. Engl.*, **8**, 89 (1969).
193. P. Bruno, M. Caselli, C. Fragale and S. Magrino, *J. Inorg. Nucl. Chem.*, **39**, 1757 (1977).
194. F. L. Kolar, R. A. Zingaro and K. Irgolic, *J. Inorg. Nucl. Chem.*, **28**, 2981 (1966).
195. P. A. W. Dean, *Can. J. Chem.*, **57**, 754 (1979).
196. M. S. Raasch, *J. Org. Chem.*, **45**, 3517 (1980).
197. T. H. Chan and J. R. Finkenbine, *Tetrahedron Lett.*, 2091 (1974).
198. D. L. J. Clive and C. V. Denyer, *J. Chem. Soc., Chem. Commun.*, 253 (1973).
199. D. L. J. Clive, W. A. Kiel, S. M. Menchen and C. K. Wong, *J. Chem. Soc., Chem. Commun.*, 657 (1977).

CHAPTER **16**

Free radical reactions of organoselenium and organotellurium compounds

LAURENCE CASTLE and M. JOHN PERKINS

Department of Chemistry, Royal Holloway and Bedford New College, University of London, Egham, Surrey TW20 0EX, UK

I. INTRODUCTION

The review[1] by Shine in Klayman and Gunther's 1973 book on organic selenium compounds is punctuated by statements such as '···very little is known about the preparation and chemistry of organoselenium radicals'. It is also clear from that review that there is mechanistic uncertainty about many of the reactions of organoselenium compounds. In many respects little has changed, although analogy with the extensive and relatively well understood organic free-radical chemistry of sulphur has led recently to a small number of key papers in which quantitative kinetic data, or clearly defined synthetic applications, have begun to appear.

The synthetic work depends largely on qualitative ideas. For example, it seems reasonable to assume that Se—H, Se—C and Se—Se bonds are weaker than their counterparts in sulphur chemistry and that one-electron oxidation of organoselenium compounds occurs more readily than does that of the corresponding organosulphur species. Many of these ideas are borne out by qualitative experience, such as the facile air

657

oxidation of the evil-smelling selenols to give diselenides. Some also appear to be backed by quantitative experimental data, such as the first ionization potentials of the dimethyl chalcogenides[2]. On the other hand, values for the strength of the Se—Se bond in organic compounds that differ by 20 kcal mol^{-1} can be found among the pages of these volumes. Even the comment on oxidation of selenols must be viewed in the light of the different pK_a values of selenols; much greater concentrations of the readily oxidized conjugate base are likely to be present in solutions of the more acidic selenols than in those of corresponding thiols.

Despite these words of caution, the qualitative picture seems reasonable and can no doubt be extrapolated to tellurium, for which even less quantitative information is available.

Analogy with sulphur chemistry suggests that the major emphasis in this chapter will be on selenyl radicals, RSe·, and on their formation (e.g. from diselenides and selenols) and this is reflected in Section II. Almost equally important, however, is Section III on S_H2 reactions[3] at selenium, in which radical attack proceeds (at least in some cases) via a discrete selenuranyl radical (1) which then dissociates.

$$Y· + R_2Se \rightarrow R_2\overset{·}{Se}Y \rightarrow R· + RSeY$$

$$(1)$$
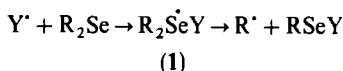
Section IV describes S_{RN} processes involving selenium radicals, and Section V briefly considers α-selenoalkyl radicals. There is special interest here in examples in which the radical centre also carries an electron-withdrawing group, for which 'capto-dative' stabilization appears to be important.

The emphasis throughout this chapter is on organic reactions involving selenium- or tellurium-containing radicals. Structure and spectroscopic properties (ESR) are formally addressed elsewhere. Therefore, relatively scant attention is given to radicals RSeO$_2$· and RSeO· in the final section (Section VI), since there seems to be little documented 'organic chemistry' for these species.

II. SELENYL RADICALS (RSe·)

A. From Diselenides

Studies of the thermolysis and photolyis of diselenides have been largely mechanistic in intent, with a central question being the relative importance of C—Se versus Se—Se bond fission. Little chemistry of a preparative nature has been described.

Whilst the pyrolytic equilibration of monomeric and polymeric trimethylene di-selenide[4], $(CH_2)_3Se_2$ (equation 1), is suggestive of a weak Se—Se bond, the bulk of the reaction may well involve an S_H2 chain process rather than diradical intermediates. On the other hand, there seems little doubt that photolysis of diselenides does produce selenyl radicals. Experiments[5] in which solutions of dimethyl diselenide were directly photolysed in the cavity of an ESR spectrometer failed to reveal methylselenyl radicals but, in the presence of a nitrone spin trap (for a review of spin trapping, see Ref. 6), or of di-*tert*-butyl selenoketone, spin adducts 2 and 3, respectively, were easily detected. The spectrum of the spin adduct 2 showed no ^{77}Se satellites, but had an unusually high g-factor attributable to the presence of selenium.

$$\text{(1)}$$

$$MeSeSeMe \xrightarrow{h\nu} 2\ MeSe^{\bullet}$$

$$\xrightarrow{PhCH=NBu^{\prime}} \quad \underset{(2)}{\overset{MeSe}{\underset{}{PhCHN}}}\diagdown \overset{O^{\bullet}}{Bu^{\prime}}$$

$$\xrightarrow{(Bu^{\prime})_2C=Se} \quad (Bu^{\prime})_2\overset{\bullet}{C}SeSeMe \qquad (3)$$
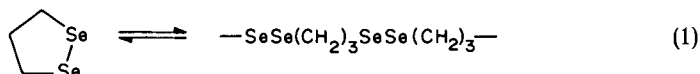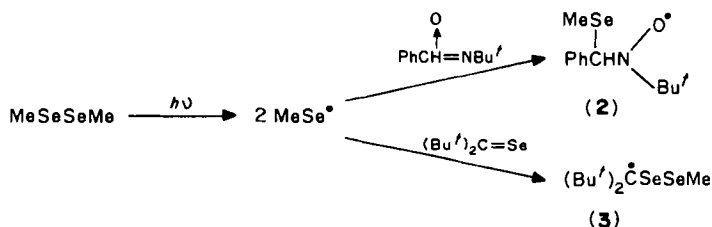
Spin trapping has also been employed to examine the photolytic scission of diphenyl and dibenzyl diselenides[7]. Using nitrosodurene, compelling evidence for scission of the former to give PhSe$^{\bullet}$ was presented; in this case the spectrum of the spin adduct (4) ($a_N = 18.5\ G$) shows not only a very high g-value (2.0099) but also well resolved ^{77}Se satellite lines.

(4)
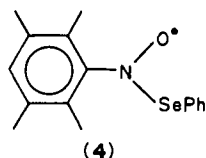
In contrast, dibenzyl diselenide gave only spin adducts of the benzyl radical. Earlier workers had already suggested[8] that both C—Se and Se—Se scission occur competitively when this diselenide is exposed to ultraviolet light. Photoreaction in an inert atmosphere gives quantitative yields of dibenzyl selenide and red selenium, while benzyl chloride and benzaldehyde are among the products of reaction in the presence of CCl_4 and O_2, respectively. Analogous products have been identified from the photolysis of dibenzyl ditelluride in the presence and absence of oxygen[9]. The products from diselenide photolysis have been accounted for in terms of C—Se scission alone; scission of the weaker Se—Se bond is considered to occur but judged to be a non-productive process.

$$R_2Se_2 \underset{h\nu}{\overset{h\nu}{\rightleftharpoons}} 2\ RSe^{\bullet} \xrightarrow{2R_2Se_2} 2\ R_2Se_2 \ + \ 2\ RSe^{\bullet} \quad \text{(Identity reaction)}$$

$$\downarrow$$

$$R_2Se_2$$

$$R_2Se_2 \xrightarrow{h\nu} R^{\bullet} + RSe_2^{\bullet} \xrightarrow{2R_2Se_2} RSeSeSeR \ + \ RSeR \ (+2RSe^{\bullet})$$

added CCl_4 or O_2 $\downarrow$

Products

$$RSeSeSeR \to Se_8 \quad \text{Observed products}$$
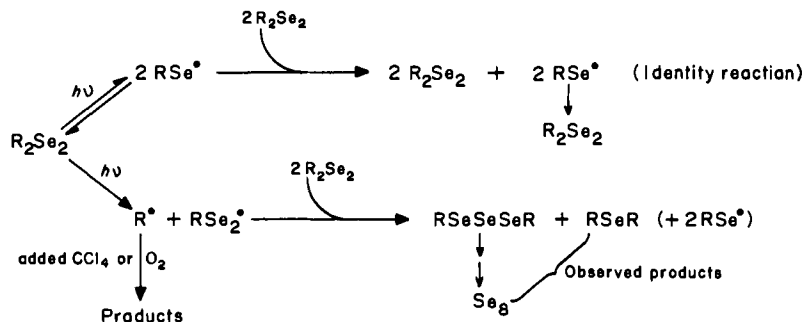
This suggested unimportance of Se—Se scission in the pathway to product formation contrasts with the results of experiments where a trap for the RSe$^{\bullet}$ radical is present. Thus Millington's group[10,11] and also Chu and Marsh[12] studied the photolysis of diselenides (RSeSeR) in the presence of tertiary phosphines (equation 2; Ch = Se) and found similar overall results when R = Me, Ph or PhCH$_2$. They interpreted their findings in terms of the chain reaction shown in Scheme 1 involving a selenophosphoranyl intermediate, and initiated by Se—Se bond fission. Of course, initiation by C—Se fission could, by addition

$$RSeSeR \xrightarrow{h\nu} 2RSe^{\cdot} \qquad\qquad \text{initiation}$$

$$
\left.
\begin{aligned}
RSe^{\cdot} + PMePh_2 &\longrightarrow RSe\overset{\cdot}{P}MePh_2 \\
RSe\overset{\cdot}{P}MePh_2 &\longrightarrow SePMePh_2 + R^{\cdot} \\
R^{\cdot} + RSeSeR &\longrightarrow RSeR + RSe^{\cdot}
\end{aligned}
\right\} \qquad \text{propagation}
$$

<div align="center">SCHEME 1</div>
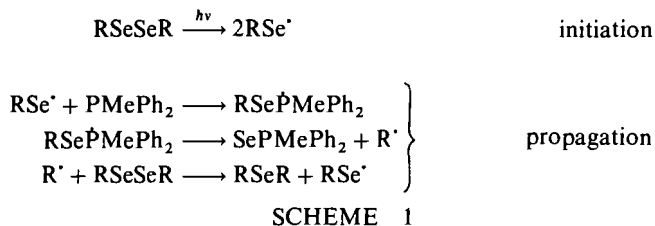
of reaction 3, give stoichiometric formation of the phosphine selenide and RSeR by the same propagation sequence.

$$RChChR + R'_3P \xrightarrow{h\nu} R'_3PCh + RChR \tag{2}$$
$$Ch = S \text{ or } Se$$

$$RSeSe^{\cdot} + PMePh_2 \longrightarrow RSe^{\cdot} + SePMePh_2 \tag{3}$$
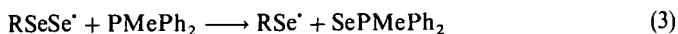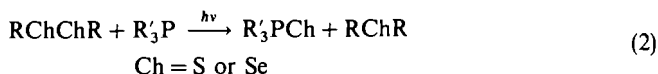
Subsequently, Brown et al.[13] demonstrated a similar photochemical transfer of tellurium from ditellurides to tertiary phosphines (equation 2; Ch = Te).

A CIDNP study[14] of the dibenzyl diselenide/tertiary phosphine system appears to indicate both C—Se and Se—Se fission.

In view of the general similarity between allylic and benzylic systems, the thermal and photochemical stability of dibenzyl telluride[9] contrasts with the instability of bis-3-cyclohexenyl telluride (5); this compound has been observed by NMR but decomposes rapidly in solution to bicyclohexenyl and tellurium[15].

(5)

Other extrusion processes involving tellurium are seen in the formation of diaryls from diaryl tellurium dichlorides, Ar_2TeCl_2[16], or from aryl tellurium trichlorides, $ArTeCl_3$[17], on treatment with degassed Raney nickel.

Bis(diphenylmethyl)diselenide, which must have a particularly weak Se—C bond, decomposes thermally to give sym-tetraphenylethane at 200 °C[18]. Some monoselenide is isolated at lower temperatures, and this appears to be a key primary product; it undergoes thermolysis at 140 °C to give the hydrocarbon, diselenide and selenium as major products.

Trifluoromethylselenyl radicals from photolysis of the corresponding diselenide have been found to displace carbon monoxide from manganese and iron carbonyls[19]. Contrasting behaviour is found with $PhSe^{\cdot}$ (from Ph_2Se_2) and vinyl mercurials, in which attack by $PhSe^{\cdot}$ is apparently not at the metal atom but at the mercury-substituted carbon centre[20]. The products are those of displacement reactions at vinyl carbon (Scheme 2). An alternative mechanism, involving S_H2 displacement of vinyl radicals from mercury, was discounted.

When Ph_2Se_2 is photolysed in the presence of allyltin derivatives an addition–elimination sequence occurs with high efficiency. A chain reaction is propagated by S_H2 displacement of $PhSe^{\cdot}$ from diselenide by the displaced tin radical (Scheme 3)[21].

Discussions of the addition of selenyl radicals to alkenes and alkynes have most frequently drawn examples from reactions of selenols, for which there is in fact usually some mechanistic uncertainty. The position is much clearer where the photolysis of

$$Ph_2Se_2 \xrightarrow{h\upsilon} 2\,PhSe^{\bullet}$$

$$PhSe^{\bullet} + RCH = CHHgHal \longrightarrow R\overset{\bullet}{C}H - \underset{SePh}{\overset{\overset{\displaystyle HgHal}{\diagup}}{C}H}$$

$$RCH = CHSePh + {}^{\bullet}HgHal$$

$${}^{\bullet}HgHal + Ph_2Se_2 \longrightarrow HalHgSePh + PhSe^{\bullet}$$

<div align="center">SCHEME   2</div>

$$PhSeSePh \xrightarrow{h\upsilon} 2PhSe^{\bullet}$$

$$PhSe^{\bullet} + RCH = CHCH_2SnBu_3 \longrightarrow PhSeCH(R)CH = CH_2 + Bu_3Sn^{\bullet}$$

$$Bu_3Sn^{\bullet} + Ph_2Se_2 \longrightarrow Bu_3SnSePh + PhSe^{\bullet}$$
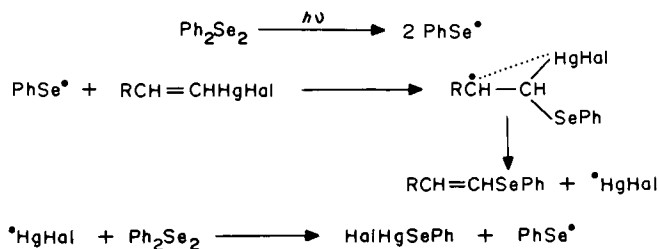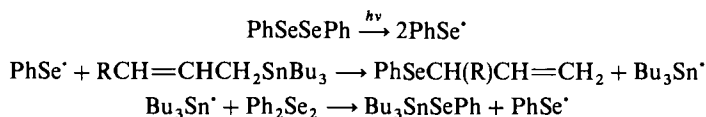
<div align="center">SCHEME   3</div>

diselenides is used as a source of authentic selenyl radicals. Although radical adducts of MeSe$^{\bullet}$ to 1,1-di-*tert*-butylethene could not be observed by ESR[5], a flash photolysis study[22] of diphenyl diselenide in the presence of various vinyl monomers has yielded not only rate data for addition of PhSe$^{\bullet}$ to these substrates but also for the facile reverse of this reaction, i.e. fragmentation of the adducts. The experiments involved direct observation of the transient absorption of PhSe$^{\bullet}$ at 490 nm. The self-reaction of this species in CCl$_4$ was found to have a second-order rate constant of 7×10^9 l mol^{-1} s^{-1} at 23 °C. Although this bimolecular decay is unaffected by the presence either of oxygen or of an alkene, its rate is reduced when both are present together; the (reversibly formed) adducts with the vinyl monomers may be intercepted by oxygen (Scheme 4). Kinetic analysis yields values for k_1 and the ratio k_{-1}/k_2. Selected values are given in Table 1. The rates of PhSe$^{\bullet}$ addition were consistently between one and two orders of magnitude lower than those for the corresponding addition reactions of PhS$^{\bullet}$. Hexane, like CCl$_4$, was found to be inert towards PhSe$^{\bullet}$.

$$PhSe^{\bullet} + CH_2 = CHX \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} PhSeCH_2\overset{\bullet}{C}HX$$

$$PhSeCH_2\overset{\bullet}{C}HX + O_2 \xrightarrow{k_2} PhSeCH_2CHX$$

$$\underset{\underset{\text{products}}{O - O^{\bullet}}}{|}$$
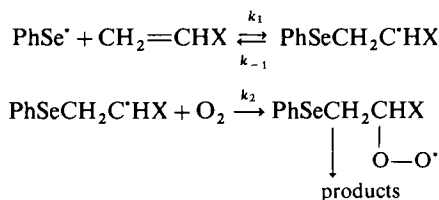
<div align="center">SCHEME   4</div>

TABLE 1. Rate data for Scheme 4

X	k_1 (l mol^{-1} s^{-1})	k_{-1}/k_2 (mol l^{-1})
Ph	2.2×10^6	$3.1 + 10^{-2}$
CN	1.4×10^4	1.8×10^{-2}
EtO	1.5×10^4	5.9×10^{-3}
AcO	$\sim 10^3$	—

Diaryl diselenides will also undergo an apparent homolysis under the influence of Group III halides[23,24]. Thus, with $AlBr_3$ ESR signals attributed to both $[ArSe_2AlBr_3]^{\cdot}$ and $[ArSeAlBr_3]^{\cdot}$ have been detected, both of which are persistent in the absence of oxygen and moisture. Hydrolysis yields Ph_2Se_2 (50%), Ph_2Se (43%) and Ph_2 (7%); neither benzeneselenol nor bromobenzene was detected.

B. From Selenols

In contrast to the largely mechanistic studies described above for diselenides, examples of the use of selenols in radical-mediated chemistry are generally of synthetic utility, and the intermediacy of selenyl radicals is presumed (albeit with sound chemical reasoning on occasions) rather than proved.

The mechanistic ambiguity of selenol additions to carbon—carbon multiple bonds was addressed by Shine[1]. Several more recent examples seem to proceed by unambiguous radical mechanisms. Benzeneselenol undergoes nucleophilic (Michael) addition to $PhC{\equiv}CCO_2Et$ under basic conditions to give 6 (predominantly the Z-isomer), but reacts by radical addition under neutral conditions to give 7 (stereochemistry not assigned)[25]. Earlier workers had apparently made an incorrect structural assignment to the product of the neutral reaction[26].

$$PhSeH \;+\; PhC{\equiv}CCO_2Et$$

base →
$$\overset{\displaystyle SeAr}{\underset{(6)}{PhC{=}CHCO_2Et}}$$

neutral →
$$PhCH{=}C\overset{\displaystyle CO_2Et}{\underset{SePh}{}}$$
(7)
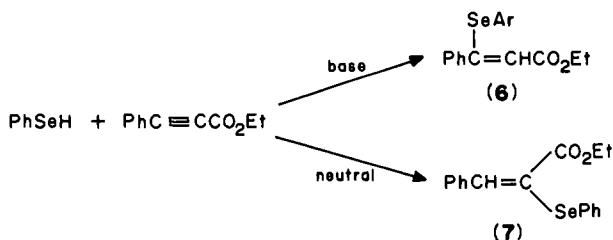
A clear distinction has also been reported between base-promoted and neutral attack of benzeneselenol on alkene 8[27]. Addition to other alkynes has been found to be complicated by reversibility[28]; for example, neat PhSeH with 1-phenylbutyne gives nearly pure (Z)-9 on reaction at 50 °C in the absence of base, but at 120 °C the Z/E ratio approaches unity and the monomeric alkene 10 is an additional product. Under these latter reaction conditions (sealed tube, 120 °C), pure (Z)-9 was found to isomerize to a Z–E mixture, but no comment was made on whether or not alkene 10 also formed in this control experiment. There is also no discussion of how it might arise in the selenol reactions. It seems likely that 9 is indeed an intermediate in the formation of 10.

$$PhSeH \;+\; CH_2{=}CHCH\overset{\displaystyle O}{\diagup\!\!\diagdown}CH_2$$
(8)

base →
$$\underset{OH}{\overset{}{CH_2{=}CHCHCH_2SePh}}$$

neutral →
$$PhSeCH_2CH{=}CHCH_2OH$$

$$CH_3CH_2C{\equiv}CPh \xrightarrow{\;PhSeH\;} \underset{(9)}{CH_3CH_2\overset{\displaystyle SePh}{C}{=}CHPh} \left(+ \underset{(10)}{CH_3CH{=}\overset{\displaystyle SePh}{C}CH_2Ph} \right)$$
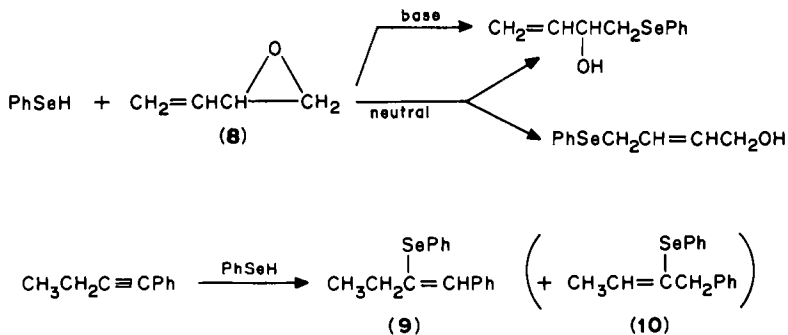
Photo-initiated additions of $Et_3M—SeH$, where $M = Si$ or Ge, to a variety of alkenes have also been reported[29].

The ease of oxidation of selenols has prompted investigation of the use of these compounds as reducing agents. In various successful examples diselenides are produced but, as is so often the case, there is no compelling evidence for radical involvement. One of the oldest examples is reduction of disulphides to thiols (equation 4). This may be effected with stoichiometric amounts of selenol, or by using catalytic amounts of selenol or diselenide and a suitable reagent which will effect the reduction of diselenide to selenol, such as hypophosphorous acid[30]. The catalytic system is also effective with sulphoxides[30]. Neither disulphides nor sulphoxides are reduced by hypophosphorous acid alone. The efficient deoxygenation of a cephalosporin S-oxide by stoichiometric amounts of PhSeH is indicative of the mildness of this procedure[31]. Sulphoxides have also been reduced by O,O-diethyl hydrogen phosphoroselenate[32], and by the Se—B heterocycle 11[33], but there has been little speculation on the mechanisms of these reactions[32,34].

$$R_2S_2 + 2R'SeH \longrightarrow 2RSH + R'_2Se_2 \qquad (4)$$
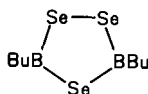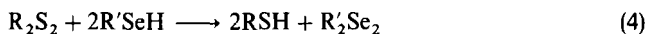
(11)

The reaction of diazonium salts with iodide ion is generally considered to be initiated by electron transfer (equation 5); this is followed by reactions of the derived aryl radicals. When diazonium decomposition is promoted by hydrogen iodide, reduction products can be isolated[35]. Diazonium decomposition may also be brought about by $ArSe^-$ and this affords a recognized route to unsymmetrical diaryl selenides (equation 6)[36]. When a suspension of p-$ClC_6H_4N_2{}^+BF_4{}^-$ in dichloromethane–acetone (10:1) is treated with PhSeH there is rapid evolution of nitrogen and formation of chlorobenzene and p-chlorophenyl phenyl selenide[37]. The mechanism outlined in Scheme 5 was suggested. Very different chemistry results when the solvent is dichloromethane alone. In this case there is no evolution of nitrogen, and a solid remains in suspension. Diphenyl diselenide is formed, however, and the suspended solid is transformed quantitatively to hydrazinium fluoroborate (equation 7). Whilst the reaction in the presence of acetone seems to be a straightforward free-radical process, the reaction in its absence, although synthetically useful, is less easily understood. Possibly the influence of the acetone is to change the redox potentials of species present in the system; in its absence a species $ArN{=}NSePh$ may be sufficiently long-lived to be reduced by hydrogen atom transfer from the selenol. It is known that azobenzene is easily reduced to hydrazobenzene[30].

$$ArN_2{}^+ + I^- \longrightarrow I^{\cdot} + [ArN_2{}^{\cdot}] \longrightarrow Ar^{\cdot} + N_2 \qquad (5)$$

$$ArN_2{}^+ + PhSe^- \longrightarrow ArSePh + N_2 \qquad (6)$$

$$ArN_2{}^+ + PhSeH \longrightarrow Ar^{\cdot} + N_2 + PhSe^{\cdot} + H^+$$
$$Ar^{\cdot} + PhSeH \longrightarrow ArH + PhSe^{\cdot}$$
$$2PhSe^{\cdot} \longrightarrow Ph_2Se_2$$
$$Ar^{\cdot} + PhSeSePh \longrightarrow ArSePh + PhSe^{\cdot}$$

SCHEME   5

$$4PhSeH + PhN_2{}^+BF_4{}^- \longrightarrow 2Ph_2Se_2 + PhNHNH_3{}^+BF_4{}^- \qquad (7)$$
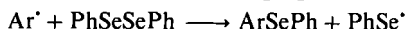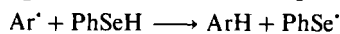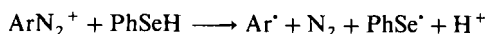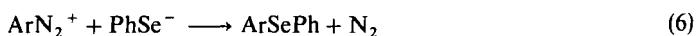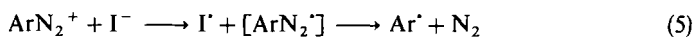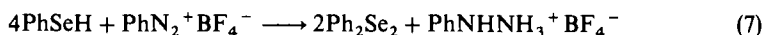
Other reductions by benzeneselenol include the conversion of nitro, nitroso and hydroxylamino groups to amino[38]. These transformations may also be achieved by the use of hydrogen telluride, H_2Te[39], which will also reduce aromatic and aliphatic aldehydes to alcohols[40,41]. Benzenetellurol has recently been employed for these reactions[42] and, for aromatic nitro compounds, reduction has been made catalytic in tellurol by the use of sodium borohydride as the stoichiometric reducing agent[43].

It has long been known that certain carbon—carbon double bonds may be reduced by selenols, and that hydrogen transfer reductions, e.g. of cinnamic acid by tetralin, may be promoted by diphenyl diselenide[44]. Comparison of this type of behaviour with the use of elemental selenium to dehydrogenate hydroaromatic compounds has been drawn by Orchin and coworkers[45,46], who have had success in using diselenides and other organoselenium compounds for dehydrogenations, and have concluded that $ArSe^\bullet$ is likely to be a key hydrogen acceptor in these reactions.

In related work, simple alkyl radicals generated in the gas phase have been adsorbed on to a freshly deposited film of amorphous selenium; on heating to ca. 150°C the film releases the alkyl radicals and not, as might have been expected, alkylselenyl radicals[47].

The reduction of chalcone by benzeneselenol is promoted by ultraviolet irradiation, and this probably involves photolysis of the initial adduct 12[48]. By analogy, benzyl phenyl selenide is rapidly photoreduced by PhSeH to give toluene.
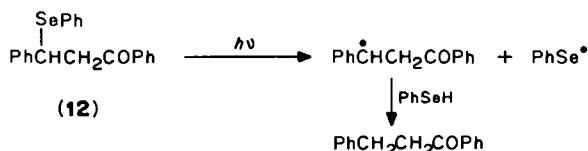
Photoreduction of several compounds containing the C=N group in the presence of benzeneselenol has also been demonstrated[48]. Benzaldehyde oxime gives benzylhydroxyl-amine, and benzylideneaniline gives *N*-benzylaniline. Benzaldehyde phenylhydrazone yields benzylphenylhydrazine, not necessarily via the azo tautomer, since the *N*-methyl derivative (13) is also reduced.

$$PhCH = NNMePh \xrightarrow[\text{PhSeH}]{hv} PhCH_2NHNMePh$$

(13)
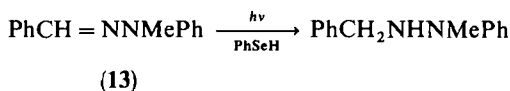
It seems possible that hydrogen atom transfer is involved in most, if not all, of the above reactions, but it must again be stressed that there is little firm evidence for this.

III. S_H2 DISPLACEMENTS AT SELENIUM

In a 1971 book on the S_H2 reaction (substitution, homolytic, bimolecular), Ingold and Roberts[3] were able to report only one example of such a displacement reaction in Group VIA (Se, Te, Po) organometallic compounds. This situation has altered dramatically in recent years and the S_H2 reaction at selenium is now firmly established in a number of synthetic strategies.

Radical attack at selenium proceeds formally via a selenuranyl radical and, in certain cases, this species may be observed directly by ESR. Examples of this include 14 and 15, which were observed in liquid solution and are believed to have the structures indicated[49]. Selenuranyl species have also been detected by ESR in solid matrices at low tempera-

tures[50,51]. The precise fates of **14** and **15** are not clear, but where one of the substituents is weakly bonded it can be expected to break away in a fragmentation step. As we shall see, control of the direction of this fragmentation is the key to the use of the S_H2 reaction in synthesis.

(14)

(15)
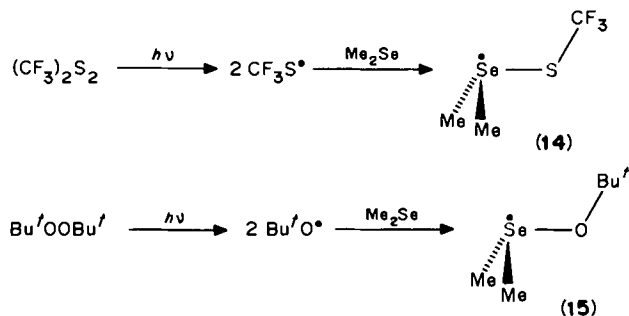
A. Reactions of Monoselenides

There are many methods for elaboration of complex organic structures which depend on the use of selenium-containing reagents. Intermediates are produced incorporating the selenium, which must then be removed. Commonly this is achieved oxidatively via selenoxide elimination, but increasingly a reductive procedure using tin hydrides is being adopted. In this reaction, alkyl phenyl selenides are cleaved to give alkane, presumably by the chain propagation sequence shown in Scheme 6[52]. An application of this procedure is given in Scheme 7[53]; similar chemistry has been deployed by Nicolaou and coworkers[54,55]

$$R'SePh + R_3Sn^{\bullet} \xrightarrow{S_H2} R'^{\bullet} + PhSeSnR_3$$

$$R'^{\bullet} + R_3SnH \longrightarrow R'H + R_3Sn^{\bullet}$$

SCHEME   6

SCHEME   7

SCHEME   8

and Corey et al.[56,49] in syntheses of various lactones, including prostacyclin, in which carboxyl instead of hydroxyl is used as the neighbouring group in the phenylselenation step.

Clive and coworkers[52,57] have extended the reaction to the reduction of selenoketals; this affords a new alternative to the Wolff–Kishner reduction of carbonyl to methylene They have also demonstrated that the phenyltelluryl group may be removed in the same way. In the absence of a radical initiator, such as 2,2'-azobis(2-methylpropionitrile) (AIBN), the reactions with tellurium compounds generally proceed at lower temperatures (ca. 50 °C) than do those of the selenium analogues (ca. 100 °C), but the organotellurium compounds are very sensitive to photolysis, extending the precautions that have to be taken to include working in red light.

Modifications of this hydride procedure whereby the intermediate alkyl radical is intercepted either inter-[58,59] or intra-molecularly[60,61] by addition to an alkene have been developed. The phenylselenyl leaving group in reductive alkylation with methyl acrylate (Scheme 8)[58] proved superior to either iodine or acetoxymercury. In a variation of this intramolecular trapping procedure[59], the alkene group to be appended is present originally in the tin reagent and a simplified chain process involving only two reagents leads to the product (Scheme 9).

Intramolecular examples of this process include the cyclization of 16 where results with different leaving groups were comparable[60]. A final example[61] of this approach shows the use of acrylate esters as lactone precursors (Scheme 10).

The success of the above reactions depends on the efficiency of the attack on selenium by the trialkyltin radicals and the mode of fragmentation of the intermediate selenuranyl radical. Some quantitative estimates of the rates of such S_H2 displacements by $(n\text{-}Bu)_3Sn^\bullet$

$$RSePh \xrightarrow[\text{or AIBN}]{h\nu} R\cdot$$

$$R\cdot + CH_2 = CHCH_2SnBu_3 \longrightarrow RCH_2CH = CH_2 + Bu_3Sn\cdot$$

$$Bu_3Sn\cdot + RSePh \longrightarrow Bu_3SnSePh + R\cdot$$

SCHEME   9

SCHEME   10

are available from the work of Scaiano et al.[62], who found the expected order of reactivity $Me_2Te > Me_2Se > Me_2S$. For $(n\text{-}Bu)_3Sn\cdot + Me_2Se$ at 25 °C in a hydrocarbon solvent, a rate constant of $3.7 \times 10^5 \, l\,mol^{-1}\,s^{-1}$ was determined. Concerning the fragmentation of the $R^1R^2R^3Se\cdot$ intermediate, the substituents are invariably $R^1 = Ph$, $R^2 = $ tin reagent and $R^3 = $ alkyl (sp^3) carbon of the compound to be modified. Preferential scission of the Se— R^3 bond ensures synthetic utility.

B. Reactions with Diselenides

S_H2 reactions of diselenides lead to selenium-containing products (equation 8). In many cases ionic routes to the selenium-containing products are more convenient, but the radical process is often efficient and may permit unusual precursors to be used. A probable early example of this reaction, not recognized as such, involved mercury dialkyls and diselenides which, when heated together in dioxane, gave good yields of unsymmetrical selenide and mercury metal (equation 9)[63].

$$R'' + RSeSeR \longrightarrow R'SeR + RSe\cdot \tag{8}$$

$$R_2Hg + R'_2Se_2 \longrightarrow 2R'SeR + Hg^0 \tag{9}$$
$$R = alkyl$$
$$R' = alkyl \text{ or } aryl$$
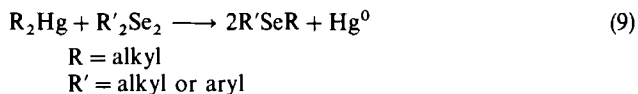
The first example[69] of a thermal S_H2 reaction involving diselenide precursors to be recognized is that sole example reported in the book by Ingold and Roberts[3] and involves the redistribution reactions of dichlorodiselenide with either dimethyl selenide or dimethyl diselenide to give first CH_3Se_4Cl and thence methyl-terminated selenium chains and

elemental selenium by a sequence of condensation plus scrambling reactions. A further early example is the pyrolytic equilibration of monomeric and polymeric trimethylene diselenide, discussed in Section II.A (equation 1).

The final step of Scheme 5 proposes S_H2 displacement on diselenide by an aryl radical. This has been adapted to a convenient and efficient synthesis of unsymmetrical diaryl selenides using copper-promoted decomposition of the diazonium salt in the presence of diphenyl diselenide[65]. When a neighbouring double bond is present, the aryl radical intermediate may be intercepted to give a cyclic product, e.g. 17.

(17)
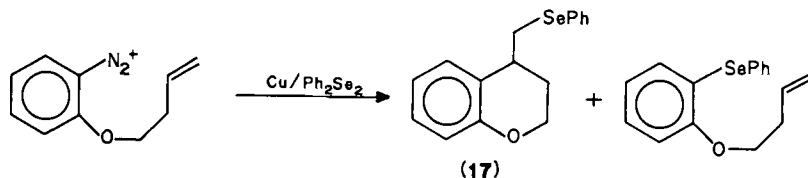
This approach has also been employed as a means of generating bridgehead selenides not accessible by conventional nucleophilic displacement reactions[66]. Thus, lead tetraacetate oxidation of 1-adamantanecarboxylic acid in the presence of diphenyl diselenide gives the unsymmetrical 1-adamantyl phenyl selenide. It was found, however, that a much better yield could be obtained by displacement of trifluoroacetate from 1-adamantyl trifluoroacetate using benzeneselenol. Other leaving groups were ineffective, and an electron-transfer mechanism is suspected.

More recently, a general strategy for synthesizing unsymmetrical disubstituted chalcogenides (19) has been developed by Barton's group[67]. In this, chain decomposition of the readily prepared carboxylate (18) occurs in the presence of the appropriate dichalcogenide. Among the products obtained this way was a bridgehead adamantyl telluride.

(19)
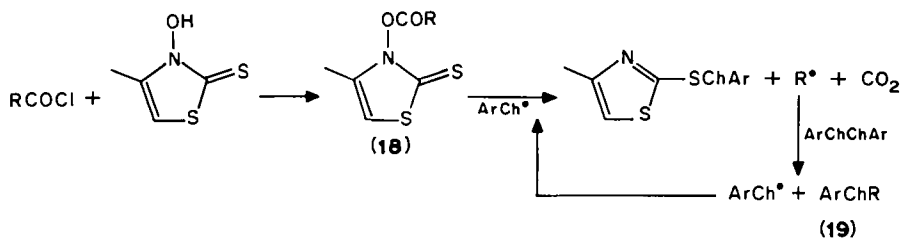
The rate of reaction of Ph_2Se_2 with primary alkyl radicals has been the subject of two independent studies[66,68], both of which used the 5-hexenyl radical 'clock', in which the bimolecular reaction of 5-hexenyl radical (20) with diselenide competes with cyclization, the rate constant (k_1) for which is known. In one investigation, the hexenyl radicals were generated by thermolysis of the corresponding heptenoyl peroxide[66]; the other employed a photoinitiated chain reaction with hexenylmercury(II) halides in which the selenyl radical displaces hexenyl from mercury[68]. In both cases, the rate constant for the bimolecular process (k_2) can then be calculated from a knowledge of the ratio of selenides 21 and 22 and of the concentration of Ph_2Se_2. The values of k_2 are ca. 1×10^7 and $5 \times 10^7 \, \mathrm{l\,mol^{-1}\,s^{-1}}$ for reaction in benzene at 45 and 80 °C, respectively. A value for the corresponding reaction with diphenyl ditelluride at 45 °C is $5 \times 10^7 \, \mathrm{l\,mol^{-1}\,s^{-1}}$[68]. These reactions are preparatively more efficient with the diselenides and ditellurides; reactions of primary alkyl radicals with diphenyl disulphide are significantly slower ($k \approx 10^5 \, \mathrm{l\,mol^{-1}\,s^{-1}}$ at 80 °C)[65,68].

$(C_6H_{11}CO_2)_2 \longrightarrow$ (20) $\xleftarrow[-PhSeHgX]{+PhSe^\bullet} C_6H_{11}HgX$

$k_2 \Big/ Ph_2Se_2$

(21) $\diagdown$ SePh

$CH_2^\bullet$ + PhSe$^\bullet$

$\xrightarrow{Ph_2Se_2}$ CH_2SePh + PhSe$^\bullet$

(22)
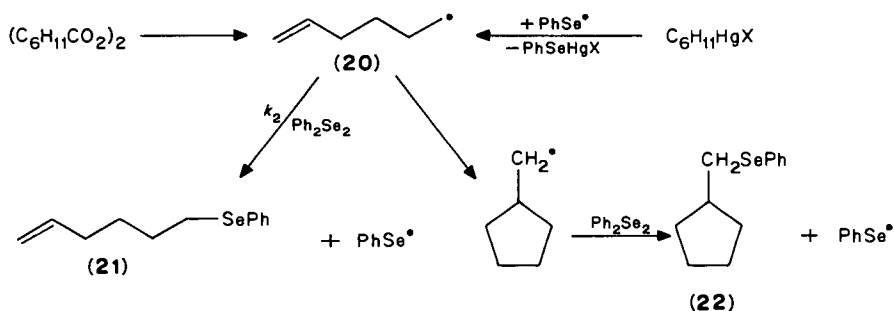
Alkyl cobaloximes will also react with diphenyl diselenide to give the mixed alkyl phenyl selenide[69]. If the alkyl group is attached to cobalt via a chiral carbon then racemization is observed in the product, consistent with a mechanism involving free alkyl radicals.

IV. SELENIUM RADICALS IN S_{RN} SUBSTITUTION PROCESSES

Radical nucleophilic substitution reactions (S_{RN}) of both aliphatic and aromatic systems are now well documented, and many such reactions have been effected with selenium and tellurium nucleophiles. Rossi's group has been particularly active in this field[70,71]. A typical reaction sequence is illustrated in Scheme 11[72], in which the reactions, in liquid ammonia, are stimulated by ultraviolet light. Table 2 shows some representative results.

This is a procedure that is generally satisfactory for the preparation of unsymmetrical diaryl chalcogenides[73,74]; it has also been extended to the use of Se^{2-} and Te^{2-} in

$$ArHal + PhSe^- \xrightarrow[NH_3]{h\nu} [ArHal]^{-\bullet} + PhSe^\bullet \qquad \text{(initiation)}$$

$$[ArHal]^{-\bullet} \longrightarrow Ar^\bullet + Hal^-$$
$$Ar^\bullet + PhSe^- \longrightarrow [PhSeAr]^{-\bullet}$$
$$[PhSeAr]^{-\bullet} + ArHal \longrightarrow PhSeAr + [ArHal]^{-\bullet}$$
$$\text{Overall:} \ ArHal + PhSe^- \longrightarrow PhSeAr + Hal^-$$

propagation
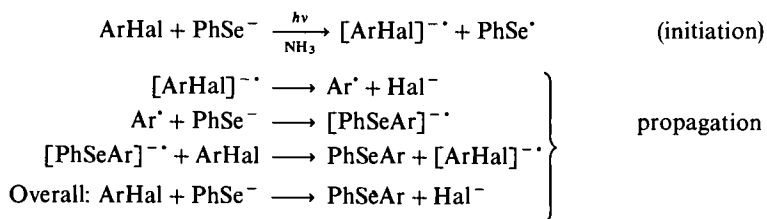
SCHEME 11

TABLE 2. Yields (%) of diaryl chalcogenides (ArChPh; Ch = Se, Te) from the photostimulated reactions ArX + PhCh$^-$ $\longrightarrow$ ArChPh + X$^-$

	PhCh$^-$	
ArX	PhSe$^-$	PhTe$^-$
PhBr	0	0
PhI	–	90
1-Chloronaphthalene	73	37
4-Chlorobiphenyl	52	–
9-Bromophenanthrene	72	–

reactions which can be adjusted to produce either areneselenol, symmetrical diselenide or unsymmetrical diaryl or alkyl aryl selenides (or their tellurium analogues)[75]. A puzzling diversion, reported recently[76], is that a by-product from the PhSe$^-$/PhI reaction is benzene, and that the formation of this is enhanced by a high PhSe$^-$/PhI ratio or by high light intensity. It was suggested that the benzene arises by abstraction of hydrogen by phenyl radicals; however, it is not clear that this is consistent with the overall mechanism, and alternative possibilities should perhaps be considered.

Investigation of the relative reactivities of nucleophiles employed in these studies has provided clear evidence for the reversibility of the formation of [ArChPh]$^{-\cdot}$[77]. Produced from Ar$^\cdot$ and PhCh$^-$, this may cleave to ArCh$^-$ and Ph$^\cdot$. The phenyl radical then reacts to form symmetrical diphenyl chalcogenide. Whether or not significant reversal is encountered is determined by the reduction potentials of the aryl halide and the chalcogen product. Reversal has not been observed when Ch = S and is most important for Ch = Te.

A similar photostimulated displacement of iodide from trifluoromethyl iodide by PhSe$^-$ has also been reported[78].

V. α-SELENOALKYL RADICALS

Hydrogen abstraction by tert-butoxy radicals from dimethyl selenide is more facile than that from saturated alkanes[5], yet whilst in the latter reactions alkyl radicals are detectable by ESR the methylselenomethyl radicals are not. This has been attributed to strong electron interaction with the selenium lone pair, resulting in line broadening by both spin–rotation and spin–orbit mechanisms. In contrast, hindered selenoalkyl radicals formed by radical addition to the selenium atom of di-tert-butyl selenoketone are readily observable[5,79]. They are forced by steric effects to adopt conformations in which there is little interaction of the unpaired electron with the selenium electrons; at low temperatures they exist in equilibrium with diamagnetic dimers. The butoxyl adduct of the selenoketone, t-BuOSeC$^\cdot$(Bu-t)$_2$, decays unimolecularly by fission of the C—O bond to give initially t-Bu$^\cdot$ and the selone oxide. In an interesting extension of this work, Scaiano[80] found that di-tert-butyl selenoketone could be used to intercept triplet Norrish Type II biradicals generated by ultraviolet irradiation of aryl ketone (equation 10).

$$\text{(10)}$$
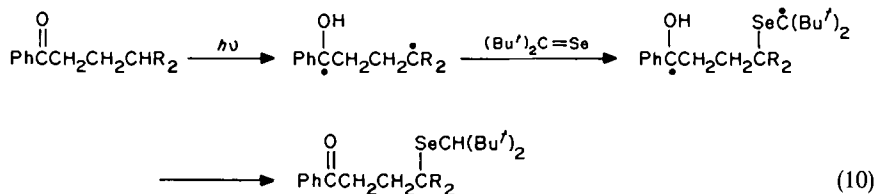
'Captodative' radical stabilization, i.e. stabilization achieved by the simultaneous action of electron-donor and electron-acceptor substituents at the radical centre, is not yet a universally accepted phenomenon. Nevertheless, radical addition, e.g. of cyanopropyl radicals, to α-phenylselenoacrylonitrile (23; X = CN) or to methyl phenylselenoacrylate (23; X = CO$_2$Me) is particularly facile and leads, presumably via the dimer of radical 24 (which is formally captodatively stabilized), to alkene 25[81]. It was suggested that the elimination of Ph$_2$Se$_2$ is initiated by an S_H2 attack on selenium.

VI. OXYSELENIUM AND OXYTELLURIUM SPECIES

We have been unable to locate any organic chemistry to report in this section. Studies by ESR of, for example, PhSeO$^\cdot$ and PhSeO$_2{}^\cdot$ have been described, but not their organic

(23)   (24)

(25)
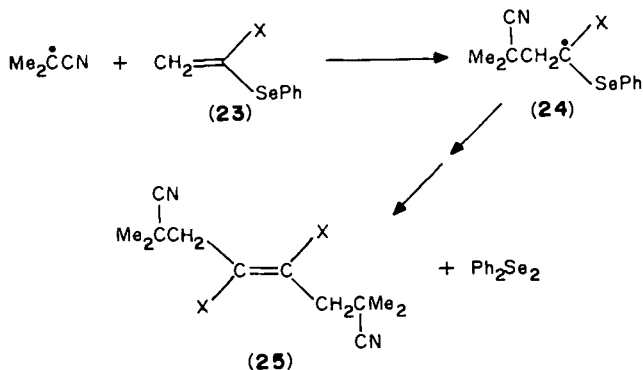
reactions. Benzeneselenenic anhydride has been used extensively as an oxidizing agent, but these reactions are generally written as two-electron processes. Such was the case for the interesting oxidation of N-phenylbenzohydroxamic acid[82], which gives, *inter alia*, the oxygenated product (26), but in unpublished work this system has been found to give intense ESR signals attributable to benzoyl phenyl nitroxide (27). The possibility of one-electron processes in the chemistry of this important oxidant may therefore merit further study.

(26)

(27)
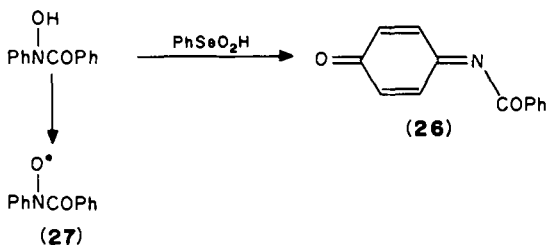
Finally, we are unaware of any selenium or tellurium analogues of the release of methyl radical from dimethyl sulphoxide by HO·.

VII. REFERENCES

1. H. J. Shine, in *Organic Selenium Compounds: Their Chemistry and Biology* (Eds. D. L. Klayman and W. H. H. Gunther), Wiley-Interscience, New York, 1973.
2. G. D. Sturgeon and M. L. Gross, in *The Chemistry of Organic Selenium and Tellurium Compounds* (Eds. S. Patai and Z. Rappoport), Vol. 1, Chapter 7, Section I.A.
3. K. U. Ingold and B. P. Roberts, *Free Radical Substitution Reactions*, Wiley–Interscience, New York, 1971.
4. J. R. Brown, G. P. Gillman and M. H. George, *J. Polym. Sci., Part A*, **5**, 903 (1967).
5. J. C. Scaiano and K. U. Ingold, *J. Am. Chem. Soc.*, **99**, 2079 (1977).
6. M. J. Perkins, *Adv. Phys. Org. Chem.*, **17**, 1 (1980).
7. R. Franzi and M. Geoffroy, *J. Organomet. Chem.*, **218**, 321 (1981).
8. J. Y. C. Chu, D. G. Marsh and W. H. H. Gunther, *J. Am. Chem. Soc.*, **97**, 4905 (1975).
9. H. K. Spencer and M. P. Cava, *J. Org. Chem.*, **42**, 2937 (1977).
10. D. H. Brown, R. J. Cross and D. Millington, *J. Chem. Soc., Dalton Trans.*, 159 (1977).
11. R. J. Cross and D. Millington, *J. Chem. Soc., Chem. Commun.*, 455 (1975).
12. J. Y. C. Chu and D. G. Marsh, *J. Org. Chem.*, **41**, 204 (1976).
13. D. H. Brown, R. J. Cross and D. Millington, *J. Organomet. Chem.*, **125**, 219 (1977).

14. G. Vermeersch, N. Febvay-Garot, S. Caplain, A. Couture and A. Lablanche-Combier, *Tetrahedron Lett.*, **7**, 609 (1979).
15. D. L. J. Clive, P. C. Anderson, N. Moss and A. Singh, *J. Org. Chem.*, **47**, 1641 (1982).
16. G. Bergman, *Tetrahedron*, **28**, 3323 (1972).
17. J. Bergman and L. Engman, *Tetrahedron*, **36**, 1275 (1980).
18. J. Y. C. Chu and J. W. Lewicki, *J. Org. Chem.*, **42**, 2491 (1977).
19. M. K. Chaudhuri, A. Haas and A. Wensky, *J. Organomet. Chem.*, **116**, 323 (1976).
20. G. A. Russell and J. Hershberger, *J. Am. Chem. Soc.*, **102**, 7603 (1980).
21. G. A. Russell and L. L. Herold, *J. Org. Chem.*, **50**, 1037 (1985).
22. O. Ito, *J. Am. Chem. Soc.*, **105**, 850 (1983).
23. I. P. Romm, I. V. Olifirenko, E. N. Guryanova, V. V. Troitskii, V. A. Chernoplekova, L. M. Kataeva and E. G. Kataeva, *Zh. Obshch. Khim.*, **53**, 477 (1983).
24. I. V. Olifirenko, I. P. Romm, E. N. Guryanova, V. V. Troitskii, L. M. Kataeva, V. A. Chernoplekova and E. G. Kataeva, *J. Organomet. Chem.*, **265**, 272 (1984).
25. D. H. Wadsworth and M. R. Detty, *J. Org. Chem.*, **45**, 4611 (1980).
26. J. Gosselck and E. Wolters, *Chem. Ber.*, **95**, 1237 (1962).
27. G. I. Zaitseva and V. M. Al'bitskaya, *J. Org. Chem. USSR*, **4**, 1987 (1968).
28. J. V. Comasseto and J. T. B. Ferreira, *J. Organomet. Chem.*, **216**, 287 (1981).
29. N. S. Vyazankin, M. N. Bochkarev and L. P. Maiorova, *Zh. Obshch. Khim.*, **39**, 468 (1969).
30. W. H. H. Gunther, *J. Org. Chem.*, **31**, 1202 (1966).
31. M. J. Perkins, B. V. Smith, B. Terem and E. S. Turner, *J. Chem. Res. (S)*, 341 (1979).
32. D. L. J. Clive, W. A. Kiel, S. M. Menchen and C. K. Wong, *J. Chem. Soc., Chem. Commun.*, 657 (1977).
33. D. L. J. Clive and S. M. Menchen, *J. Chem. Soc., Chem. Commun.*, 168 (1979).
34. M. Mikolajczyk, *Chem. Ind. (London)*, 2059 (1966).
35. D. H. Hey, G. H. Jones and M. J. Perkins, *J. Chem. Soc., Chem. Commun.*, 1375 (1969).
36. L. Chieriu and R. Passerini, *Boll. Sci. Fac. Chim. Ind. Bologna*, **12**, 56 (1954).
37. F. G. James, M. J. Perkins, O. Porta and B. V. Smith, *J. Chem. Soc., Chem. Commun.*, 131 (1977).
38. K. Fujimori, H. Yoshimoto and S. Oae, *Tetrahedron Lett.*, 4397 (1979).
39. L. Engman, *Acc. Chem. Res.*, **18**, 274 (1985).
40. N. Kambe, K. Kondo, S. Morita, S. Murai and N. Sonoda, *Angew. Chem., Int. Ed. Engl.*, **19**, 1009 (1980).
41. N. Kambe, K. Kondo and N. Sonoda, *Angew. Chem., Int. Ed. Engl.*, **19**, 1009 (1980).
42. M. Akiba and M. P. Cava, *Synth. Commun.*, **14**, 1119 (1984).
43. N. Ohira, Y. Aso, T. Otsubo and F. Ogura, *Chem. Lett.*, 853 (1984).
44. S. Morimoto, *J. Chem. Soc. Jpn.*, **75**, 557 (1954).
45. H. A. Silverwood and M. Orchin, *J. Org. Chem.*, **27**, 3401 (1962).
46. E. J. Levi and M. Orchin, *J. Org. Chem.*, **31**, 4302 (1966).
47. S. A. Zavyalov, I. A. Myasnikov and E. E. Gutman, *Zh. Fiz. Khim.*, **53**, 1303 (1979).
48. M. J. Perkins, B. V. Smith and E. S. Turner, *J. Chem. Soc., Chem. Commun.*, 977 (1980).
49. J. R. M. Giles, B. P. Roberts, M. J. Perkins and E. S. Turner, *J. Chem. Soc., Chem. Commun.*, 504 (1980).
50. M. Geoffrey, *J. Chem. Phys.*, **70**, 1497 (1979).
51. R. Franzi, M. Geoffrey, L. Givet and V. Leray, *J. Phys. Chem.*, **83**, 2898 (1979).
52. D. L. J. Clive, G. Chittattu and C. K. Wong, *J. Chem. Soc., Chem. Commun.*, 41 (1978).
53. K. C. Nicolaou, R. L. Magolda, W. J. Spiro, W. E. Barnette, Z. Lysenko and M. M. Joullie, *J. Am. Chem. Soc.*, **102**, 3784 (1980).
54. K. C. Nicolaou, G. P. Gasic and W. E. Barnette, *Angew. Chem., Int. Ed. Engl.*, **17**, 293 (1978).
55. K. C. Nicolaou, S. P. Seitz, W. J. Spiro and J. F. Blount, *J. Am. Chem. Soc.*, **101**, 3884 (1979).
56. E. J. Corey, H. L. Pearce, I. Szekely and M. Ishiguro, *Tetrahedron Lett.*, 1023 (1978).
57. D. L. J. Clive, G. J. Chittattu, V. Farina, W. A. Kiel, S. M. Menchen, C. G. Russell, A. Singh, C. K. Wong and N. J. Curtis, *J. Am. Chem. Soc.*, **102**, 4438 (1980).
58. S. D. Burke, W. F. Fobare and D. M. Armistead, *J. Org. Chem.*, **47**, 3348 (1982).
59. G. E. Keck and J. B. Yates, *J. Am. Chem. Soc.*, **104**, 5829 (1982).
60. M. D. Bachi and C. Hoornaert, *Tetrahedron Lett.*, **22**, 2693 (1981).
61. D. L. J. Clive and P. L. Beaulien, *J. Chem. Soc., Chem. Commun.*, 307 (1983).
62. J. C. Scaiano, P. Schmid and K. U. Ingold, *J. Organomet. Chem.*, **121**, C4 (1976).
63. Y. Okamoto and T Yano, *J. Organomet. Chem.*, **29**, 99 (1971).

64. D. Grant and J. R. Van Wazer, *J. Am. Chem. Soc.*, **86**, 3012 (1964).
65. P. Bishop, *PhD Thesis*, London, 1985.
66. M. J. Perkins and E. S. Turner, *J. Chem. Soc., Chem. Commun.*, 139 (1981).
67. D. H. R. Barton, D. Bridon and S. Z. Zard, *Tetrahedron Lett.*, **25**, 5777 (1984).
68. G. A. Russell and H. Tashtoush, *J. Am. Chem. Soc.*, **105**, 1398 (1983).
69. J. Deniau, K. N. V. Duong, A. Gaudener, P. Bougeard and M. D. Johnson, *J. Chem. Soc., Perkin Trans. 2*, 393 (1981).
70. R. A. Rossi, *Acc. Chem. Res.*, **15**, 164 (1982).
71. R. A. Rossi, *J. Chem. Educ.*, **59**, 310 (1982).
72. A. B. Pierini and R. A. Rossi *J. Org. Chem.*, **44**, 4667 (1979).
73. A. B. Pierini and R. A. Rossi, *J. Organomet. Chem.*, **144**, C12 (1978).
74. A. B. Pierini and R. A. Rossi, *J. Organomet. Chem.*, **168**, 163 (1979).
75. R. A. Rossi and A. B. Penenory, *J. Org. Chem.*, **46**, 4580 (1981).
76. A. B. Penenory, A. B. Pierini and R. A. Rossi, *J. Org. Chem.*, **49**, 3834 (1984).
77. A. B. Pierini, A. B. Penenory and R. A. Rossi, *J. Org. Chem.*, **49**, 486 (1984).
78. V. G. Voloshocnuk, V. N. Bioko and L. M. Yagupolskii, *Zh. Org. Khim.*, **13**, 2008 (1977).
79. J. C. Scaiano and K. U. Ingold, *J. Chem. Soc., Chem. Commun.*, 205 (1976).
80. J. C. Scaiano, *J. Am. Chem. Soc.*, **99**, 1494 (1977).
81. Z. Janousek, S. Piettre, F. Gorissen-Hervens and H. G. Viehe, *J. Organomet. Chem.*, **250**, 197 (1983).
82. T. Frejd and K. B. Sharpless, *Tetrahedron Lett.*, 2239 (1978).

CHAPTER **17**

Synthesis of selenium and tellurium ylides and carbanions: application to organic synthesis*

A. KRIEF

Universitaires Notre-Dame Facultés de la Paix, Namur, Belgium

*This contribution involves the work published prior to 1985.

I. α-SELENOORGANOMETALLICS: SYNTHESIS AND SYNTHETIC USEFULNESS

A. General Aspects

When present in organic molecules, the Se atom confers on them unique properties[1-8]. These properties result from the location of Se in the Periodic Table in the neighbourhood of C and Br, two atoms which play an important role in organic chemistry.

The C—Se bond (243 kJ mol^{-1}) is weaker than the C—S bond (272 kJ mol^{-1}) and the C—Br bond (285 kJ mol^{-1}). On the other hand the electronegativity* of Se (2.55) is very close to that of C (2.55) (S 2.58, Br 2.96).

1. Reactivity of selenides

Selenides are usually stable compounds. They are however transformed selectively to several other functional groups by use of the proper reagents.

The high nucleophilicity and oxidizability of the Se atom plays an important role in the reactivity of selenides and functionalized selenides. These properties are usually not observed with alkyl bromides and are much more pronounced than those found in sulphides[7,9], two types of molecules possessing a heteroatom located in the Periodic Table of elements in the neighbourhood of the Se atom. The electrophilicity of the Se atom in selenides allows valuable synthetic transformations. The same type of electrophilicity is often observed in the case of alkyl bromides (i.e. halogen–metal exchange) but is unusual for sulphides[8].

The electrophilic properties of the Se atom in selenides is probably due to the presence of low-energy, unoccupied 4d orbitals. These are responsible for the unusual reactivity of alkyllithiums which cleave the C—Se bond of selenides rather than metalate them[8,10-12]

---

*These values refer to Pauling's method [A. L. Albred, *J. Inorg. Nucl. Chem.*, **17**, 215 (1961)]. Other methods give C 250, Se 248 [Albred–Rochow values; *J. Inorg. Nucl. Chem.*, **5**, 264 (1958)] and C 263, Se 233 [Mulliken-type values H. O. Pritchard and H. A. Skinner, Journal, **55**, 745 (1955)].

$$PhSeMe + BuLi \rightarrow [PhLi] + BuSeMe$$
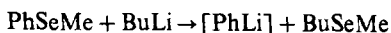
n-BuLi: ether, reflux/19 h	30%	(as PhCOOH after carbonation)[10]
n-BuLi: THF/hexane, 20°C/0.5 h	93%[a]	(as Ph_2CHOH after reaction with $PhCH{=}O$)[11]
n-BuLi: THF/hexane, -78°C/1.3 h	20%[a]	(as Ph_2CHOH after reaction with $PhCH{=}O$)[12]
n-BuLi: THF/hexane, -50°C/1.75 h	89%	(as Ph_2CHOH after reaction with $PhCH{=}O$)[12]
s-BuLi: ether/hexane, -50°C/1.5 h	57%[b]	(as Ph_2CHOH after reaction with $PhCH{=}O$)[12]
t-BuLi: ether/hexane, -78°C/1.5 h	81%[a]	(as Ph_2CHOH after reaction with $PhCH{=}O$)[12]
n-BuLi: ether/hexane, -50°C/1.5 h	10%[c]	(as Ph_2CHOH after reaction with $PhCH{=}O$)[12]

[a] These reactions have also been followed by ^{77}Se-NMR: the time given is the minimum required for complete reaction at that temperature.
[b] 41% recovery of the starting selenide.
[c] 88% recovery of the starting selenide.

SCHEME 1

(Scheme 1) as observed in sulphides[8,10]. Since metalloamides are not strong enough to metalate dialkyl or phenylalkyl selenides (α-seleno carbanions are less stabilized than their thio analogues)[13], these are not valuable starting materials for the synthesis of α-selenoalkyllithiums[8]. The Se–metal exchange is less easy than the Br–metal exchange but several orders of magnitude faster than the S–metal exchange in sulphides[8].

· Selenides can be reduced to alkanes with Raney nickel[14], lithium in ethylamine[14] or tin hydrides[15,16,221] more efficiently than sulphides[16] (Scheme 2).

$$C_{11}H_{23}CH(SeR)Me \rightarrow C_{11}H_{23}CH_2Me \qquad (a)$$
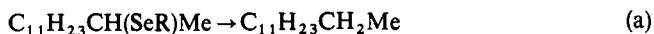
R = Ph, Me: Raney Ni/ethanol, 80°C/24 h   65%[14]
R = Ph, Me: Li/EtNH$_2$, -10°C/2 h   80%[14]

(Ref. 15)   (b)
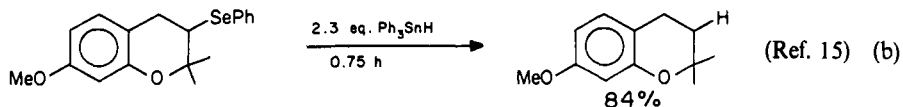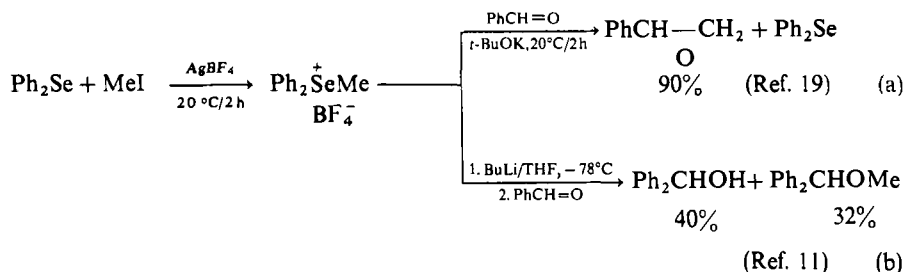
SCHEME 2

SCHEME 3

They are very good complexing agents for metal ions[3] and powerful nucleophiles. Selenonium salts are therefore readily available on reaction with halogens[17,18] or alkyl halides[3,17,19], dialkyl sulphates[19] or alkyl fluorosulphonates[20] (Schemes 3 and 4).
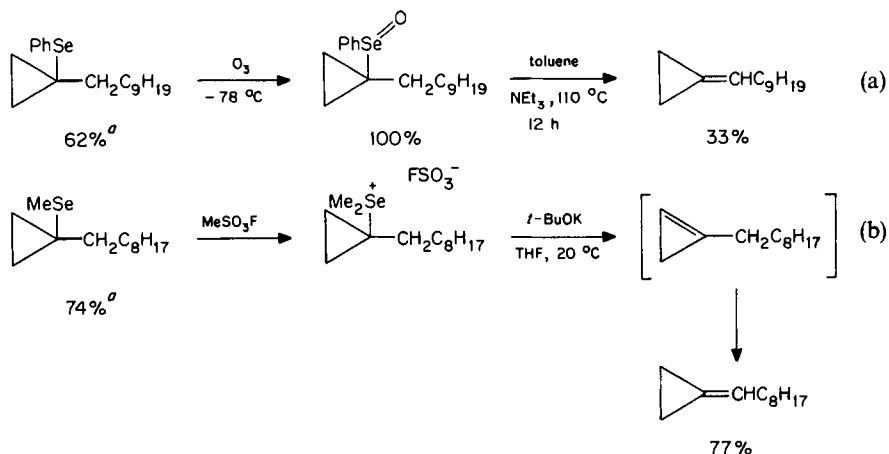
^{a} This yield refers to the synthesis of the compound by formation of the bond shown by a heavy line.

SCHEME 4[20]

Selenides are easily oxidized to selenoxides[3,6,8] under a large variety of conditions (see Section i.e. 3a and Schemes 4a and 7). The overoxidation to selenone has been described as being particularly difficult[5,6]. It was however recently shown in the author's laboratory that under suitable conditions (m-chloroperbenzoic acid or $KMnO_4$, 20 °C) selenones can be obtained in good yield*.

Selenonium salts and selenoxides are more prone to metalation than selenides. t-BuOK in DMSO and KOH in water under phase-transfer catalysis are strong enough to allow the hydrogen–metal exchange in selenonium salts[11,19,20] (Scheme 3a). In the case of selenoxides metalation has been achieved[21,22] with LDA in THF even at $-78\,°C$ (Scheme 5). Again alkyllithiums do not act as bases and react on the Se atom of these derivatives leading, for example, in the case of n-BuLi and diphenylmethylselenonium fluoroborate to an exchange of ligand on the Se atom producing phenyllithium[11]. This is further trapped
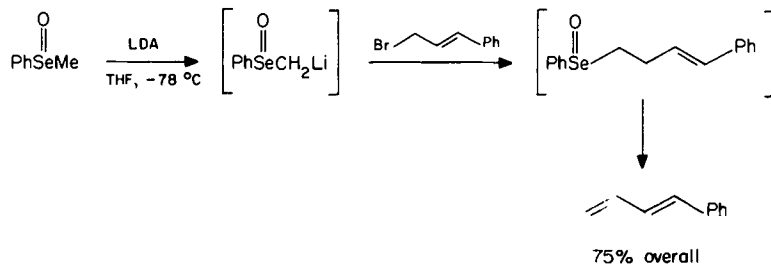
SCHEME 5[22]

*A. Krief and J. N. Denis, unpublished results. It was in several instances noticed[3-6,8] that selenides are much more easily oxidized to selenoxides than sulphides are to sulphoxides, but that the reverse was found in further oxidation to selenone and sulphone.

by addition of benzaldehyde to the medium and results in the formation of diphenylcar-binol (Scheme 3b).

Compounds possessing a positively charged Se atom are valuable derivatives in which the selenyl moiety becomes a good leaving group. Hence they have been used for a variety of substitution or elimination reactions:

(a) Selenonium salts are very good precursors of alkyl iodides, chlorides or bromides. For example, selenides react with bromine at room temperature in CH_2Cl_2 producing instantaneously selenonium salts which decompose slowly (2 h) to alkyl bromides[17,18] in the presence of triethylamine. The reaction is highly stereoselective and occurs with complete inversion of configuration at the substituted carbon atom[18] (Scheme 6). Similar transformations have been achieved[23] from selenoxides and hydrochloric or hydrobromic acids.

90 % (stereochemical purity 95.5)
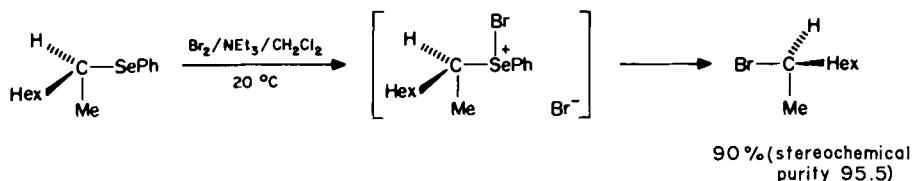
SCHEME 6[18]
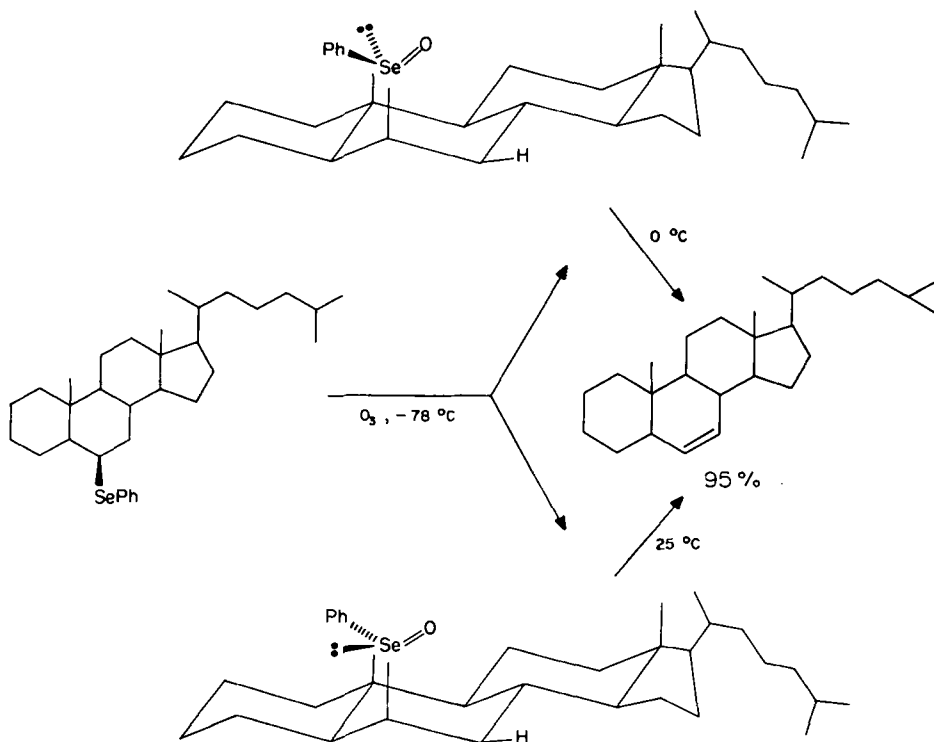
SCHEME 7[26]

(*b*) Elimination reactions leading to olefins have also been specifically achieved from selenoxides[2,4-6,8,27,28] and selenonium salts[8,20,24,25] (Schemes 4, 5, 7 and 8). Since the discovery, by Jones and coworkers[26] (Scheme 7), and development of the method simultaneously by Sharpless[2,27], Reich[5,6] and Clive[4], the selenoxide elimination leading to olefins has been frequently used for the total synthesis of natural products[28] (Scheme 8). This reaction has contributed much to the development of the chemistry of organoselenium compounds. Selenoxides decompose thermally to produce olefins in high yield. The reaction is analogous to the aminoxide and sulphoxide elimination reactions[29], but whereas these occur respectively at 260° and 160 °C, the selenoxide elimination takes place even at 20 °C. The stereochemistry of the reaction has been determined and the elimination of selenenic acid is found to occur in a *syn* fashion[27] (Scheme 8).
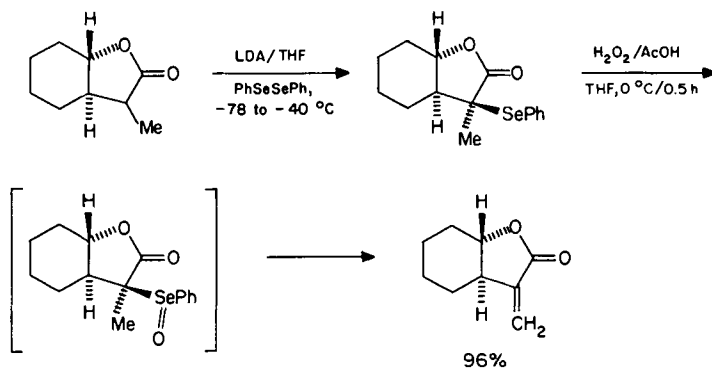
SCHEME 8[28]

(*c*) Olefins can be prepared[20] by reaction of selenonium salts with bases. The transformation probably involves the intermediary formation of an ylide which is thought to produce the olefin via a process related to selenoxide elimination (compare a and b, Scheme 4).

2. Synthesis of selenides

Selenides and functionalized selenides can be easily prepared from selenols or selenolates and compounds containing an electrophilic carbon atom. The high nucleophilicity of the Se atom in these derivatives and the high acidity of the selenols make them versatile compounds for the synthesis of Se-containing molecules[1-6,8].

The selenyl moiety can also be introduced as an electrophilic species into molecules possessing a nucleophilic carbon atom. Diselenides, selenenyl halides, selenenic acids and esters and seleninic halides and anhydrides are now the choice reagents[2,4-6]. These methods are very useful but they usually do not allow the introduction of the selenyl moiety with the concomitant formation of C—C bonds between two different entities. However, the reaction of α-selenoalkylmetals with electrophiles fulfills this requirement[2,4-68]. We shall discuss below:

  (*a*) the synthesis of α-selenoalkylmetals,
  (*b*) their reactivity towards electrophiles,
  (*c*) some transformations which allow the selective removal of the selenyl moiety on the products prepared, and
  (*d*) the description of functional group transformations using α-selenoalkylmetals.

B. Synthesis and Reactivity of α-Selenoorganometallics

1. Synthesis of α-selenoalkylmetals in which the carbanionic centre is sp³-hybridized and the selenyl moiety is uncharged

a. General. α-Selenoalkylmetals belong to the well-known family of α-heterosubstituted organometallics[30-66]. Those bearing nitrogen, phosphorus or sulphur moieties (charged or not), alkoxy or silyl groups and halogens have been prepared during the last thirty years[8].

There are several synthetic routes to such organometallics which have all their advantages and inconveniences[8]. These include hydrogen–metal exchange, halogen–metal exchange, addition of organometallics to α-heterosubstituted olefins heteroatom–metal and metal–metal exchange reactions.

Hydrogen–metal exchange is one of the most useful methods because the starting materials are usually easily available; however, it works only when the carbanionic species is sufficiently stabilized. Halogen–metal exchange is often limited by the accessibility of the starting materials and the addition of organometallics to α-heterosubstituted olefins is generally limited to heterosubstituted ethylenes, especially those bearing a stabilizing group adjacent to the heteroatom.

We will present the different synthetic methods used for the preparation of α-selenoalkyllithiums shown in Scheme 9.

$$RSeCR^1R^2M$$

$$R^1 = H, \text{ alkyl}; R^2 = H, \text{ alkyl}$$
$$R^1 = H, \text{ alkyl}, SeR; R^2 = SeR, SiR'_3$$
$$R^1 = H, \text{ alkyl}; R^2 = RCO, CO_2R, CONR_2,$$

CN, Ph, Ar,

$$RS(=O)CR^1R^2M \qquad R_2\overset{+}{Se}CR^1R^2M$$
$$X^-$$
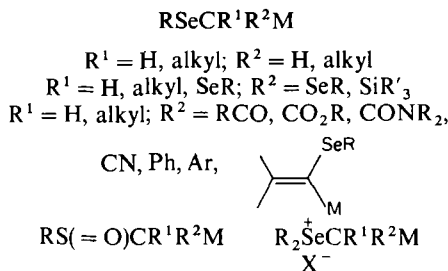
SCHEME 9

b. Theoretical and practical aspects. The strategy used for the synthesis of α-selenoalkylmetals greatly depends upon the substituents present around the carbanionic centre expected to be formed.

(i) Synthesis of α-selenoalkylmetals by metalation. Dialkyl or aryl alkyl selenides cannot usually be metalated since metalloamides are not strong enough to perform the reaction and alkylmetals usually react on the Se atom of these compounds (Scheme 1). It has been shown however[67] that (phenylselenomethyl) lithium can be prepared, although in modest yield, by metalation of methyl phenyl selenide with *n*-BuLi when tetramethylethylene diamine (TMEDA) is used as the cosolvent (Scheme 10).

$$PhSeCH_3 \xrightarrow[> 0°C]{BuLi/TMEDA/THF} PhSeCH_2Li$$
$$38\%$$
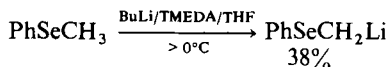
SCHEME 10[67]

The presence of a substituent able to produce extra stabilization at the expected carbanionic centre often permits the synthesis of the α-selenoalkylmetals from the corresponding selenides and metalloamides:

(a) Aryl selenides bearing another heteroatomic moiety in the α-position, such as phenylselenoacetals[67-72] (Scheme 11), α-thiophenyl selenides[73] (Scheme 12), α-silyl-phenylselenomethane[22,72,74-76] (Scheme 13), α-methoxyarylselenomethane[72] as well as α-phosphono[101], α-phosphonatophenyl selenides[102], α-nitrophenyl selenides[103], α-stannylphenyl selenides[34] and α-germylphenyl selenides[300] have been successfully metalated. There is in fact a big difference of reactivity between the parent compounds which are usually metalated with lithium diisobutyramide (LiDBA) in THF[67] or lithium diisopropylamide (LDA) in THF[68,75,76], and the higher homologues which require stronger basic systems such as lithium tetramethylpiperidide (LiTMP) in THF–HMPT[68] or diglyme[73] or potassium diisopropylamide (KDA) in THF[69] (Schemes 11–13). Methylseleno derivatives of these types are however completely inert under all these conditions.

$$(RSe)_2CHR^1 \xrightarrow{\text{base}} (RSe)_2CMR^1 \xrightarrow{\text{HexBr}} (RSe)_2C(Hex)R^1$$

$R = Ph, R^1 = H:(i\text{-}Bu)_2NLi/THF\text{–}hexane, -78°C$ then $30°C/0.2\,h$ $80\%^{67,68}$
$R = Ph, R^1 = Me:LDA/THF\text{–}HMPT, -30°C$ then $30°C/0.2\,h$ $74\%^{68}$
$R = Ph, R^1 = Me:LiTMP/THF/HMPT, -30°C$ then $30°C/0.2\,h$ $83\%^{68}$
$R = Ph, R^1 = Hex:LDA/THF/HMPT, -30°C$ then $30°C/0.2\,h$ $44\%^{68}$
$R = Ph, R^1 = Hex:LiTMP/THF/HMPT, -30°C$ then $30°C/0.2\,h$ $86\%^{68}$
$R = Ph, R^1 = Me:KDA/THF, -78°C$ $95\%^{69}$
$R = Me, R^1 = H:LiTMP/THF/HMPT, -30°C$ then $30°C/0.2\,h$ $0\%^{68}$
$R = m\text{-}CF_3C_6H_4, R^1 = H:LDA/THF, -78°C/0.1\,h$ $85\%^{a\,70}$

^{a} This yield refers to the β-hydroxyselenoacetal derived from benzaldehyde.

SCHEME 11

$$RSeCH(SR^2)R^1 \xrightarrow{\text{base}} RSeCLi(SR^2)R^1 \xrightarrow{\text{PhCHO}} RSeC(SR^2)R^1CH(OH)Ph$$
$$(A)$$
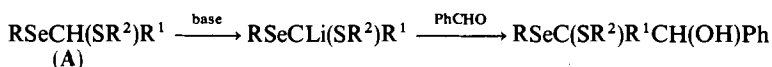
$R = R^2 = Ph, R^1 = H:LiTMP/THF, -24°C/1.5\,h$ 91%
$R = R^2 = Ph, R^1 = Me:LiTMP/THF, -24°C/1.5\,h$ $68\%(A:10\%)$
$R = R^2 = Ph, R^1 = Pen:LiTMP/THF, -24°C/1.5\,h$ $0\%(A:85\%)$
$R = R^2 = Ph, R^1 = Pen:LiTMP/DME, -24°C/0.5\,h$ $21\%(A:64\%)$
$R = R^2 = Ph, R^1 = Pen:LiTMP/diglyme, -24°C/0.5\,h$ $65\%(A:17\%)$
$R = Ph, R^2 = Me, R^1 = H:LiTMP/THF, -78°C/1\,h$ $0\%(A:80\%)$
$R = Ph, R^2 = Me, R^1 = H:LiTMP/DME, -78°C/1\,h$ 45% —
$R = Ph, R^2 = Me, R^1 = H:LiTMP/diglyme, -78°C/1\,h$ 75% —

SCHEME 12[73]

$$RSeCH_2SiMe_3 \xrightarrow[\text{THF/hexane}]{\text{LDA}} [RSeCHLiSiMe_3] \xrightarrow{C_{10}H_{21}Br} RSeCH(C_{10}H_{21})SiMe_3$$

$$\xrightarrow{H_2O_2} C_{10}H_{21}CHO$$
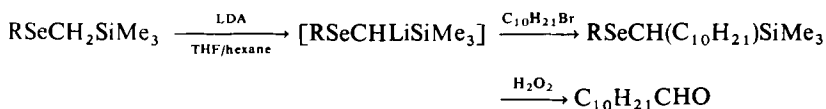
$R = Ph$	$-78°C/3\,h$	$-78°C$	$5\%^{74}$
	$-30°C/0.5\,h$	$-30°C$	$75\%^{74,75}$
$R = Me$	$-30°C/0.5\,h$	$-30°C$	$0\%^{74}$

SCHEME 13

(*b*) Selenides bearing two other heteroatomic moieties are more acidic than those presented above and have been in both the phenylseleno[67] and the methylseleno[68,74] series readily metalated with LiDBA[67,71] or LDA[68,74] in THF (Scheme 14). This is for example the case for trisphenylseleno-[67] and trismethylseleno-[68,74] methane as well as α-silyldiselenomethane[71].

$$(PhSe)_3CH \xrightarrow{\text{LiDBA/THF, } -78°C} (PhSe)_3CLi \xrightarrow{\text{MeI}} (PhSe)_3CMe \qquad \text{(Ref. 67)} \quad \text{(a)}$$
$$93\%$$

$$(MeSe)_3CH \xrightarrow{\text{LDA/THF, } -78°C} (MeSe)_3CLi \xrightarrow{\text{MeI}} (MeSe)_3CMe \qquad \text{(Ref. 68)} \quad \text{(b)}$$
$$80\%$$

$$(PhSe)_2CHSiMe_3 \rightarrow [(PhSe)_2CLiSiMe_3]$$

$$\xrightarrow{\text{EtCHO}} [(PhSe)_2C(SiMe_3)CHEt] \rightarrow (PhSe)_2C{=}CHEt \qquad \text{(Ref. 71)} \quad \text{(c)}$$
$$\underset{O^-}{|} \qquad 70\%$$

SCHEME 14

(*c*) Primary allyl[72,77–79,321,326], benzyl[22,72,78,80,83] and ethynyl[72,81] aryl selenides as well as their methylseleno analogues[78,83] are readily metalated at − 78 °C with LDA and LiTMP/THF, respectively (Scheme 15), but the reaction seems to be restricted to the parent compounds and does not work in the case of higher homologues[22,77].

$$PhCH_2SePh \xrightarrow{\text{LDA/THF}} PhC(SePh)HLi \xrightarrow{\text{EtBr}} PhC(SePh)HEt$$
$$80\% \quad \text{(Ref. 80)} \quad \text{(c)}$$

$$PhCH_2SeMe \xrightarrow[-78°C/0.5h]{\text{LiTMP/THF}} PhC(SeMe)HLi \xrightarrow{\text{PhCHO}} PhC(SeMe)HC(OH)HPh$$
$$68\% \quad \text{(Ref. 78)} \quad \text{(d)}$$

$$\text{PhCHRSePh} \xrightarrow{\text{LDA/THF}} \text{PhCRLiSePh} \qquad \text{(Ref. 72)} \quad \text{(e)}$$

R = Me, SiMe$_3$

SCHEME 15

(d) Finally, α-seleno ketones[72,84-86,256b], esters[72,87-89], acids[72,90], lactones[88,91] and nitriles[92] produce the corresponding lithio derivatives on reaction with LDA in THF (Scheme 16 and 17). α-Phenylselenoacetonitrile has also been successfully metalated under phase-transfer catalysis and produces[93] 1-phenylseleno-1-cyanocyclopropane if the reaction is conducted in the presence of 1,2-dibromopropane.

$$\text{RSeCH}_2\text{COOMe} \xrightarrow[\sim 78\,^\circ\text{C}]{\text{LDA/THF}} \text{RSe—CHLiCOOMe} \xrightarrow{\text{C}_6\text{H}_{13}\text{CHO}} \underset{\substack{| \qquad | \\ \text{MeOOC} \quad \text{OH}}}{\text{RSeCH—CH—C}_6\text{H}_{13}} \quad \text{(a)}$$

R = Ph   93%
R = Me   80%
R = p-ClC$_6$H$_4$ 96%

$$\text{PhSeCHMeCOOMe} \xrightarrow[\sim 78\,^\circ\text{C}]{\text{LDA/THF}} \text{PhSeCLiMeCOOMe} \xrightarrow{\text{C}_6\text{H}_{13}\text{CHO}} \underset{\substack{| \qquad | \\ \text{MeOOC} \quad \text{OH} \\ 60\%}}{\overset{\substack{\text{CH}_3 \\ |}}{\text{PhSe—C—CH—C}_6\text{H}_{13}}} \quad \text{(b)}$$
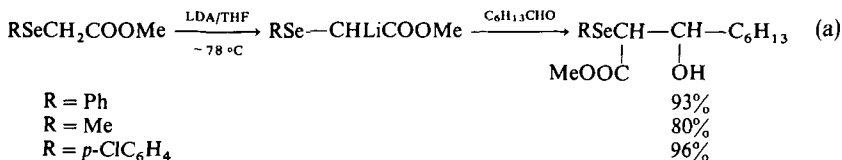
SCHEME 16[88]
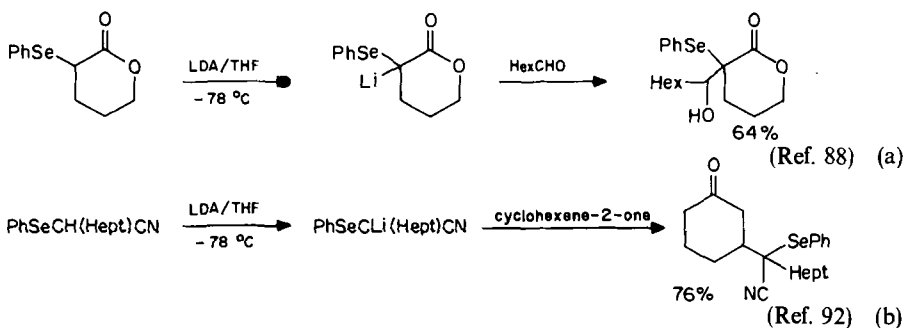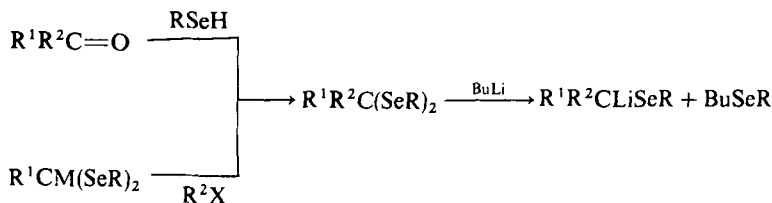
SCHEME 17

R,R^2 = H, alkyl, aryl
R = alkyl, aryl

SCHEME 18

(ii) Synthesis of α-selenoalkyllithiums by cleavage of the C—Se bond of selenoacetals. Except in the case of (phenylseleno) methyllithium, the general route to α-selenoalkyllithiums is the reaction of selenoacetals with alkyllithiums[2,4-6,8,11,67,94,126,127,133] (Scheme 18). Most of the work has been carried out with phenyl- and methyl-selenoacetals themselves, readily available from carbonyl compounds[11,19,67,94-99,126b,127] or by alkylation of 1-metallo-1,1-bisselenoalkanes[67-69,74,133].

The Se—metal exchange in selenoacetals is usually performed at − 78 °C with *n*-BuLi in THF/hexane (1:1) and leads to the quantitative formation of the selenoalkyllithiums and aryl or alkyl butyl selenides. Under these conditions the selenoalkyllithiums are stable for prolonged periods (~1 day), they are completely unreactive towards the selenides formed, but are particularly reactive towards electrophiles such as carbonyl compounds, alkyl halides, epoxides, etc.

The reaction seems to be a general one, and allows the synthesis of α-selenoalkyllithiums bearing two hydrogens[67,94], one hydrogen and one alkyl group[11,94,126] or even two alkyl or cycloalkyl groups[11,94,126,127,133]. Before this work none of the organometallics possessing an uncharged heteroatom and two alkyl groups on the carbanionic centre had been described.

The reaction also permits the synthesis of selenoalkyllithiums bearing aryl[78], silyl[74,100], selenyl[67,68] or methoxy[72] moieties on the carbanionic centre (Scheme 19).

$$R^1C(SeR)_2X \xrightarrow[\substack{-78\ °C/0.1-4\ h}]{\substack{BuLi \\ THF/hexane}} BuSeR$$

$$+ \left[R^1CLi(SeR)X\right]$$

$$\xrightarrow{R^2Y} R^1R^2C(SeR)X \quad \textbf{(A)}$$

$$\xrightarrow{R^3CHO} R^1(RSe)CXCHR^3(OH) \quad \textbf{(B)}$$
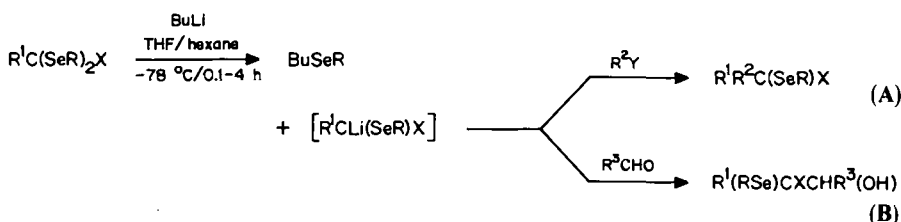
R	X	R^1	Electrophile	Yield (%) in A or B	Ref.
Me	Ph	H	PhCHO	(B) 87	78
Ph	Ph	H	PhCHO	(B) 83	78
Me	Ph	Me	PhCHO	(B) 85	78
Me	Me$_3$Si	H	C$_{10}$H$_{21}$CHO	(B) 54	100
Me	Me$_3$Si	Me	C$_{10}$H$_{21}$CHO	(B) 50	100
			C$_{10}$H$_{21}$Br	(A) 95	74
Me	MeSe	H	Me$_3$SiCl	(A) 72	68
Me	MeSe	Me	Me$_3$SiCl	(A) 83	68
			C$_6$H$_{13}$CHO	(B) 65	68
Ph	PhSe	Me	MeI	(A) 72	67
Ph	PhSe	PhSe	H$_2$O	(A) —	67

SCHEME 19

The Se—metal exchange in selenoacetals, α-silylselenoacetals and selenoorthoesters is dramatically favoured over the hydrogen—metal exchange when the latter is formally also possible, and only in very special cases such as trisphenylselenoorthoformate does competitive metalation occur[67] (Scheme 20).

$$(PhSe)_3CH \xrightarrow[\text{n-BuSePh}]{\text{BuLi/THF/hexane}} (PhSe)_2CHLi + (PhSe)_3CLi$$

SCHEME 20[67]

α-Selenoalkyllithiums are stable at − 78 °C in THF/hexane and isomerization to the ring-metalated derivatives or to the more stable selenomethyllithium is usually not observed under these conditions but can occur at higher temperatures[104] (Scheme 21). This isomerization has been reported once in a very special case[105] (Scheme 22).

$$R^1R^2CLi(SePh) \xrightarrow[]{\text{ether or THF, − 78°C}} \!\!\!\!\!\! \times \!\!\!\!\!\! \longrightarrow R^1R^2CH(O\text{-}C_6H_4Li) \qquad \text{(Refs. 8, 78)} \quad \text{(a)}$$

$$R^1R^2CLi(SeCH_3) \xrightarrow[]{\text{ether or THF, − 78°C}} \!\!\!\!\!\! \times \!\!\!\!\!\! \longrightarrow R^1R^2CH(SeCH_2Li) \qquad \text{(Refs. 8, 78)} \quad \text{(b)}$$

$$BuCH_2CH(SePh)_2 \xrightarrow[-78°C]{\text{t-BuLi/ether}} BuCH_2CHLi(SePh) \xrightarrow[\text{2. heptanal}]{\text{1. 20°C/1 h}} \underset{16\%}{HexSePh}$$

$$+ \, HexSeC_6H_4CH(OH)Hept + BuCH{=}CHSePh \qquad \text{(Ref. 106b)} \quad \text{(c)}$$
$$26\% 16\%$$

SCHEME 21

			Individual yields (%)				
Temp (°C)	Time (h)	Overall yield (%)	A	B	C	D	E
− 78	0.1	96	—	15	85	—	—
+ 20	1	84	—	—	—	27	73

SCHEME 22[105]

Unusual products resulting from the decomposition of the selenoalkyllithiums have been reported in the reaction of α-selenomethyllithiums with epoxides[106] or of triphenylselenomethyllithium with triphenyl phosphine[67].

$$R^1R^2C(SeR)_2 \xrightarrow{\text{R'Li}} R^1R^2CLi(SeR), \; R^1R^2CLi(SeR) \xrightarrow{\text{PhCHO}} R^1R^2C(SeR)CHPh(OH)$$

Conditions; yield, % (recovery of the starting material, %)

Entries	Acetal	R	n-BuLi–THF/hexane, –78°C		s-BuLi–THF/hexane, –78°C Minimum time required for complete cleavage	n-BuLi–ether/hexane, –78°C/1 h
			0.1 h	Minimum time required for complete cleavage		
1a	CH$_2$C(SeR)$_2$	Ph	82(0)			88(0)
1b		Me	80(0)			
2a	CH$_3$CH(SeR)$_2$	Ph	70(0)			73(16)
2b		Me	81(0)			
3a	C$_{10}$H$_{21}$CH(SeR)$_2$	Ph	80(0)			40(44)
3b		Me	83(0)			
4a	t-BuCH(SeR)$_2$	Ph	92(0)			
4b		Me	82(10)			
5a	PhCH(SeR)$_2$	Ph	83(0)			81(0)
5b		Me	87(0)			89(0)
6a	MeC(Me)(SeR)$_2$	Ph	94(0)			
6b		Me	75(16)			
7a	MeC(C$_6$H$_{13}$)(SeR)$_2$	Ph	81(2)			
7b		Me	50(40)	90(0)/2 h		
8a	Me(t-Bu)C(SeR)$_2$	Ph	59(25)			
8b		Me	32(60)	76(6)/2 h		
9a	Me(p-Tol)C(SeR)$_2$	Ph	90(0)			80(0)
9b		Me	47(48)			
10a	(C$_6$H$_{13}$)$_2$C(SeR)$_2$	Ph	17(80)	93(0)/4 h	83(0)/0.1 h	
10b		Me	91(0)			
11a	(CH$_2$)$_n$C(SeR)$_2$ (n = 2)	Ph	80(0)			35(64)
11b		Me	90(0)			
12a	(n = 3)	Ph	80(0)			
12b		Me	90(0)			
13a	(n = 4)	Ph	81(0)			
13b		Me	88(0)			
14a	(n = 5)	Ph	62(35)	87(0)/2 h		
14b		Me	55(43)			
15a	1,1-Di(RSe)-2-methylcyclohexane	Ph	25(72)	82(0)/4 h		
15b		Me			87(0)/0.1 h	
16a	2,2-Di(RSe)adamantane	Ph	0(89)	0(98)/2 h		
16b		Me	0(97)		81(0)/0.5 h	

SCHEME 23[78]

As general trends, the following comments on the synthesis of α-selenoalkyllithiums by Se—metal exchange can be made:

(a) Phenylselenoacetals are more easily cleaved than their methylseleno analogues[8,78] (Scheme 23, compare entries a and b).

(b) Selenoacetals derived from aldehydes are already cleaved after 0.1 h at − 78 °C by n-BuLi in THF/hexane whereas those derived from ketones required longer times[78] (0.5 to 4 h: Scheme 23, compare entries 1–4 to entries 6–8).

(c) In the series of acetals derived from methyl ketones with more bulky R^2 groups the reaction is more difficult (Scheme 23, examples 6–10 and 15–17). It is usually better in these difficult cases to use a longer period of time at − 78 °C rather than to increase the reaction temperature since the organometallics are stable at − 78 °C, but readily decompose at higher temperatures.

(d) The presence of a stabilizing group such as aryl, selenyl or silyl enhances the speed of the reaction (Scheme 23, compare entry 9b to 6b and 7b; see also Scheme 18).

(e) Selenoacetals derived from cyclopropanone[133], cyclobutanone[127] or cyclopentanone[78] are more easily cleaved than those of cyclohexanone (Scheme 23, entries 11–16). The conditions just reported are not suitable for the synthesis of the α-seleno-alkyllithiums derived from adamantanone (Scheme 23, entry 16).

As to the reactivity of selenoacetals under various experimental conditions:

(a) Several other sets of experimental conditions have been successfully tried for the cleavage of selenoacetals, and, e.g., s-BuLi in THF/hexane has proved to be particularly powerful[78]. Thus 7,7-bis(methylseleno)tridecane, which required 4 h to be completely cleaved by n-BuLi in THF/hexane at − 78 °C (Scheme 23, entry 10b), has been completely transformed to the corresponding α-selenoalkyllithium after 0.1 h reaction at the same temperature using s-BuLi. Interestingly these conditions allow the quantitative cleavage of methylselenoacetal derived from 2-methylcyclohexanone (0.1 h instead of 4 h for n-BuLi at − 78 °C)[78] and of the one derived from adamantanone[78] (100% after 0.5 h instead of 0% after 2 h for n-BuLi at − 78 °C). Closely related results have been obtained[78] with t-BuLi used instead of s-BuLi.

(b) s-BuLi also allows the cleavage of several selenoacetals when ether/hexane[8,78,107–112] is used instead of THF/hexane[8,11,67,78,94,107–112,126,127,133]. In this solvent system s-BuLi is less reactive than in ether (see Scheme 23) but the medium offers in several instances advantages over THF/hexane[107–112]. Thus, the α-selenoalkyllithiums are more stable in this medium and do not decompose at − 50 °C. They also have a higher propensity to add across the carbonyl group of particularly hindered[108] or enolizable[107,109,110] ketones. Moreover, the ratio of axial/equatorial attack on rigid cyclohexanones is often very different if the reactions are conducted in ether rather than in THF[108].

(c) n-BuLi in ether has also been used for the cleavage of the C—Se bond in selenoacetals. At − 78 °C, only phenylselenoacetals derived from formaldehyde, and phenyl- and methyl-selenoacetals derived from aromatic aldehydes and ketones are quantitatively cleaved. The reaction is very slow and requires at least 1 h for completion (Scheme 23). Under similar conditions, phenylselenoacetals of aliphatic aldehydes and cyclopropanone are only partially cleaved (Scheme 23). Phenylselenoacetals derived from aliphatic ketones and all methylselenoacetals except those of aromatic carbonyl compounds remain unchanged. If the reaction is performed at − 50 °C, however, all the phenylselenoacetals derived from aldehydes are cleaved in 0.5 h, but those derived from ketones are cleaved very slowly[78].

(d) Methyl- and phenyl-lithiums have also been reacted[8,78] with selenoacetals in THF/hexane but, with the exclusion of selenoacetals of aromatic compounds[12], they are not suitable for the synthesis of α-selenoalkyllithiums.

Although only preliminary work has been done in this field, it seems that some chemoselectivity can be expected. In the case of molecules bearing two selenoacetal groups

derived from differently substituted carbonyl compounds, it is found[111] that phenyl- and methyl-selenoacetals behave differently.

In the case of phenylselenoacetals it is possible to cleave the selenoacetal group derived from an aldehyde without affecting the one derived from a ketone by taking advantage of the difference of reactivity of n-BuLi in ether towards these two groups (see above)[78,111]. At $-50\,°C$ the discrimination can be achieved under kinetically controlled conditions and a specific example is shown in Scheme 24.

Reaction conditions (left to right):

1. 1 mol eq. n-BuLi ether/hexane, $-45\,°C/0.5$ h
2. HexCHO
3. H_3O^+

Second step conditions:

1. 1 mol eq. n-BuLi, ether/hexane, $-78\,°C/0.1$ h
2. 1 mol eq. s-BuLi, ether/hexane, $-78\,°C/0.5$ h
3. HexCHO
4. H_3O^+

76%
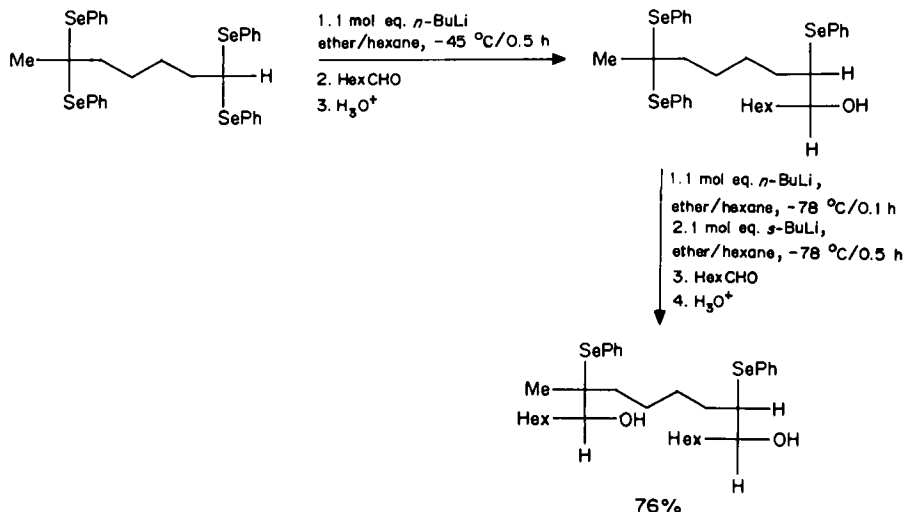
SCHEME 24[78,111]

In the case of methylselenoacetals the reactions have not been performed on one molecule bearing both different acetal functions but on a mixture of two different selenoacetals[111] (Scheme 25). The difference in reactivity of these acetals towards n-BuLi in THF or s-BuLi in ether is not strong enough to permit a high selectivity favouring the cleavage of the acetal derived from the aldehyde (Scheme 25a–d) (75/25). It was found however[111] that α-selenoalkyllithiums derived from aldehydes are thermodynamically more stable than those derived from ketones. It is therefore possible to increase the

$$HexCH(SeMe)_2 + HexCMe(SeMe)_2 \xrightarrow[\text{2. PhCHO}]{\text{1. RLi}} HexCH(SeMe)CHPh(OH) \quad \textbf{(A)}$$

$$+ HexCMe(SeMe)CHPh(OH) \quad \textbf{(B)}$$
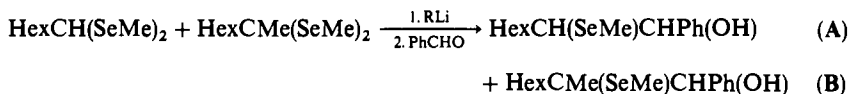
Reaction–solvent	Temp (°C)	Time (h)	A (%)	B (%)	A/(A + B)
(a) s-BuLi–ether/hexane	-78	0.5	55	20	73
(b) n-BuLi–THF/hexane	-100	0.5	15	5	75
(c) n-BuLi–THF/hexane	-78	0.05	37	11	77
(d) n-BuLi–THF/hexane	-78	0.1	67	23	74
(e) n-BuLi–THF/hexane	-78 then -40	0.1 } 1 }	78	8	90

SCHEME 25[78,111]

formation of the former derivatives by carrying out the reaction under thermodynamically controlled experimental conditions[111]. If the reaction is performed in the more polar THF at $-78\,°C$ and then stirred for two hours at $-4\,°C$, a net increase of the percentage of the organometallic derived from aldehyde is observed as compared with the results obtained by quenching the mixture after 0.1 h reaction at $-78\,°C$ (Scheme 25e).

Preliminary results show that phenylselenoacetals are much more easily cleaved than their methylseleno analogues. Experiments have been performed on a 1:1 mixture of

TABLE 1. ^{77}Se-NMR data for selenoacetals, $R^1R^2C(SeR)_2$, and their corresponding α-selenoalkyllithiums, $R^1R^2CLi(SeR)$[78 a,b]

			$R^1R^2C(SeR)_2$	$R^1R^2CLi(SeR)$
R^1	R^2	R	^{77}Se-NMR (ppm)	^{77}Se-NMR (ppm)
H	H	Ph	324	278
		Me	104	61
H	Me	Ph	422	389
		Me	194	180
H	Et	Ph	378	335
		Me	155	126
H	$C_{10}H_{21}$	Ph	388	347
		Me	163	138
H	t-Bu	Ph	382	307
		Me	155	95
H	Ph	Me	237	54
Me	Me	Ph	530	475
		Me	277	249
Me	Et	Ph	479	408
		Me	241	187
Me	$C_{10}H_{21}$	Ph	490	425
		Me	249	202
Me	t-Bu	Ph	479	397
		Me	247	179
Hex	Hex	Ph	448	405
		Me	207	182
Me	Ph	Me	359	168
CH_2—CH_2		Ph	527	492
		Me	297	184
CH_2—CH_2—CH_2		Ph	479	452
		Me	253	213
CH_2—$(CH_2)_2$—CH_2		Ph	439	401
		Me	235	186
CH_2—$(CH_2)_3$—CH_2		Ph	558–402	476
		Me	313–166	246

[a] ^{77}Se-NMR Jeol FX 90Q, solvent THF/hexane, standard conditions for 10^{-3} mol of the Se compound (Me_2Se as external standard), temperature $-78\,°C$.

[b] ^{77}Se-NMR shift (ppm) of some selenides in THF: Me_2Se (0), MeSeBu (82), MeSePh (196), PhSeBu (288), Ph_2Se (408).
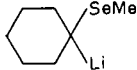
phenylseleno- and methylseleno-acetals derived from acetone, using n-BuLi in THF. After 0.1 h at $-78\,^\circ$C a 86:14 ratio of 2-phenylseleno-: 2-methylseleno-2-propyllithiums is observed.

Most of the work we have done for synthetic purposes has been recently carefully reinvestigated by monitoring the reactions by ^{77}Se-NMR. In the case of reactions between selenoacetals and alkyllithiums, the peaks attributed to the Se atom in the acetals, α-selenoalkyllithiums and butyl selenides are well differentiated[78] (Table 1). Hence one can follow the changes depending upon the experimental conditions. From the temperature at which the reaction starts[78] (Scheme 23), information related to the speed of the reaction[78] and the temperature at which it occurs[8,78] have been derived.

Little information is available on the intimate mechanism of the Se bond cleavage of selenoacetals by alkyllithiums. If the reaction is followed by ^{77}Se-NMR, even at $-85\,^\circ$C only peaks attributed to the organometallic and to the butyl selenide are concomitantly formed at the expense of the one corresponding to the selenoacetals, and in no case has an intermediate, such as for example an ate complex, been detected[8,78].
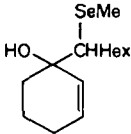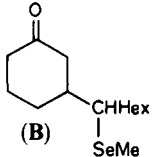
The metal plays an important role in the further reaction of organometallics, but only a little is known in the case of α-selenoalkyl derivatives. For example, up to now, alkyllithiums are the only organometallics which have been used to cleave the C—Se bond of selenoacetals. No reports have appeared concerning the reaction of alkylsodiums, Grignard or organozinc reagents or cuprates with selenoacetals.

The metal–metal interchange on α-selenoalkyllithiums has been successfully achieved by adding $MgBr_2$[78] at $-78\,^\circ$C or CuI[112-117] at $-110\,^\circ$C. In both cases the ^{77}Se-NMR of the solution of the selenoalkyllithiums before and after the addition of the metal salts were different. Specific examples concerning the addition of CuI are presented in Scheme 26.

	C_6H_{13}CHLiSeMe	C_9H_{19}CLi(Me)(SeMe)	cyclohexyl SeMe/Li
THF/hexane, $-78\,^\circ$C, $SeMe_2$ as external standard	136 ppm	202 ppm	245 ppm
As above, but after addition of 0.5 mol eq. CuI–SMe_2	102 ppm 103 ppm	178 ppm 179 ppm	208 ppm 209 ppm

SCHEME 26[78]

As expected, the reactivity of the new species is somewhat different from the one of the α-selenoalkyllithiums. For example, in the presence of $MgBr_2$ the percentage of the C(3) additions of the selenoalkyllithiums to cyclohexenone increases[78] (Scheme 27) and in the presence of 0.5 eq. of CuI the yield of allylation of α-selenoalkyllithiums is greatly enhanced[113-116] (Scheme 28).

	A (%)	B (%)	A/(A + B)
Without additive	90	0	100
In the presence of $MgBr_2$	17	17	50

SCHEME 27[78]

THF, − 78°C   0%
THF/HMPT, − 78°C   0%
THF, − 78°C in the presence of 0.5 eq. CuI   70%

THF, − 100°C/0.5 h   50%
THF, − 100°C in the presence of CuI/Me_2S 83%
Ether, − 100°C in the presence of CuI/Me_2S 85%
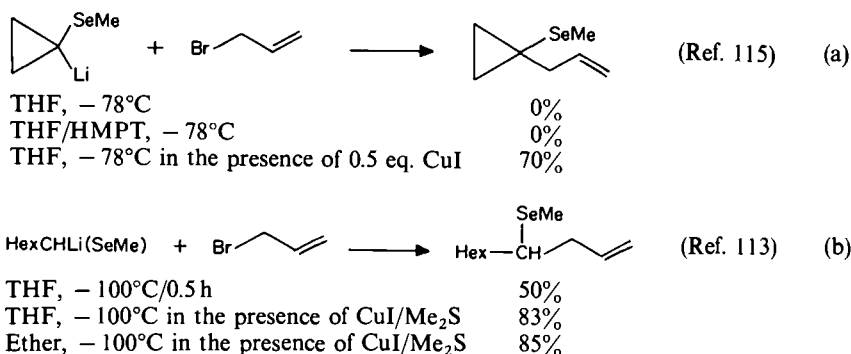
SCHEME 28

Finally it was found[112,117] that oxidative coupling of the α-selenoalkyllithiums takes place around − 40 °C in the presence of CuI, and produces olefins in high yield (Scheme 29). The mechanism of the process still remains unknown.

$$HexCHLi(SeMe) + 0.5\,mol\,eq.\ CuI/SMe_2 \longrightarrow HexCH=CHHex$$

THF, − 78 to + 20°C/0.7 h   80%
Ether, − 78 to + 20°C/0.7 h   85%
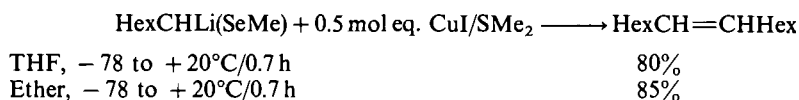
SCHEME 29[112,117]

(iii) *Synthesis of α-selenoalkyllithiums* via *halogen–metal exchange*. The whole series of α-phenylselenoalkyllithiums, even the dialkyl-substituted ones, have been successfully synthesized[118,119] from the corresponding α-bromophenyl selenides and *n*-BuLi in THF/hexane (Scheme 31). The cleavage of the C—Br bond is highly selective and occurs quite instantaneously at − 78 °C, but the yields of α-selenoalkyllithiums (60–75%) are lower than those obtained by the route involving the cleavage of the C—Se bond in selenoacetals. Moreover, the α-bromoselenides are not in all cases stable and they must often be prepared just before they are reacted.

$R^1CH=CR^2(SePh) + HBr$

$R^1R^2C=O + PhSeH + HBr$

$R^1R^2C(SePh)OSiMe_3 + HBr$

$$R^1R^2CH(SePh)Br \xrightarrow[THF,\,-78\,°C]{n\text{-BuLi}} R^1R^2CH(SePh)Li$$

$$\xrightarrow{HexCHO} R^1R^2CH(SePh)CHHex(OH)$$

$R^1 = H, R^2 = H$:   70%
$R^1 = Me, R^2 = H$:   69%
$R^1 = Hex, R^2 = H$:   63%
$R^1 = Me, R^2 = H$:   62%
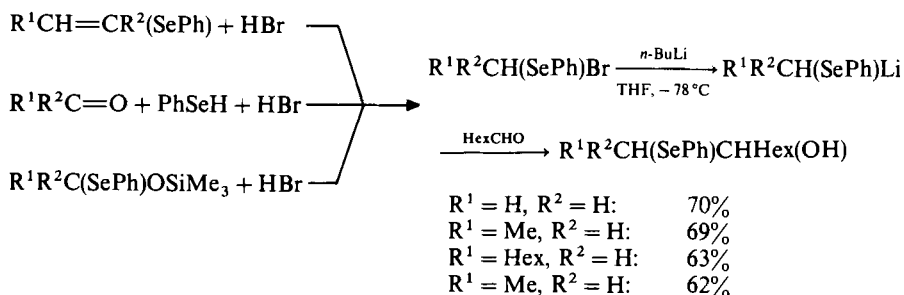
SCHEME 30[118]

This synthetic route to α-selenoalkyllithiums is not general and does not work for methylseleno derivatives. Moreover, C—Se rather than C—Cl bond cleavage is observed if α-chlorophenyl selenides are reacted[118] instead of α-bromophenyl selenides.

$CH_3CH(SePh)_2 \xrightarrow[P_2I_4 \text{ or } PI_3, 20-80°C]{MeI/DMF, 80°C/5h}$ (Refs. 123, 124) $\longrightarrow CH_2=CHSePh$ (Ref. 125)

$\xrightarrow[THF, -78°C/1h]{R=n-Bu} CH_2=CHSeBu + PhLi$ (Ref. 121) 70%

$ClCH_2CH_2SePh + t-BuOK \xrightarrow{THF, 25°C}$

RLi ↓

$\xrightarrow{} RCH_2CHLi(SePh) \xrightarrow{E'} RCH_2CHE(SePh)$

(A)
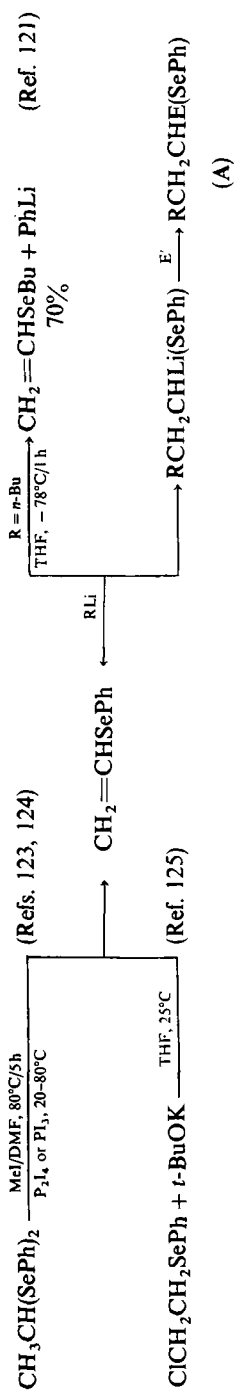
R	Conditions	E'	E	A (%)	Ref.
n-Bu	Ether, 20°C/0.5–1 h	H_2O	H	75	120
n-Bu	Ether, 20°C/0.2 h	HexCHO	HexCHOH	40	121
n-Bu	DME, 0°C	PhCHO	PhCHOH	71	122
i-Pr	Ether, 0°C	Me_2CO	Me_2CHOH	72	122
s-Bu	Ether, 20°C/0.5–1 h	H_2O	H	25	121
t-Bu	Ether, 0°C	D_2O	D	85	122
t-Bu	Ether, 20°C/0.5–1 h	H_2O	H	25	121

SCHEME 31

(iv) Synthesis of α-selenoalkyllithiums by addition of alkyllithiums to phenyl vinyl selenides. Three research groups[120-122] have simultaneously but independently described the addition of alkyllithiums to phenyl vinyl selenide. The reaction proceeds readily in DME or ether between 0 and 20 °C producing α-lithioalkyl phenyl selenides which may be trapped with various electrophiles (Scheme 31). The reaction must be performed as rapidly as possible since the organometallic formed is unstable at this temperature and isomerizes easily to the corresponding aryllithium[106b,121] (Scheme 32, compare also to Scheme 21c).

$$BuLi + CH_2=CHSePh \xrightarrow[20°C/0.2h]{\text{ether}} BuCH_2CHLi(SePh) \xrightarrow[\text{HexCHO}]{20°C/0.8h} HexSePh + HexSeC_6H_4CHOH$$

$$30\% \qquad\qquad 18\%$$
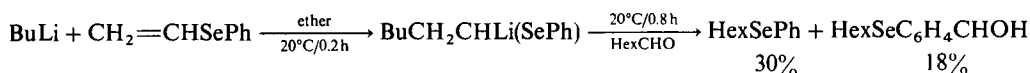
SCHEME 32[106b,121]

The proper choice of reaction conditions is essential for the success of the addition since α-deprotonation leading to 1-lithio-1-phenylselenoethylene or cleavage of the C—Se bond producing butyl phenyl selenides may also occur[121,122]. The last reaction is in fact the predominant one if THF is used instead of ether or DME as the solvent and is particularly favoured if the reactions are performed at low temperature[121,122] (Scheme 31).

2. Reactivity of α-selenoalkylmetals in which the carbanionic centre is sp³-hybridized and the selenyl moiety is uncharged

a. Reactivity of α-selenoalkylmetals bearing hydrogens or one or two alkyl groups on the carbanionic centre. These derivatives have proved to be particularly reactive. They have been protonated[14,120,121], deuteriated[14,67b,122,126a], reacted with primary alkyl halides[14,20,106b,122,127], allyl halides[14,113,114], trialkyl and triallyl boranes[128], terminal epoxides[106,127,129], oxetanes[106], aldehydes[11,21,94,107,118,126,127,130-133] and ketones[11,21,67,72,94,107,118,122,126,127,130,131,133-135,137], as well as α-seleno aldehydes[139], α,β-unsaturated aldehydes[138,154] and ketones[72,138,154], esters[136], acid chlorides[136,140], anhydrides[136], chlorocarbonates[136] and carbonic anhydride[115,136], dimethylformamide[136,139], diphenyl disulphide[126,141] and related derivatives[126b], silyl chlorides[122,141-143], phenylselenenyl halides[122] and nitriles[122].

b. Reactivity of α-functionalized α-selenoalkylmetals. The following functional groups attached to α-selenoalkyllithiums were investigated:
(i) Allyl moieties react with primary[77,321] and secondary[72,78,321] alkyl halides, epoxides[77,321], silyl chlorides[77,78,321], aldehydes[78], ketones[77,78,321] and enones[79].
(ii) Benzyl groups react with primary and secondary alkyl halides[72,78,80], epoxides[72], allyl bromides[72] and aldehydes[72,78,145] and ketones[145] including hindered ones.
(iii) Ethynyl groups react with primary and secondary alkyl halides[82] and benzyl halides[82].
(iv) Ketone groups react with allyl halides[85].
(v) Carboxyl groups react with secondary allyl bromides[90], terminal epoxides[90] and aromatic aldehydes[72].
(vi) Ester groups react with primary alkyl halides[87,88a], aldehydes and ketones[88a] and α,β-unsaturated carbonyl compounds[88a,b,89].
(vii) Lactone rings react with primary alkyl halides[91], aldehydes and ketones[88a].
(viii) Nitrile groups react with enones[92] and alkyl halides[93].
(ix) Silyl groups react with primary alkyl halides[74,75], benzyl halides[76], epoxides[147] and aldehydes and ketones[74].
(x) The α-thio moiety reacts with aldehydes[73].

(*xi*) α-Selenyl moieties react with trimethyl silyl chloride[68,71,74], deuteriated water[67], primary alkyl halides[67-69,126,133], secondary alkyl halides[69], tosylates[133], benzyl halides[69], epoxides[68,69], aldehydes[68,69,72,187] and ketones[21,67-69], α,β-unsaturated ketones[69,148,149], α,β-unsaturated aldehydes[150] and α,β-unsaturated esters[150].

(*xii*) α-Methoxy groups react with aldehydes[72] and ketones[72].

(*xiii*) The α-nitro group reacts with formaldehyde[103].

(*xiv*) An α-phosphonium salt reacts with aldehydes[67,87], but it does not react with ketones.

(*xv*) An α-phosphonato group reacts with aldehydes[67,187], but it does not react with ketones.

(*xvi*) α,α-Diseleno groups (orthoesters) react with D_2O[67], primary alkyl halides[67,74], trimethylsilyl chloride[74], epoxides[133] and aldehydes[67].

c. Further comments on the reactivity of α-selenoalkylmetals. Some of the reactions presented require further comments which are given below.

(*i*) *Reaction with alkyl and allyl halides, epoxides and oxetanes.* (*a*) Selenoalkyllithiums react in THF at − 78 °C exclusively with terminal alkylhalides, epoxides or oxetanes to form, respectively, selenides, γ- or δ-hydroxyselenides. In the last two cases the reaction occurs exclusively at the less hindered side of the heterocycle.

(*b*) Selenomethyllithiums are less reactive than their higher homologues. The reaction with primary alkyl halides and terminal epoxides or oxetanes occurs around − 30 °C instead of around − 60 °C for the higher homologues. At that temperature however part of the organometallic decomposes and produces selenolates which further react with the electrophiles present. The side-reactions can be avoided if the substitution is performed in THF at − 78 °C but in the presence of HMPT[106].

(*c*) When secondary or tertiary alkyl halides are used instead of primary ones, no alkylation is observed in THF at from − 100 °C to − 20 °C and not even in the presence of CuI.

(*d*) Selenoalkyllithiums are not efficiently allylated[113,115] in THF at − 78 °C or − 100 °C. However, at − 100 °C in the presence of 0.5 mol eq. of CuI the reaction works particularly well[113-115] (Scheme 28). In the case of geranyl and neryl chlorides the reaction is both regio- and also highly stereo-selective[113,114]. It occurs in an S_N instead of an $S_{N'}$ manner and with retention of the stereochemistry of the C=C bonds. When CuI is used the reaction must be performed around − 100 °C, since at higher temperatures a side-reaction occurs[112,117] (Scheme 29) which leads to an olefin resulting from the coupling of two selenoalkyl moieties followed formally by the elimination of diselenide.

(*ii*) *Reaction with carbonyl compounds.* α-Selenoalkyllithiums react with a large variety of aldehydes and ketones including α,β-unsaturated, highly enolizable or hindered ones.
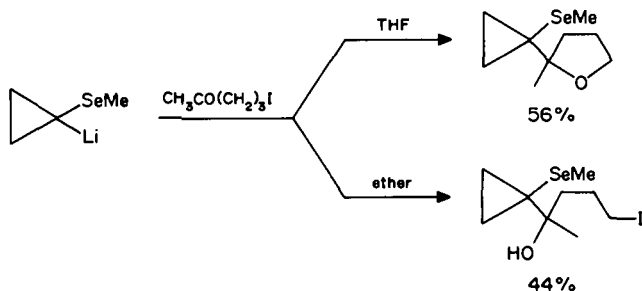
SCHEME 33[115]

(a) The reaction of α-selenoalkyllithiums, even of those possessing two alkyl groups on the carbanionic centre is readily (few minutes) achieved in THF/or ether/hexane usually at − 78 °C. The reaction proceeds much more readily with carbonyl compounds than, for example, with alkyl halides[115] (Scheme 33).

(b) The reaction is not usually stereoselective with aliphatic or aromatic aldehydes and ketones since a mixture (1:1 to 7:3) of the two possible stereoisomers around the newly formed C—C bond is usually obtained without any regard to the solvent or the conditions used.

(c) In the case of rigid cyclohexanones high stereoselectivity is observed and products resulting from an axial or equatorial attack are found depending upon the solvent used (THF/ or ether/hexane, − 78 °C)[108,144] (Scheme 34). With α-seleno aldehydes, β-hydroxyselenides are formed with a very high stereoselectivity. The Cram[291] and Felkin[292] rules can account for the results observed[139] (Scheme 35).
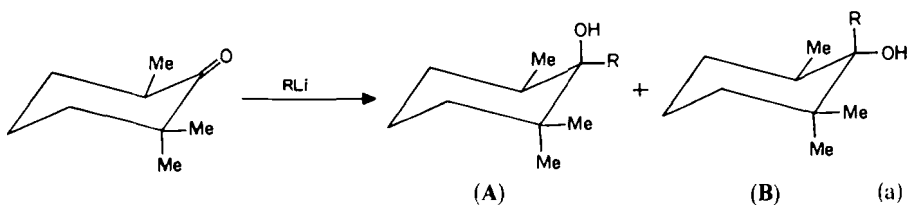
R	Conditions	Total yield (%)	A (%)	B (%)	Ref.
MeSeCH₂	Ether/hexane, − 78°C	86	31	69	144
	THF/hexane, − 78°C	92	18	82	
MeSeCHMe	Ether/hexane, − 78°C	84	95	5	144
	THF/hexane, − 78°C	85	95	5	
MeSeCMe₂	Ether/hexane, − 78°C	85	95	5	108
	THF/hexane, − 45°C	48	33	67	
PhSeCMe₂	Ether/hexane, − 78°C	84	95	5	108
	THF/hexane, − 78°C	0	—	—	

(Ref. 144)   (b)
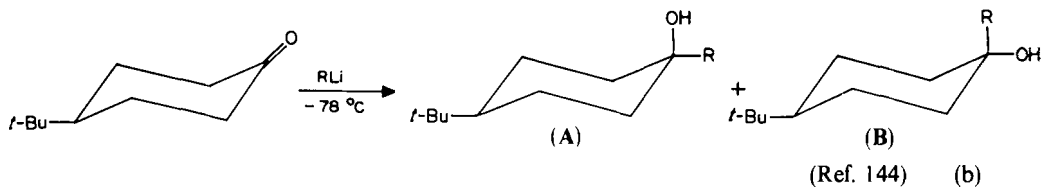
R	Conditions	Total yield (%)	A (%)	B (%)
MeSeCH₂	THF	85	75	25
	Ether	75	69	31
MeSeCHMe	THF	70	90	10
	Ether	79	90	10
MeSeCMe₂	THF	75	100	00
	Ether	75	100	00

SCHEME 34

2%   98%

Overall yield 71%
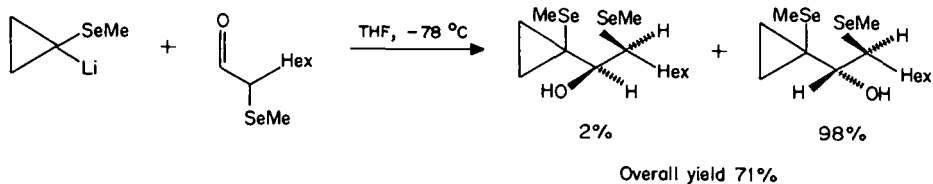
SCHEME 35[139]

(d) α-Selenoalkyllithiums exhibit particularly high nucleophilicity towards aldehydes and ketones even those bearing a highly hindered or enolizable carbonyl group. Best results are obtained with methylseleno derivatives, especially if the reactions are performed in ether/hexane rather than in THF/hexane and at low temperatures (usually −78 °C). Some representative examples are presented in Scheme 36. Thus 2-lithio-2-

$$RSeCR^1R^2Li + R^3R^4C{=}O \rightarrow RSeCR^1R^2CR^3R^4OH$$

THF/hexane	77%[94]	72%[144]	—
Ether/hexane	83%[144]	—	23%[151]

	R = Me	R = Ph		
THF/hexane	59%[108]	0%[108]	63%[115]	0%[155]
Ether/hexane	83%[108]	88%[108]	—	0%[115]

			n = 1	n = 2
THF/hexane	75%[144]	80%[94]	56%[115]	68%[115]
Ether/hexane	80%[144]	80%[144]	70%[115]	—
Ether/hexane/ HMPT(1 eq.)	12%[144]	—	—	—

			R = Me	R = Ph
THF/hexane	45%[115]	44%[115]	0%	0%
Ether/hexane	—	—	66%[109]	49%[109]
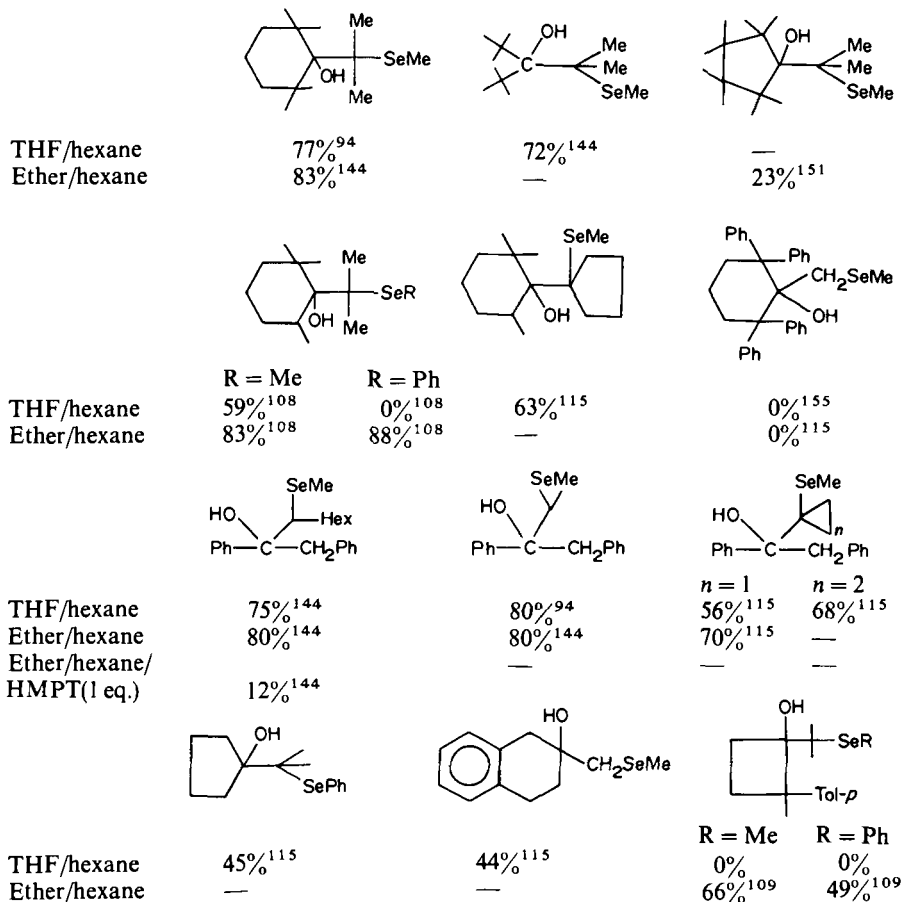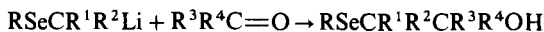
SCHEME 36

methylselenopropane and α-lithiocyclopropyl selenides lead to a high yield of β-hydroxyselenides on reaction with deoxybenzoin[94, 130,131], 2,2,6,6-tetramethylcyclohexanone[94,108,144], 2,2,6-trimethylcyclohexanone[108,115] and di(t-butyl) ketone[144] (Scheme 36). Rather modest yields are found in the case of cyclopentanone[144], tetralone[144] and permethylcyclopentanone[151]. The last reaction is exceptional since the permethylcyclopentanone carbonyl is so hindered that it is not reduced by $AlLiH_4$ (Scheme 36). 2,2,6,6-Tetraphenylcyclohexanone[152] however was reluctant to form a new carbon–carbon bond, even with the less hindered (methylseleno) methyllithium.

(e) α-Heterosubstituted α-selenoalkyllithiums are much less nucleophilic towards carbonyl compounds than polyalkylated α-selenoalkyllithiums. Thus α-selenyl α-lithioselenides lead to modest to good yields of the corresponding alcohol on reaction with carbonyl compounds[68]. A comparison between the yield of C—C bond formation of various organometallics bearing an α-Se atom and some carbonyl compounds is presented in Scheme 37.

$$R^1R^2CXLi + HexCH{=}O \xrightarrow{\text{THF}} R^1R^2CXCH(OH)Hex \qquad (a)$$
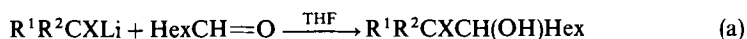
X	R^1	R^2	Yield (%)	Ref.
PhSe	Me	Me	70	11
MeSe	Me	Et	82	94
MeSe	MeSe	Me	65	68
MeSe	Me$_3$Si	Me	40	74
MeSe	MeSe	MeSe	75	68

$$\text{Me}_2\text{CXLi} \;+\; \text{cyclohexanone} \xrightarrow{\text{THF}} \qquad (b)$$
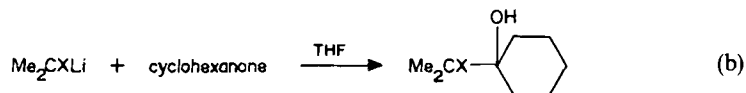
X	Yield (%)	Ref.
PhSe	78	11
	85	126a
MeSe	82	135
PhSeO	55	22

$$+ \;\text{Me}_2\text{CXLi}\; \xrightarrow{\text{THF}} \qquad (c)$$
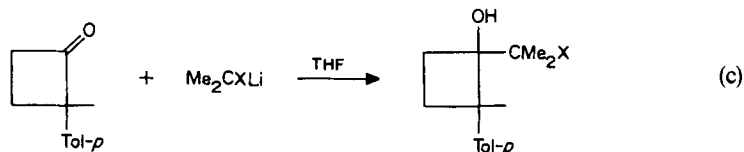
X	THF/hexane		Ether/hexane	
	Yield (%)	Ref.	Yield (%)	Ref.
SeMe	0	109	66	109
SePh	0	109	49	109
Se(O)Ph	39	153	—	—

SCHEME 37

(iii) Reaction with enals, enones and enoates. α-Selenoalkyllithiums bearing hydrogen or alkyl groups on the carbanionic centre have a very high tendency to add at the C(1) site of enals[138,154] and enones[138,154]. Chalcone[138,154] however produces a significant percentage of C(3) addition (Scheme 38). Due to side-reactions addition of CuI[112,117] (Scheme 29) or of HMPT[8,155], known for favouring the C(3) addition of organometallics at the C(3) site of α, β-unsaturated carbonyl compounds, has proved to be successful for favouring the C(3) addition of α-selenoalkyllithiums.

$$\text{MeSeCR}^1\text{R}^2\text{Li} + \text{PhCH=CHCOPh} \xrightarrow[\text{or} -78\text{ to }+20\,°\text{C}]{\text{THF, }-78\,°\text{C}} \text{PhCH}\equiv\text{CH}$$

$$—\text{CPh(OH)CR}^1\text{R}^2(\text{SeMe}) + \text{MeSeCR}^1\text{R}^2\text{CHPhCH}_2\text{COPh}$$

$R^1 = R^2 = H$:   35%   35%
$R^1 = R^2 = Me$:   21%   47%

(c)
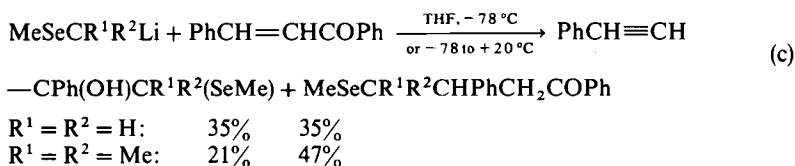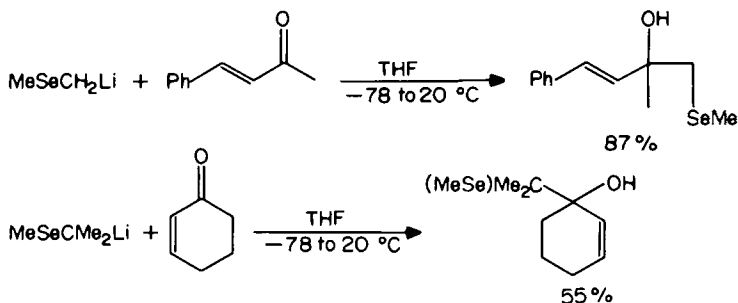
SCHEME 38[154]

The presence of a group which stabilizes the carbanionic centre greatly modifies the course of the reaction[8].
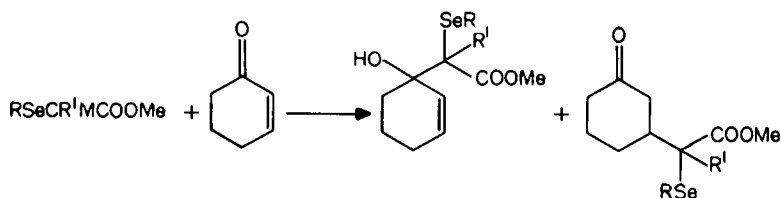
R	R^1	M	Conditions	Overall yield (%)	C(1)(%)	C(3)(%)
Me	Me	K	1. Ether or THF, − 110 or − 78 °C, 0.2 or 1 h 2. H_3O^+ at − 110 or − 78 °C	75	0	100
Me	Me	Li	1. Ether, − 110 or − 78 °C, 0.2 or 1 h 2. H_3O^+ at − 110 or − 78 °C	60	100	0
Me	Me	Li	THF, − 110 or − 78 °C, 0.2 or 1 h	75	85	15

SCHEME 39[89]

Exclusive addition at the C(3) site of cyclohexanone is observed with α-lithiophenyl-selenonitrile[92] and α-potassioseleno esters[89] (Scheme 39) and in the case of chalcone with α-lithioseleno esters[88b,89] (Scheme 40).

$$MeSeCMMeCOOMe + PhCH{=}CHCOPh$$

$$\longrightarrow (MeSe)MeC(COOMe)CHPhCH_2COPh$$
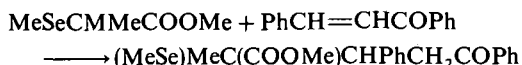
M = Li:THF, − 78 or − 110°C, 0.2 h or 1 h   83%
M = Li:ether, − 78 or − 110°C   67%
M = K:THF or ether, − 78 or − 110°C   75%

SCHEME 40[89]

In the case of α-lithioseleno esters and enones (excluding chalcone) it is possible to control the regiochemistry of the addition: C(1) adducts are formed under kinetically controlled conditions especially if the reactions are performed[88b,89] in THF or, better, in ether at low temperature (− 78 °C) (Scheme 39). At higher temperature or when HMPT is added C(3) adducts are exclusively obtained[88b,89] and have been shown to be formed under thermodynamically controlled conditions[88b,89]. Whatever the conditions used, phenylseleno derivatives have a higher tendency to add at C(3) to enones than their methylseleno analogues and higher substitution at the carbanionic centre enhances this tendency[89] (Scheme 41).
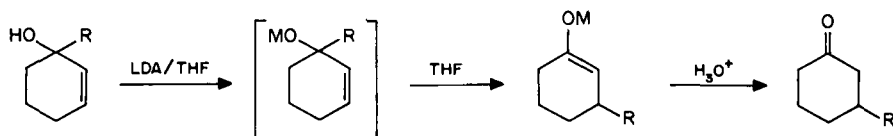
R	R^1	Temp. (°C)	t(h)^a
MeSeCR^1(COOMe)	Me	− 50	1
PhSeCR^1(COOMe)	H	− 25	1.5
	Me	− 25	inst.
		− 40	0.1
		− 60	0.2

^{a}Minimum time required for complete C(1) to C(3) isomerization. If potassium replaces lithium, the reaction produces the C(3) adduct instantaneously.

SCHEME 41[89]

In the case of 1-metallo-1,1-bis(seleno) alkanes[8,117] the temperature does not seem to have a significant effect on the ratio of product resulting from the C(1)/C(3) addition to enones. The structure of the organometallic, the nature of the metal and especially the nature of the solvent used controls the regiochemistry of the reactions (Schemes 42 and 43):

(a) This it is found that C(1) additions to enones[8,69,148,149] and enals[8,150] usually occur regioselectively if ether is used whereas C(3) adducts are formed[148,149] in THF in the presence of HMPT. Interestingly, both reactions were found to occur under kinetic control[18,148–150] (Scheme 42).
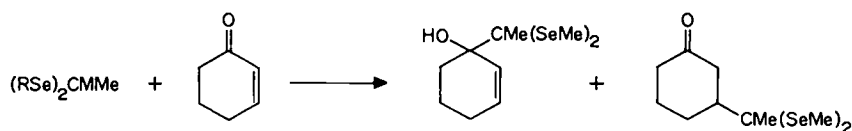
Conditions	R	M	Overall yield (%)	C(1)(%)	C(3)(%)	Ref.
Ether/hexane, − 70°C/0.2 h, then H$_3$O$^+$, − 78°C	Me	Li	78	97	03	117
	Ph	Li	71	93	07	117
THF/hexane, − 78°C/0.2 h, then H$_3$O$^+$, − 78°C	Me	Li	63	73	27	117
	Ph	Li	80	00	100	117
	Ph	K	76	100	0	69
THF/hexane + HMPT(1.1 eq.)^a, − 78°C/0.2 h then H$_3$O$^+$, − 78°C	Me	Li	78	00	100	117, 149
	Ph	Li	80	00	100	117, 149
THF/hexane + Ph$_3$PO(1.1 eq.)^a, − 78°C/0.2 h, then H$_3$O$^+$, − 78°C	Me	Li	68	23	77	117
Ether/hexane + HMPT(0.5 eq.)^a, − 78°C/0.2 h, then H$_3$O$^+$, − 78°C	Me	Li	74	75	25	117
Ether/hexane + kryptofix 2.2.2 (1 eq.), − 78°C/0.2 h, then H$_3$O$^+$, − 78°C	Me	Li	60	28	72	149
DME/hexane, − 78°C/0.2 h, then H$_3$O$^+$, − 78°C	Me	Li	61	13	87	149

^{a} With reference to the organometallic.
^{b}Trade name (Merck, Dormstat) for hexaoxa—4, 7, 13, 16, 21, 24—diaza—1, 10-bicyclo[8.8.8]-hexacosane.

SCHEME 42

(RSe)$_2$CMMe + PhCH=CHCOPh ⟶ PhCH=CH(OH)PhC(SeR)$_2$Me

+ PhCHC(SeR)$_2$MeCH$_2$COPh
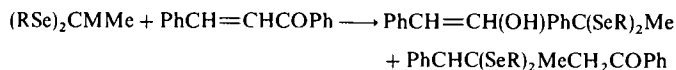
Conditions	R	Overall yield (%)	C(1)(%)	C(3)(%)
THF/hexane, − 78°C/0.2 h, then H$_3$O$^+$, − 78°C	Me	91	25	75
	Ph	60	55	45
THF/hexane + HMPT(1.1 eq.)^a, − 78°C/0.2 h, then H$_3$O$^+$, − 78°C	Me	77	95	5
	Ph	63	98	2

^{a} With reference to the organometallic.

SCHEME 43[156]

(b) In the case of enoates again the C(1) adduct is found in ether or THF and the C(3) adduct is obtained if the reactions are performed in THF–HMPT or in dimethoxyethane[150] (Scheme 42). Surprisingly, chalcone has, as the only one among various enones used, the reverse tendency[156] (Scheme 43).

(c) As a general trend phenylseleno derivatives have a higher tendency to add C(3) to enones and enoates[150] (Schemes 42 and 44) than their methylseleno analogues and surprisingly the reverse is found with enals[117,150] (Scheme 45).

$$(MeSe)_2CMeLi + PenCH=CHCO_2Me \longrightarrow (MeSe)_2CMeCHPenCH_2CO_2Me$$

THF/hexane + HMPT(1.1 eq.), $- 78°C/0.2$ h, then H_3O^+, $- 78°C$ 48%

DME, $- 78°C/0.2$ h, then H_3O^+, $- 78°C$ 40%

SCHEME 44[150]

$$(RSe)_2CMeLi + PrCH=CHCH=O \longrightarrow PrCH=CHCH(OH)C(SeR)_2Me$$
$$+ PrCHC(SeR)_2MeCH_2CHO$$
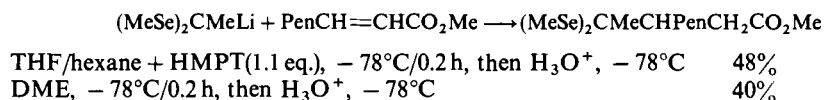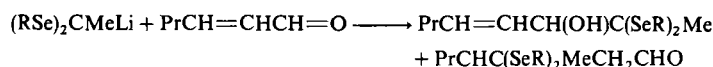
Conditions	R	Overall yield (%)	C(1)(%)	C(3)(%)	Ref.
THF/hexane, $- 78°C/0.2$ h,	Me	74	100	0	150
then H_3O^+, $- 78°C$	Ph	80	100	0	150
THF/hexane + HMPT(1.1 eq.)[a],	Me	68	28	72	150
$- 78°C/0.2$ h, then H_3O^+, $- 78°C$	Ph	60	100	0	150
THF/hexane + HMPT(2.2 eq.)	Me	51	21	79	117
THF/hexane + HMPT(4.4 eq.)	Me	27	18	82	117
THF/hexane + kryptofix 2.2.1	Me	[b]	68	32	117
DMF/hexane + TPPT[c]	Me	58	24	76	117
DME	Me	[b]	83	17	117

[a] With reference to the organometallic.
[b] GC^2 ratio.
[c] Trimethyl pyrrolidinophosphotriamide.

SCHEME 45

(d) The addition of organometallics to enones produces enolates which have been trapped with various electrophiles[117,148]. Silylated enolates are obtained[117] on reaction with Me_3SiCl and 2-alkylated ketones are formed[117] on reaction with alkyl halides. The stereochemistry of the C(3) addition of 1-lithio-1,1-bis(methylseleno)ethane with methyl-cyclohexenones has been established[117,148] as well as that of products resulting from the methylation of the adduct between the same organometallics and cyclohexenone[117,148] (Scheme 46).

(e) Finally the cleavage of the C—Se bond of highly functionalized selenoacetals (Scheme 47) has been successfully achieved[148] and the resulting α-selenoalkyllithium has been subjected to further reaction (Scheme 47).

3. Synthesis and reactivity of sp³-hybridized α-selenoalkylmetals bearing a charged selenyl moiety

The presence of a positive charge on the selenyl moiety as in selenoxides[21,22] and selenonium salts[19] allows, unlike most of the selenides, easy metalation of such compounds by metalloamides in the first case ($- 78$ °C, 0.3 h) or by t-BuOK in the second one.

Scheme 45 (top, with 6-methyl through 2-methyl cyclohexenones):

+ (MeSe)₂CMeLi

1. THF/hexane + HMPT(11 eq.), −78 °C
2. NH₄Cl/H₂O

C(SeMe)₂Me (two diastereomers)

a:6–Me	68%	32%
b:5–Me	87%	13%
c:4–Me	5%	95%
d:3–Me	0%	0%
e:2–Me	1%	99%

Overall yield

76%
56%
0%
0%
65%

+ (MeSe)₂CMeLi

1. THF/hexane + HMPT(11 eq.), −78 °C
2. MeI(5 eq.) + HMPT(5 eq.)/THF

Me, C(SeMe)₂Me

99%   +   1%

Overall yield = 77%

SCHEME 46[148]

+ (MeSe)₂CMeLi

1. THF/hexane + HMPT, −78 °C
2. Me₃SiCl/NEt₃/THF

OSiMe₃ C(SeMe)₂Me

70%

1. n-BuLi/THF, −78 °C
2. PenCHO
3. MeLi, 20 °C

C(SeMe)MeCHPenOH

63%

CH₂Cl₂ / P₂I₄/NEt₃

CMe=CHPen

78%

SCHEME 47[157]

a. Synthesis of α-metalloselenoxides. Selenoxides must in most cases be handled below 0 °C to avoid olefin formation[22,153,158]. A procedure has been therefore developed by Reich and Shah[22], in which the phenyl alkyl selenide is oxidized by *m*-chloroperbenzoic acid in THF at 0 °C[21,158] or at − 10 °C[22,158] or by ozone in ether[22] at − 78 °C and then immediately deprotonated by LDA/THF at − 78 °C (2 eq. of LDA, if perbenzoic acid is used) (Scheme 48).

$$PhSe(O)CHR^1R^2 \xrightarrow[-78\,°C]{LDA, THF} PhSe(O)CR^1R^2Li \xrightarrow{E'} PhSe(O)CR^1R^2E$$
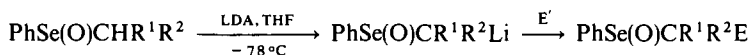
R^1	R^2	E'	E	Yield (%)
H	H	PhCH=CHCH$_2$Br	PhCH=CHCH$_2$—	75
H	(CH$_2$)$_2$Ph	Me$_2$C=CHCH$_2$Br	Me$_2$C=CHCH$_2$—	64
H	(CH$_2$)$_2$Ph	EtCHO	EtCHOH	87
Me	Me	PhCHO	PhCHOH	81
Me	Me	PhCO$_2$Me	PhC=O	81

SCHEME 48[22]

b. Reactivity of α-metalloselenoxides. These organometallics react[21,22] with primary alkyl, allyl and benzyl halides[21,22,158], aldehydes[21,22,72,158], ketones[21,22,153,154] and aromatic esters[21,22,158]. The corresponding functionalized selenoxides are then allowed to fragment to olefins and selenenic acids[21,22] or are reduced to the corresponding selenides by bisulphite solution[21,22], by P$_2$I$_4$[159] or by PI$_3$[160].

c. Synthesis and reactivity of selenonium ylides. Stable selenonium ylides have been prepared by the action of active methylene compounds on selenide dichlorides in basic methanol[161-164,302,303] or on selenoxides in the presence of dicyclohexylcarbodiimide[302]. A further method involves the thermal or photolytic decomposition of diazo compounds in the presence of selenides[164a,302].

Selenonium ylides stabilized by groups in which the negative charge can delocalize are quite uncreative. Some of them have been isolated[302,303] and their structure determined by X-ray crystallography[162]. Thus, Me$_2$Se=CH—C(=O)Ph is stable at room temperature[165], although it trimerizes to tribenzoylcyclopropane when heated[165]; if the reaction is conducted in the presence of chalcone, 1,2-dibenzoyl-3-phenylcyclopropane is formed[165].

Non-stabilized selenonium ylides which bear H or R groups on the carbanionic centre are much more reactive. They have been generated[19] at 20 °C on reaction of *t*-BuOK in DMSO with selenonium salts (the latter being readily available from selenides and alkyl halides[19]), and have been trapped *in situ* with non-enolizable aldehydes and ketones producing epoxides in moderate to good yields (Scheme 49).
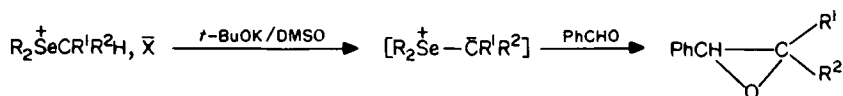
R	R^1	R^2	X	Yield (%)
Me	H	H	I	90
Ph	H	H	BF$_4$	90
Ph	H	Me	BF$_4$	69

SCHEME 49[19]

Under similar[19] or closely related[166] conditions enolizable carbonyl compounds such as heptanal, cyclohexanone and acetophenone do not form significant amounts of the corresponding oxiranes. In the case of acetophenone and trimethylselenonium fluoroborate, polymethylation of the carbonyl compound occurs. These results can be explained by enolate formation which is further alkylated by the selenonium salts[19] (Scheme 50).

$$I^-, R_2\overset{+}{S}eMe + PhC(O)Me \xrightarrow{t\text{-BuOK/DMSO}} [PhCOCH_2K] \xrightarrow{R_2{}^+SeMe, I^-} PhCOMe$$
$$R = Me, Ph \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad 40\%$$
$$+ PhCOCH_2Me + PhCOCHMe_2$$
$$13\% \qquad\qquad 28\%$$

SCHEME 50[19]

In one case the ylide has been generated[19] from diphenylmethylselenonium fluoroborate and LiCH$_2$Cl in DME at $-78\,°C$. Further addition of acetophenone leads to the formation of 1-phenyl-1-methyloxirane in 30% yield.

Selenoxides[22] and selenonium ylides[19] also react with alkyllithiums but no metalation is observed. In the case of selenonium salts[11] and BuLi $-78\,°C$ 0.2 h), selenanes are probably formed. On reaction with aldehydes and ketones selenanes release one group producing good yield of alcohols[11] (Scheme 51). Ph groups migrate in preference to Me groups or to other alkyl groups[11].

$$R\overset{+}{S}eR^1R^2, X^- + BuLi \xrightarrow{THF} [RSeBuR^1R^2] \xrightarrow{PhCHO} PhCHR^1(OH) + PhCHBu(OH)$$

R = Me, R^1 = Me, R^2 = Me, X = I:	54%	16%
R = Ph, R^1 = Ph, R^2 = Me, X = MeSO$_4$:	40%	0%
R = Ph, R^1 = Ph, R^2 = Ph, X = BF$_4$:	56%	0%

SCHEME 51[11]

4. Synthesis and reactivity of 1-metallo-1-selenoalkenes

a. Synthesis. The synthesis of these organometallics has been successfully achieved by metalation of vinyl selenides or by cleavage of the C—Se bond of 1,1-bis(seleno)alkanes.

(i) By metalation of vinyl selenides. Vinyl aryl selenides are valuable precursors of metallo-1-selenoalkenes. They have been prepared by several routes[324] including addition of selenols to terminal acetylenes[101,167], dehydrohalogenation of β-halo-[125,169-173,180] and α-halo-selenides[174,175,325] reaction of selenoacetals[123,124,176] (Scheme 31), reaction of alkynyl trialkylborate[177], alkenylborane[180], alkenyllithium[178], magnesium[179] and alkenylmercurial derivatives[180] with selenyl halides, and the reduction of 1-(phenylseleno)alkynes[180]. The reaction of Wittig[101] or Wittig–Horner[101,102] reagents with aldehydes and α-lithiosilylselenides with aldehydes[74,181] as well as the addition of selenamides to acetylene[183] and base-catalysed isomerization of allyl selenides[184] have also been used for the synthesis of vinyl selenides.

Deprotonation of the parent compound phenyl vinyl selenide has been successfully achieved by LDA at $-78\,°C$ in THF[70,121] by KDA[69] under similar conditions (Scheme 52) or with LDA in THF in the presence of HMPT[121]. Deprotonation with LDA is shown to be reversible[70] and during competitive deprotonation studies (LDA, THF) aryl vinyl sulphides are found to be thermodynamically less acidic than aryl vinyl selenides[70] [$K_{S/Se} = 0.21$ for phenyl vinyl and 0.3 for *m*-(trifluoromethyl)phenyl vinyl]. Metalation with LiTMP is irreversible and competitive deprotonation studies show vinyl

$$R^1R^2C=CH(SeAr) \xrightarrow{\text{base}} R^1R^2C=CM(SeAr) \xrightarrow{E'} R^1R^2C=CM(SeAr) \xrightarrow{E'} R^1R^2C=CE(SeAr)$$

Ar	R^1	R^2	Conditions	E'	E	Yield (%)	Ref.
Ph	H	H	1.5 eq. LDA/THF, −78°C/1 h	D_2O	D	80	70,121
			LDA/THF–HMPT(20:1)	HexCHO	HexCHOH	40	121
			KDA/THF, −78°C	DecBr	Dec	80	121
m-CF$_3$C$_6$H$_4$	H	H	LDA/THF–HMPT, −78°C	DecBr	Dec	94	69
Ph	H	Me[a]	LDA/THF, −78°C/5.8 h	BuI	Bu	85	70
m-CF$_3$C$_6$H$_4$	H	Me[a]	LDA/THF, −78°C/5 h	MeI	Me	3[b]	70
m-CH$_3$C$_6$H$_4$	H	Et	1.5 eq. LiTMP/THF, −50°C	MeI	Me	17[b]	70
Ph	Bu	H	KDA/THF, −78°C	MeI	Me	61	70
	H	nBu	KDA/THF, −78°C	MeI	Me	85	69
Ph	Me	Me	KDA/THF or LiTMP	MeI	Me	85	69
			—	—	—	—	69

[a] Mixture of isomers used.
[b] Deprotonation at the allylic position is also observed.

SCHEME 52

selenides to be kinetically more acidic than their thio analogues [$K_{S/Se} = 0.37$ for phenyl vinyl and 0.42 for m-(trifluoromethylphenyl) vinyl].

Phenyl vinyl selenides with β-monoalkyl substituents are not completely metalated with LDA in THF. Deprotonation proceeds quite readily until half of the LDA is used up and then slows down[70]. Both vinyl and allyl protons are removed under these conditions[70]. In these cases, LiTMP is not satisfactory at $-78\,°C$ and the reaction requires an excess of reagent (1.5 mol eq.) and high temperatures to go to completion[70]. KDA in THF[69] works much better and metalation is complete at $-78\,°C$. The metalation is found to be highly regio- and stereo-selective and occurs with retention of configuration[69].

β,β-Dialkyl-substituted phenyl vinyl selenides are metalated at the allylic positions with LiTMP[70] or KDA[69] but not at the vinylic one. The other substituent present on the Se atom has a big influence on the feasibility of the reaction. m-(Trifluoromethyl)phenylseleno derivatives are much more acidic than the phenyl ones[70] and methylseleno derivatives have not yet been metalated[185].

(ii) By cleavage of the C—Se bond of 1,1-bis(seleno)alkenes. 1-Metallo-1-selenoalkenes can be conveniently prepared from 1,1-bis(seleno)alkenes and BuLi in THF[185,186], taking advantage of the cleavage of the C—Se bond (Scheme 53). 1,1-Bis(selenoalkenes, are readily available from alkyl[124] or β-hydroxyalkyl[187] orthoesters which in turn have been prepared from α-metallo orthoesters[67,68] and alkyl halides[67,68], aldehydes or ketones, respectively. The alkenes have also been directly prepared from carbonyl compounds and 1,1-bis(seleno)-1-silylalkanes[186] taking advantage of the Peterson elimination of the silyloxy group.

$$R^1R^2C{=}C(SeR)_2 \xrightarrow[-78°C/1\,h]{BuLi/THF} R^1R^2C{=}C(SeR)Li \xrightarrow{E'} R^1R^2C{=}C(SeR)E$$
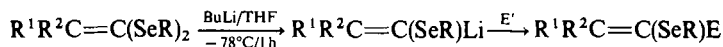
R	R^1	R^2	E′	E	Yield (%)	Ref.
Ph	H	Ph	H$_2$O	H	61(E)	186
			PhCOBr	PhCO	55(E)	186
Me	H	Dec	MeI	Me	80($Z + E$)	185
			HexCHO	HexCHOH	69($E + Z$)	185
			DMF	CHO	79(E)	185
			CO$_2$	CO$_2$H	80($E + Z$)	185

SCHEME 53

The synthesis of 1-metalloseleno alkenes from the corresponding ketene selenoacetal and BuLi is an easy reaction which takes place rapidly (0.5 h) at $-78\,°C$ in THF/hexane. Both ketene phenylselenoacetals[186] and their methylseleno analogues[185], are cleaved under these conditions and the organometallic is obtained in both cases in quantitative yield. The stereochemistry of the reaction is not well defined. The only available results are those concerning the stereochemistry of the compounds resulting from further reactions of the organometallic with electrophiles[185,186].

Both stereoisomers are obtained if the methylseleno organometallic[185] is hydrolysed or reacted with aldehydes and ketones whereas only one isomer, of α-seleno-α,β-unsaturated carbonyl compounds, whose stereochemistry has not been determined, has been found on reaction of α-methylseleno derivatives with DMF[185] or of a phenylseleno derivative with phenacyl bromide[186].

b. Reactivity. α-Metalloselenoalkenes react with alkyl halides[69,70,121,185], unhindered aldehydes and ketones[69,70,121,185], ethylene oxide[69], DMF[185], chlorocarbonates[185], phenacyl bromide[186], carbonic anhydride[185], trimethylsilyl chloride[70], dimethyl disulphite[70] and diphenyl diselenide[70]. 1,2-Addition is exclusively observed with cyclohexenone[69] with either Li^{+185} or K^{+69} used as a counterions.

5. Synthesis of allyllithiums, benzyllithiums, α-thioalkyllithiums and α-silylalkyllithiums from the corresponding selenides by selenium–metal exchange

a. Synthesis of allyl- and benzyl-lithiums. The cleavage of the C—Se bond of selenides and functionalized selenides by alkyllithiums is a powerful synthetic route to α-selenoalkyllithiums and bis(selenoalkyl)lithiums and permits the synthesis of other organometallics often difficult to prepare by other routes, such as allyllithiums,

CH_2=CH—CH_2Br

$\xrightarrow[\text{EtOH}]{\text{RSeH/NaOH}}$ CH_2=CHCH$_2$SeR $\xrightarrow[\text{78°C/0.1 h}]{\text{BuLi/THF}}$ CH_2=CHCH$_2$Li $\xrightarrow{\text{PhCHO}}$ CH_2=CHCH(OH)Ph

R = Ph	81%		86%
R = Me	80%		95%

SCHEME 54[12]

E

Z

SCHEME 55[188]

	ArCH$_2$X + RSeNa	X = Cl, Br	
	62–90%		
ArC(SeR)R^{1}R^2	ArCR^{1}R^{2}OH + RSeH + H$_2$SO$_4$	R^1 = alkyl; R^2 = H, alkyl	
A	55–78%		
	ArCR^1(SeR)Li + R^{2}X ⇒ ArCR^1(SeR)$_2$ or ArCHR^1(SeR)		

A $\xrightarrow[\text{-78°C/0.1 h}]{\text{BuLi/THF}}$ ArCR^{1}R^{2}Li $\xrightarrow{\text{PhCHO}}$ ArCR^{1}R^{2}CHPh(OH)
  B

Ar	R^1	R^2	R		B(%)
Ph	H	H	Ph	(reverse addition of **A** to BuLi)	86
Ph	H	H	Me		98
Ph	H	Me	Me	(reverse addition)	71
Ph	Me	Me	Me		80
p-ClC$_6$H$_4$	H	H	Me		91
p-FC$_6$H$_4$	H	H	Me		83
o-ClC$_6$H$_4$	H	H	Me		94

SCHEME 56[12]

benzyllithiums and α-thio- and α-silyl-alkyllithiums. Phenyl methyl selenide is quanti-
tatively cleaved[78] by BuLi in THF/hexane after 1.8 h at $-50\,°C$. Usually the more
stabilized of the two possible organometallics is formed and the rate of the cleavage of a
selenide is faster if the carbanionic species formed is more stabilized[78]. Allyl and benzyl
phenyl selenides as well as their methylseleno analogues are instantaneously cleaved by
BuLi in THF at $-78\,°C$, producing quantitatively allyl-[326] or benzyl-lithiums[12]. The
latter have been alkylated or hydroxyalkylated with alkyl halides[12] or carbonyl
compounds[12,326] (Schemes 54–56). The method is particularly useful since these orga-
nometallics cannot be easily prepared by simple metalation or by halogen–metal
exchange[189–193,201] and often require the reaction of lithium on the corresponding
ether[194–196] or thio ether[198] or the reaction of alkyllithiums on vinylic or benzylic tin
derivatives[197–200].

 b. Synthesis of α-thioalkyllithiums. Methylthio- and phenylthio-methyllithium can be
prepared[8] by metalation of the corresponding sulphide either with
BuLi/TMEDA[202] or BuLi/DABCO[203]. The method proved unsuitable for higher
homologues. These monoalkylated phenylthioalkyllithiums have been prepared by
addition of alkylmetals to vinyl phenyl sulphide[204,205] or by metalation of an alkyl phenyl
sulphide[206].

 The discovery that all the α-phenylthioalkyllithiums (even the most substituted ones),
and all the α-methylthio analogues can be prepared by C—Se bond cleavage of mixed S,Se
acetals is therefore an important observation[126,207–209]. The reactions are usually
performed at $-78\,°C$ with BuLi in THF and the α-thioalkyllithiums formed are trapped
with alkyl halides[126] or with carbonyl compounds[126,207,209] (Scheme 57). The
resulting β-hydroxysulphides have also been used for the synthesis of epoxides[208],
olefins[209,210], vinyl sulphides[210] and azidosulphides[210] (Scheme 57).

$$RSCR^2R^3SeR^1 \xrightarrow[-78\,C]{BuLi/THF} RSCR^2R^3Li \xrightarrow{E'} RSCR^2R^3E$$
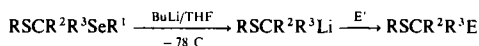
R	R¹	R²	R³	E'	E	Yield (%)	Ref.
Ph	Ph	H	H	PhCHO	PhCHOH	94	207, 208
Ph	Ph	H	Me	PhC(=O)CH₂Ph	PhC(OH)CH₂Ph	92	208
Ph	Ph	H	CHMe₂	⬡=O	⬡—OH	60	135
Ph	Ph	—CH₂(CH₂)₃CH₂—		PhCHO	PhCHOH	85	126, 207
Ph	Ph	Me	Me	HexCHO	HexCHOH	57	126, 208
Me	Me	H	Me	DecCHO	DecCHOH	73	209
Ph	Me	H	Me	DecCHO	DecCHOH	71	209
Me	Me	Me	Me	DecCHO	DecCHOH	70	209
Me	Ph	H	Me	DecCHO	DecCHOH	80	207

SCHEME 57

 c. Synthesis of α-silylalkyllithiums. The synthesis of α-silylalkyllithiums by cleavage of the
C—Se bond in α-silyl selenides is not as facile as that of α-seleno- and α-thio-alkyllithiums
which we have just presented. Thus α-silyl phenyl selenides do not produce α-
silylalkyllithiums but exclusively α-silyl butyl selenides and phenyllithium[211] (Scheme 58).

$$Et_3SiCH(Hex)SePh + BuLi \xrightarrow{THF,\ -78\,°C} Et_3SiCH(Hex)SeBu + PhLi$$
$$66\%$$
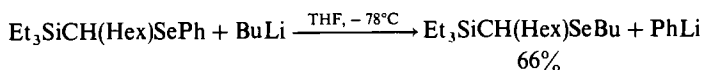
SCHEME 58[211]

If methylseleno derivatives are used, however, the α-lithioselenides are obtained. The reaction proceeds at 0 °C for monosubstituted alkyl derivatives and produces moderate ($\sim 50\%$) yields of the desired organometallics[211] (Scheme 59). Under similar conditions secondary alkyl silyl selenides do not react except for the cyclopropyl derivative which leads to α-silylcyclopropyllithium in very good yield[143] at -20 °C (last entry in Scheme 59).

$$R_3^3SiCR^1R^2SeMe + BuLi \xrightarrow[\text{BuSeMe}]{\text{THF}} R_3^3SiCR^1R^2Li \xrightarrow{R^4CHO} R_3^3SiCR^1R^2CHR^4OH$$
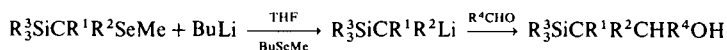
R³	R¹	R²	Conditions	R⁴	Yield (%)	Ref.
Et	H	Me	0°C/1 h	Hex	45	211
Me	H	Hex	0°C/1 h		50	211
Et	H	Hex	0°C/1 h	Hex	30	211
Me	—CH₂CH₂—		−20°C/1 h	Dec	85	143

SCHEME 59

α-Silylalkylmetals are rather difficult to prepare. The parent compound forms in low yield on metalation of tetramethylsilane[8,212,213] or by halogen–metal exchange in α-bromotriphenylsilylmethane[8,214]. The last reaction has been used for the preparation of trimethylsilyl/ethyllithium and more recently for the synthesis of α-silylcyclopropyllithium[143]. These compounds remain until now the only two examples of α-silylalkyllithiums bearing two alkyl groups on the carbanionic centre[143,215,216]. Compounds bearing only one alkyl group on the carbanionic centre (at the exclusion of α-silylethyllithiums) have also been obtained by addition of organometallics across the C=C bond of vinylsilanes[8,217-219].

d. Miscellaneous syntheses of organometallics by selenium–metal exchange. C—Se bond cleavage in selenides has also been used for the synthesis of a few aryllithiums[8,10-12], some metallo heteroaromatic compounds and α-lithiotriphenylethylgermane[34].

C. Reactions of Selenides and Functionalized Selenides

1. Reactions involving the reduction of the C—Se bond

Reactions involving the reduction of a C—Se bond to a C—H bond have been achieved using Raney nickel in ethanol[14,220], lithium in ethylamine[14] and trialkyl- or triaryl-tin hydrides[15,108,148,221] with or without azobisisobutyronitrile AIBN (Scheme 2).

Thus substituted selenides[222] and β- and γ-hydroxyselenides[108,221] have been reduced to the corresponding alkanes or hydroxyalkanes with Li/EtNH₂ or with tin hydrides.

Selenoacetals, including functionalized ones, have been reduced selectively[15,148,221] to selenides or to the corresponding alkanes depending upon the number of equivalents (1 or 2) of tin hydride used. Direct reduction to alkanes has also been performed on reaction with Raney nickel[14] or lithium in ethylamine[14].

The reduction of vinyl selenides is more complex. Thus whereas methyl vinyl selenides are transformed to the corresponding olefins on reaction with tin hydride[185], involving the reduction of the Se—sp² carbon Bond, Se—methyl bond cleavage is observed[185] if lithium in ethylamine is used (Scheme 60).

$$\text{OctCH}{=}\text{C(SeMe)Me} \longrightarrow$$

$$\xrightarrow[\text{toluene, 90°C/3h}]{\text{Bu}_3\text{SnH/AIBN}} \text{OctCH}{=}\text{CHMe}$$
$$51\%$$

$$\xrightarrow[-15°\text{C/1 h}]{\text{Li/EtNH}_2} \text{OctCH}{=}\text{C(Me)Se}{-}\text{SeC(Me)}{=}\text{CHOct}$$
$$68\%$$

SCHEME 60[185]

Aluminium amalgam[153], P_2I_4[223] and PI_3[223] efficiently reduce α-selenoketones to ketones (Scheme 61). P_2I_4 surprisingly allows the direct transformation of α-seleno-α-cyclopropyl ketones to γ-iodoketones[223] (Scheme 61b).

$$\text{OctCH(SeR)COMe} \xrightarrow[\text{R = Ph or Me}]{0.5 \text{ mol eq. P}_2\text{I}_4, 20°\text{C/0.4 h}} \text{OctCH}_2\text{COMe} \qquad \text{(Ref. 223)} \quad \text{(a)}$$
$$> 80\%$$

$$\xrightarrow[\text{acetone, 20 °C}]{\text{1 mol eq. P}_2\text{I}_4} \left[\text{ICH}_2\text{CH}_2\text{CH(SePh) COHex}\right] \longrightarrow \text{I(CH}_2)_3\text{COHex}$$
$$95\%$$
$$\text{(Ref. 223)} \quad \text{(b)}$$

$$\xrightarrow{\text{Al/Hg}}$$

$$\sim 100\%$$
$$\text{(Ref. 153)} \quad \text{(c)}$$

SCHEME 61

As already mentioned, the reduction of the C—Se bond can be performed with alkyllithiums. Thus α-selenoalkyllithiums and α-lithioselenoacetals (prepared from selenoacetals or selenoortho esters) hydrolyse or deuterolyse to selenides and selenoacetals or deuteriated analogues.

Selenides are also reduced with alkyllithiums and useful reactions have been performed on allyl or benzyl selenides which quantitatively produce allyl- and benzyl-lithiums[12] on reaction with BuLi in THF.

2. Reactions involving the transformation of the C—Se bond to a C—halogen bond

Selenides are valuable precursors of alkyl halides. The reactions can be directly achieved from dialkyl or aryl alkyl selenides and bromine (in CH_2Cl_2/NEt$_3$[17,18] or in ethanol[18]) or alkyl halides (CH_3I[17] or $BrCH_2COOMe$[106b] in DMF).

These reactions proceed through selenonium salts which can be isolated if the reactions are performed at low temperature but which decompose slowly in the presence of triethylamine or by refluxing in DMF to produce alkyl halides. The Br_2/NEt$_3$ method is particularly valuable for the synthesis of secondary or tertiary alkyl bromides from the corresponding selenides and occurs with complete inversion of configuration at the substituted carbon atom in case of the secondary alkyl selenides[18].

Coupled with the Grieco reaction[224] which allows the synthesis of selenides from alcohols with inversion of configuration[18], these reactions permit two-step synthesis of alkyl bromides from alcohols with overall retention of configuration[18] (Scheme 62).

SCHEME 62[18]

The RX/DMF method proceeds efficiently with selenides possessing a primary alkyl chain, but with secondary alkyl selenides it mainly leads to olefins.

Both methods have been successfully applied[106] to the synthesis of γ-halogenoselenides from γ-hydroxyselenides (Scheme 63a) but exclusively produce tetrahydrofurans[106] if applied to the higher homologues, namely δ-hydroxyselenides (Scheme 63b).

$$\text{HexCH(SePh)CH}_2\text{CH(OH)Me} \xrightarrow[\text{80°C/3h}]{\text{Br}_2/\text{EtOH}-\text{H}_2\text{O}} \text{HexCHBrCH}_2\text{CH(OH)Me} \quad \text{(a)}$$
$$80\%$$

R = Me	Br$_2$/EtOH–H$_2$O, 80°C/3 h	77%
R = Ph	Br$_2$/EtOH–H$_2$O, 80°C/3 h	70%
R = Me	Br$_2$/NEt$_3$–CH$_2$Cl$_2$, 20°C/3 h	80%
R = Ph	Br$_2$/NEt$_3$–CH$_2$Cl$_2$, 20°C/3 h	74%
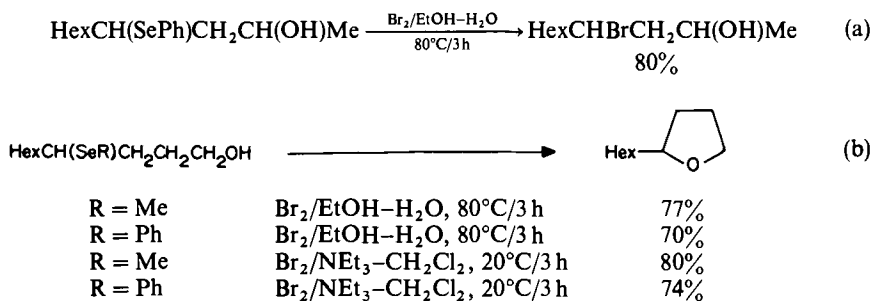
SCHEME 63[106a]

S—Br exchange has also been performed on vinyl selenides[34,120,185,225], but the addition of bromine to the C=C bond as well as to the Se atom can occur. In benzene or chlorobenzene vinylbromide was formed[34,120,185], whereas a mixture of vinyl bromide and α-bromoketone, arising presumably from the addition of bromine across the C=C bond, was observed[185] in CH$_2$Cl$_2$ or CH$_2$Cl$_2$/NEt$_3$ (Scheme 64).

$$\text{OctCH=CMe(SeMe)} \longrightarrow \text{OctCH=CBrMe} + \text{OctCHBrCOMe}$$

Br$_2$/PhH or PhCl, 20°C/15 h	51%	0%
Br$_2$/CH$_2$Cl$_2$	43%	24%
Br$_2$/NEt$_3$–CH$_2$Cl$_2$	60%	24%
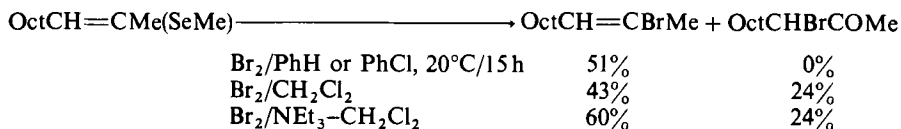
SCHEME 64[185]

3. Selenoxide synthesis and reactivity

a. Synthesis. Selenides are readily oxidized to selenoxides[3-6,8]. Among the various reagents used for selenoxide formation the following have been the most frequently used:

hydrogen peroxide in THF/water[7,226,227] or in CH_2Cl_2[125,227], sometimes in the presence of catalytic quantities of transition metal complexes[228], organic peracids[22,227,229,230], peroxides (usually t-BuO_2H) without additives[231] or in the presence of either alumina[232] or transition metal complexes[228], ozone[9,227,232] and singlet oxygen[320] (Schemes 4a, 7, 8, 65).

$$RSeM + BrCH_2CH_2R^1 \rightarrow RSeCH_2CH_2R^1$$

$$\xrightarrow{(O)} [RSe(=O)CH_2CH_2R^1] \rightarrow CH_2=CH_2R^1$$

R	R^1	Conditions	Yield (%)	Ref.
Ph	$C_{10}H_{21}$	10 eq. H_2O_2/THF, 25°C/20 h	77	233
o-$NO_2C_6H_4$	$C_{10}H_{21}$	10 eq. H_2O_2/THF, 0°C/0.5 h	62,91[a]	233
m-$CF_3C_6H_4$	$C_{10}H_{21}$	10 eq. H_2O_2/THF, 25°C/2 h	70[a]	233
p-$MeOC_6H_4$	$C_{10}H_{21}$	10 eq. H_2O_2/THF, 25°C/7 h	60[a]	233
Ph	C_8H_{17}	O_3/CH_2Cl_2, − 78°C then 45°C/24 h	30	232
		O_3/CH_2Cl_2, 3 eq. NEt_3, 45°C/24 h	75	232
		t-BuO_2H/Al_2O_3/THF, 65°C/3 h	86	232
Me	C_8H_{17}	O_3/CH_2Cl_2, − 78°C then 45°C/24 h	< 1	232
		O_3/CH_2Cl_2, 3 eq. NEt_3	23	232
		t-BuO_2H/Al_2O_3/THF, 65°C/3 h	83	232

[a]These yields were determined by GLC relative to an internal standard.

SCHEME 65

The reaction with ozone can be performed at low temperature (− 78 °C) and seems to be highly selective, selenides being oxidized selectively even in the presence of an olefin which remains unchanged. Selenoxides are stable at this low temperature and do not eliminate.

Hydrogen peroxide in THF is one of the best methods if one wishes to oxidize the selenide, followed by its decomposition to olefin. The reaction is often conducted in the presence of an excess of hydrogen peroxide which further oxidizes the selenenic acid, concomitantly formed, to seleninic acid[3-6,8,26,27], avoiding the addition of selenenic acid across the C=C bond of the olefin. The hydrogen peroxide method does not always permit selenoxide formation. In the case of vinyl selenides for example the C=C bond is cleaved and carbonyl compounds are formed[123] (Scheme 66).

(a) $\xrightarrow[20\ °C]{H_2O_2/THF}$ $MeCO(CH_2)_4COOH$ 65%

(b) $\xrightarrow[20\ °C]{H_2O_2/THF}$ $HOOC(CH_2)_4COOH$ 75%
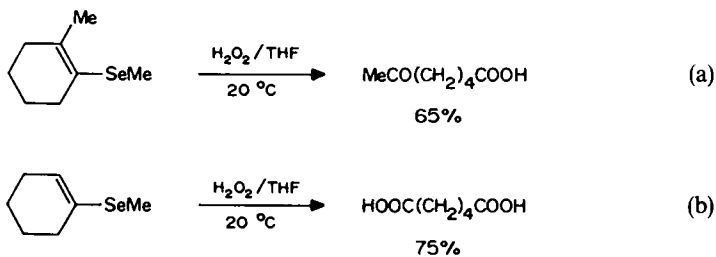
SCHEME 66[123]

If the selenoxide is used as an intermediate for olefin synthesis it is often important to remove the selenenic acid from the medium[3-6,8,26], in order to avoid its addition to the

olefin. This can be done as above with an excess of oxidant, or if the reactions are carried out in the presence of an amine[227,232,234] or basic alumina[232] which trap the selenenic acid.

b. Reactions involving the selenoxide elimination. The stereochemistry of the selenoxide elimination has been investigated[27]. It proceeds, as in the case of sulphoxide elimination, in a *syn* fashion[27,91]. Further insight into its intimate mechanism has been described[235]. The reaction is not usually regio- and stereo-selective if several hydrogens are available on the C atoms β to the one bearing the selenoxy group. In the product mixture of different olefins the less substituted ones predominate, in which the formation of the *E* isomer is greatly favoured over the *Z*. The *syn* elimination of selenenic acid is an imperative requirement and therefore olefin formation does not occur when this stereochemical requirement cannot be achieved[28,91] (Scheme 67).

$$\text{Ar} = m\text{-CF}_3\text{C}_6\text{H}_4\text{—}$$
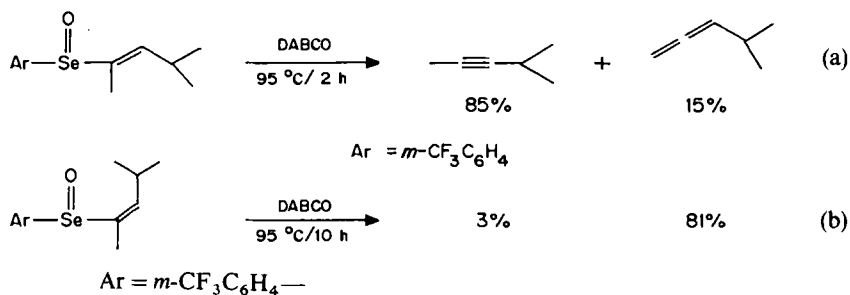
SCHEME 67[264]

c. Regiochemistry of the selenoxide elimination. In several instances the reaction is regioselective. Thus in the case of β-hydroxyselenides[11,22,108,126,127,132,233,241,252] the elimination occurs away from the hydroxyl group and produces allyl alcohols except in the case where the only hydrogen available is the one α to the hydroxyl group.

Similar observations have been made with β-acetoxy-[226] or trifluoromethylacetoxy-[242] selenoxides[220,226,243-246], β-alkoxyselenoxides[220,226,243-247], β-selenoxyacetals[248], β-halogenoselenoxides[226,249], at the exclusion of the chloro compounds, β-selenoxyalkyl-amides[250] and β-selenoxyamines[168] which lead, respectively, to allyl acetates or trifluoromethyl acetates, allyl ethers, allylic halides, enamides and amines.

β-Azidoselenoxides[251] for their part eliminate in both directions producing a mixture of vinyl and allyl azides. Finally, a series of functionalized selenoxides have been successfully transformed to functionalized olefins. That is the case among others of α-selenoxy aldehydes[14,136], α-selenoxyketones[2,22,136,227,229,253-255], α-selenoxy es-ters[136,229,256,257], α-selenoxylactones[91,258,259], α-selenoxy acids[2,136], α-selenoxyamides[260], α-selenoxynitriles[92,261], α-selenoxynitroalkanes[103,262] and α-selenoxyphosphonium salts[230], which produce respectively α,β-unsaturated aldehydes, ketones, esters, lactones, acids, amides, nitriles and nitroalkanes and vinyl phosphonium salts. In most cases the synthesis of these compounds has been directly achieved at 20 °C or below from the corresponding selenide and an oxidant, without isolation of the intermediary selenoxide.

d. Structure–reactivity relationships in the selenoxide elimination. The nature of the selenoxy group has a great influence on the elimination. The *o*-nitrophenylselenoxy[233], *m*-chlorophenylselenoxy[233], pyridylselenoxy[263] and *m*-(trifluoromethyl)phenylselenoxy[264] groups eliminate much faster than their phenylselenoxy analogues, which themselves react

at a temperature below 20 °C. Methylselenoxy derivatives[232] react much more slowly in CH_2Cl_2 or THF. In the two latter cases valuable improvements are observed if the reactions are carried out in the presence of an amine[227,232,234] or at reflux temperature in THF in the presence of t-butyl hydroperoxide and basic alumina[232].

All things being equal, secondary alkyl selenoxides react faster than primary ones and the presence of a carbonyl group on the carbon bearing the selenoxy group favours the reaction, whereas a cyclopropyl[20] or a vinyl[123,264] group disfavours it. In the latter cases the selenoxide often releases the oxygen and reverts to the starting selenide, but the presence of a group with a strong inductive effect linked to the Se atom can restore the reactivity. Thus, whereas vinyl phenyl selenoxides do not fragment[123,264] their m(trifluoromethyl)phenyl analogues afford allenic and/or acetylenic compounds by selenenic acid elimination[264] (Scheme 67).

e. α-Silyl selenoxides. In some cases the selenoxide does not eliminate but leads to other types of reactions. This is the case with α-silyl selenides[74-76] and selenoacetals[266] which possess a high tendency to produce aldehydes or ketones on reaction with hydrogen peroxide. The formation of these compounds can be accounted for by a Pummerer-type rearrangement. α-Silylacetals and selenoorthoesters behave similarly and lead to the corresponding carboxylic acids[74] in high yields.

f. Allylic, allenic and propargylic selenoxides. Allyl selenoxides[27,77,267,269] and related allenyl[5,268] and propargyl[81] selenoxides do not eliminate[82] the selenenic acid but instead produce allenyl alcohols[78,267] or α,β-unsaturated carbonyl compounds[5,81,268], respectively. The reaction therefore implies an allyl selenoxide → allyl seleninate rearrangement rather than the selenoxide elimination reaction reported previously. Arylselenoxy derivatives are much more prone to rearrangement than their methylselenoxy[264,269] or arylsulphoxy[81,269] analogues. For example the cyclopropyl allyl derivatives shown in Scheme 68 rearrange to alkylidene cyclopropane in the phenylseleno series[269] but not in the methylseleno or phenylthio series.

X = SePh	H_2O_2/THF–H_2O	0%
	H_2O_2/MeOH	0%
	$NaIO_4$/MeOH, extraction	
	then piperidine/cyclohexane	77%
X = SeMe	As above	16%
X = SPh	As above	0%
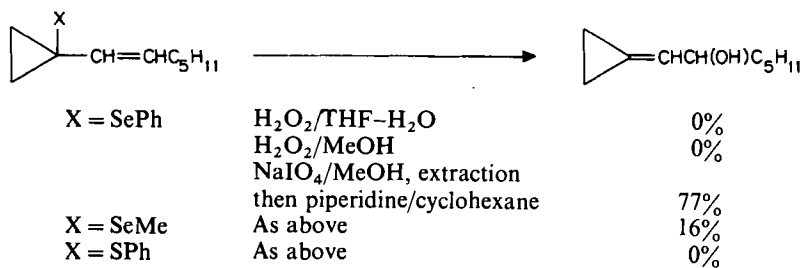
SCHEME 68[269]

g. β-Alkyloxyselenoxides. As already mentioned β-hydroxyselenides fragment to allyl alcohols. A ring-enlargement leading to cyclopentanones takes place[153] when β-alkoxyselenoxides, derived from cyclobutanones, are heated in THF (Scheme 69).

h. Vinyl selenoxides. A series of vinyl selenoxides have been reacted with enolates, and have led via α-lithioselenoxides, to α-cyclopropyl ketones and esters in fair to good yield. A specific example of this kind of reaction[271] is shown in Scheme 70.

i. Reduction of selenoxides to selenides. Selenoxides have been reduced to selenides by a large variety of reagents which include P_2I_4 and PI_3[159,160,270], phosphine, tin
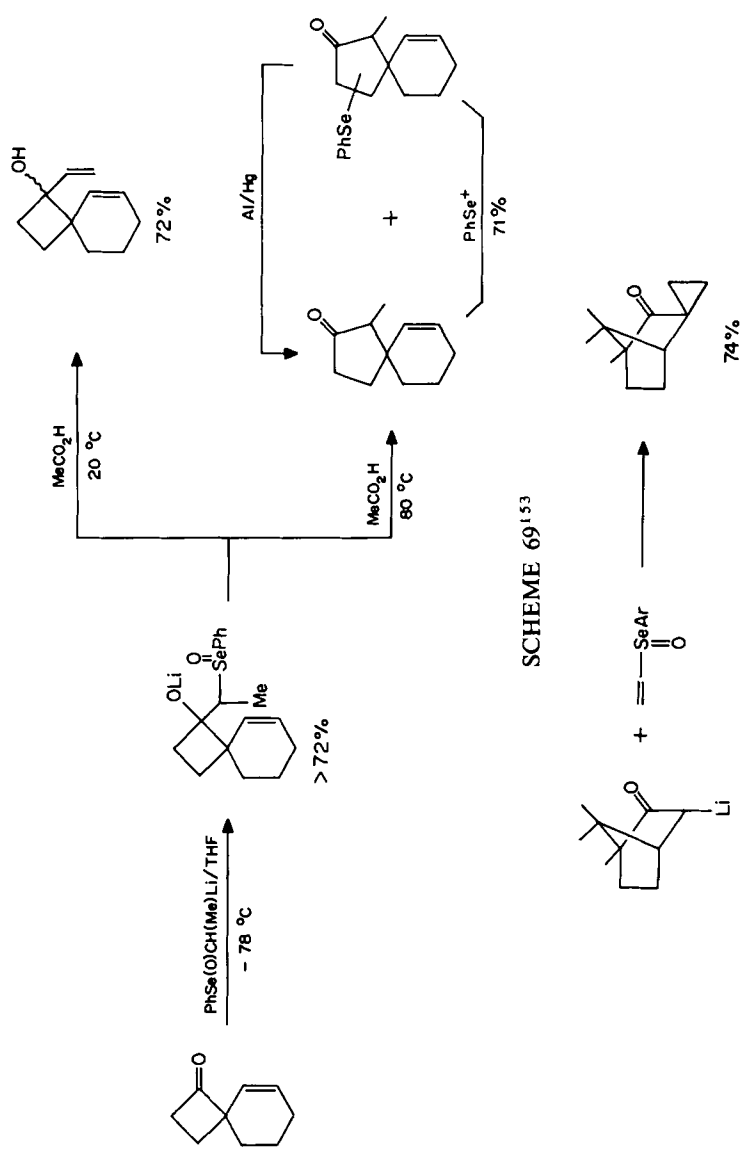
SCHEME 69[153]

SCHEME 70[271]

chloride[21] and selenolate[271]. The selenoxides have also been used as mild and selective oxidizing agents[6,272-279]. Their transformation to alkyl chlorides and bromides has been successfully performed[23] with HCl or HBr.

4. Synthesis and reactivity of selenonium salts

a. Synthesis. Selenonium salts[19,94,106,108,129,135,137,138,140,251,269,280] are usually prepared from selenides and alkylating agents such as alkyl halides[19], in the presence or not of silver tetrafluoroborate[19], dialkyl sulphates[19] and methyl fluorosulphonate[20,108] (magic methyl). The alkylation is often performed in the absence of solvent, in methylene dichloride or in ether but in the last solvent the reaction is slower. As expected, phenylseleno derivatives[19,137,140] are much less reactive than their methylseleno analogues[94,138], and are usually alkylated in the presence of silver salts. These strong conditions are not required for methylseleno derivatives. The presence of a hydroxyl group in the β-[94,135,137,138,281], γ-[106b,129] or δ-[106b] position to the selenenyl moiety has been found to greatly enhance the rate of the reaction and this is particularly observed in hte methylseleno series.

β-Hydroxyselenides substituted by alkyl groups on the two heterosubstituted carbon atoms have some tendency to rearrange to ketones[19,108] on reaction with alkyl halides[137]. This reaction is favoured in the case of very hindered derivatives, especially if the alkylation is performed in CH_2Cl_2. In the very difficult cases presented in Scheme 71, the
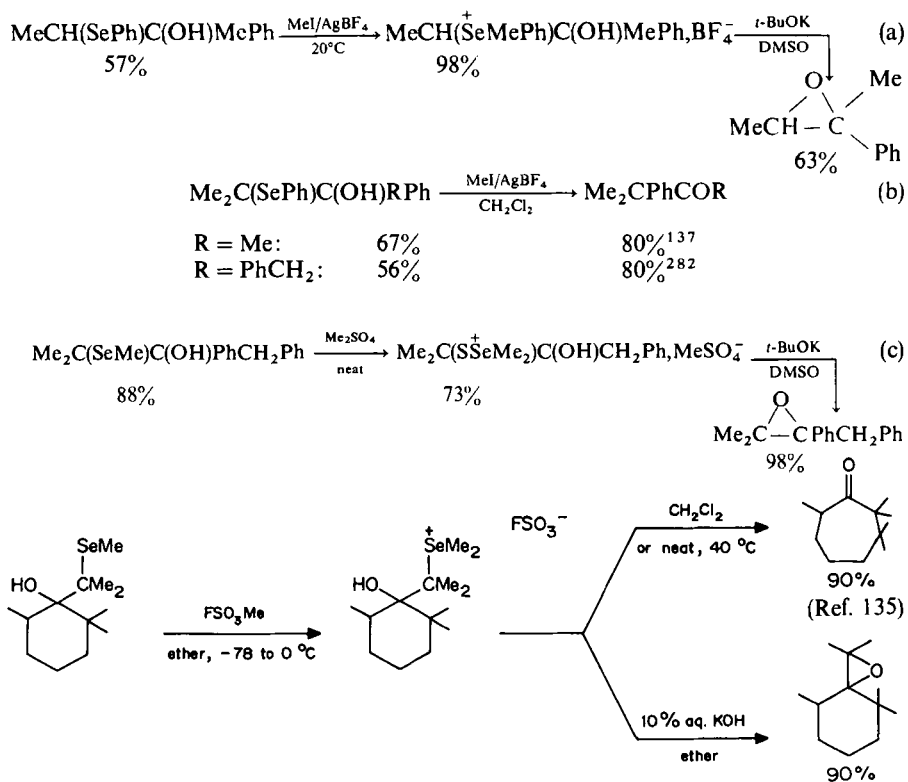
SCHEME 71

solvent was found to have a crucial role. Thus the hindered β-hydroxyselenonium salts can be quantitatively prepared if ether[108] is used as the solvent and rearrange immediately to ketones when they are dissolved in CH_2Cl_2 (Scheme 71).

b. *Reactivity.* Selenonium salts are reactive compounds. They react very specifically but in very different ways with nucleophilic/basic reagents. Substitution is observed with enolates[19] and alcoholates[19] (Schemes 3 and 50) whereas attack on the Se atom takes place with alkyllithiums[11] (Schemes 3 and 51).

Metalation has been found to occur on reaction with a base such as t-BuOK in DMSO[20] or in THF[20], with KOH in the same solvents[20] or with metalloamides[11]. The resulting ylides have been trapped *in situ* with carbonyl compounds to produce epoxides[11,166].

In the absence of carbonyl compounds an internal elimination involving the selenide and a β-hydrogen, if available, takes place and produces a very good yield of olefin. This reaction is related to the selenoxide elimination[20] but is far superior to it for the synthesis of alkylidene cyclopropanes[20,269] (Schemes 4b and 72) and allylidene cyclopropanes[269] from cyclopropyl selenides. If several hydrogens are available in the β-position, the elimination is not regiospecific and leads to a mixture of regioisomeric olefins in which the less substituted ones predominate[20]. Moreover, in the case of α,β-disubstituted olefins the E isomer is exclusively formed[20].

SCHEME 72[269]
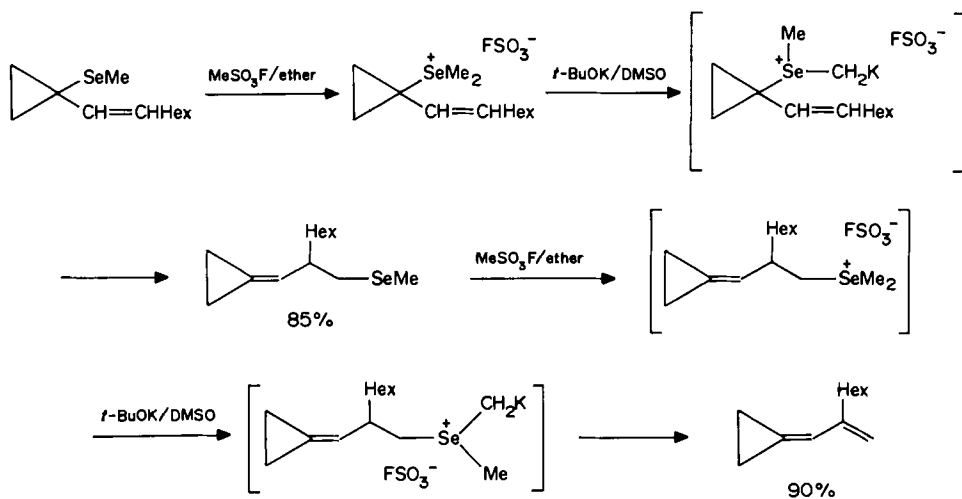
The reaction of selenonium salts with bases requires further comments. Thus the presence of a hydroxyl group in the molecule often changes the course of the reaction:

(*i*) β-Hydroxyselenonium salts do not usually produce allyl alcohols[108] by the elimination reaction just reported but instead lead to epoxides by an internal substitution reaction. The reaction proceeds stereospecifically[2,140] and allows the synthesis of terminal[94,137] and polyalkylated derivatives[94,137,140] and hindered[108] and α,β-unsaturated compounds[138] (Scheme 73).

(*ii*) γ-Hydroxyselenonium salts in which the selenyl moiety is attached to a methylene group produce oxetanes[106b,307] (Scheme 74a), whereas homoallyl alcohols are exclusively observed[129] if a hydrogen is present on the carbon δ to the hydroxyl group (Scheme 74b).

OH

$\overset{+}{SePh}$

Et   X⁻

NaH/THF

O

(Ref. 2)   (a)

Dec   OH

H

$Me_2\overset{+}{Se}$ Bu

cis : *trans* = 85:15

t-BuOK/DMSO

O

H   H

Dec   Bu

70%

cis : *trans* = 85:15

(Ref. 140)   (b)

HexCH($\overset{+}{Se}$Me₂)CH(OH)Hex   MeSO₄⁻

aq. KOH/CH₂Cl₂

O

Hex —⟍⟋— Hex

86%

(Ref. 144)   (c)

SO₃F⁻

Me₂$\overset{+}{Se}$ HO

aq. KOH/ether

O

99%

(Ref. 108)   (d)

$\overset{+}{Se}Me_2$ I⁻

HO

t-BuOK/DMSO

O

80%

(Ref. 138)   (e)
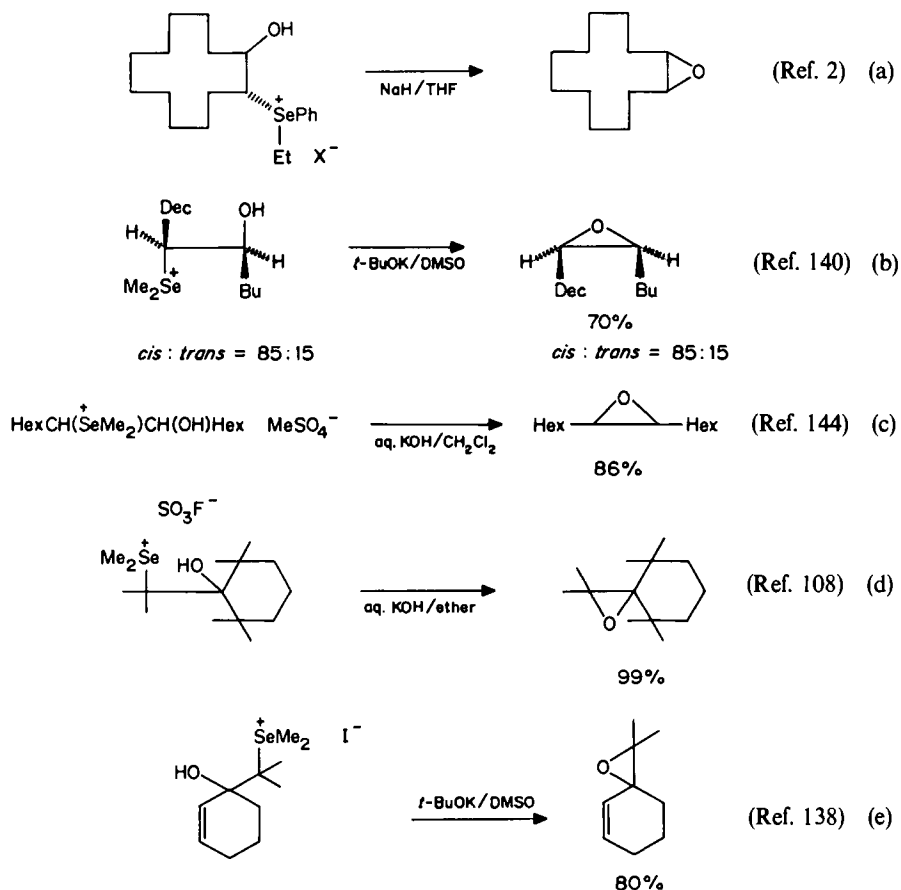
SCHEME 73

The high regioselectivity of the reaction (no allyl alcohol formed) suggests an anchimeric assistance of the alkoxide group[127,129].

(*iii*) δ-Hydroxyselenonium salts are also cyclized on reaction with bases[106b]. The yields of tetrahydrofurans are modest and other unidentified products are formed (Scheme 75). Similar results are observed if the selenonium salts are heated at 80 °C in chloroform[106b] in the absence of base.

5. Synthesis using functionalized selenides

a. Synthesis of olefins from β-hydroxyselenides. As already shown selenides are valuable precursors of olefins taking advantage of the easy thermal elimination involving the corresponding selenoxides or selenonium ylides. Other reactions producing olefins are in some cases more flexible than the just reported ones. While oxidation of selenoacetals[266], orthoseleno esters[128] and α-silyl selenides[74-76] leads to the formation of carbonyl compounds, vinyl selenides[123,124,324,325] and ketene selenoacetals[124] are however prepared from selenoacetals[266] and orthoesters[74], respectively, on reaction with MeI in DMF at 80 °C[123] or with PI₃ or P₂I₄ in chlorinated solvents[124].

$$Me_2\overset{+}{Se}CH_2CH_2CH(OH)Hex \quad \overset{t\text{-}BuOK/DMSO}{\underset{20\ ^\circ C/4\ h}{\xrightarrow{\hspace{2cm}}}} \quad \boxed{}\text{-Hex} \quad + \quad CH_2{=}CHCH(OH)Hex$$

$$I^-$$

25% 25%

$$+ \quad MeSeCH_2CH_2CH(OH)Hex \qquad\qquad \text{(Ref. 307)} \quad \text{(a)}$$

10%

PhCH$_2$—H OH
$\overset{+}{Me_2Se}$ Hex
I$^-$
$\xrightarrow{\text{base}}$
[PhCH$_2$—H O$^-$ $\overset{+}{Me_2Se}$ Hex I$^-$]

$$\xrightarrow{\hspace{1.5cm}} \quad PhCH_2CH{=}CHCH_2CH(OH)Hex \qquad \text{(Ref. 129)} \quad \text{(b)}$$
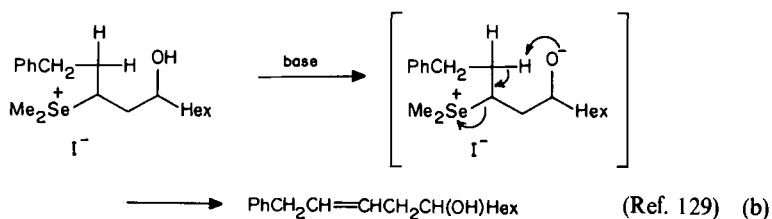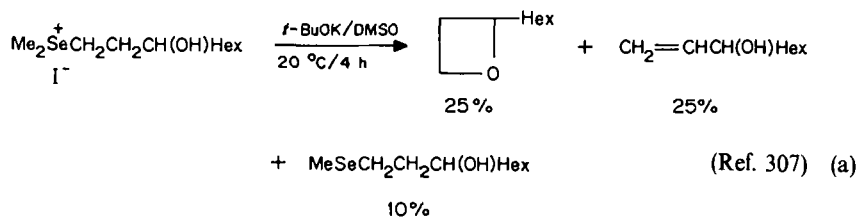
1 mol eq. t-BuOK/DMSO, 20°C/4 h   91%
aq. 50% KOH, Adogen 464^a, CH$_2$Cl$_2$, 20°C/4 h   73%

^{a} Trade name (Ashland Chemical Co.) for methyltrialkyl (C_8–C_{10}) ammonium chlorides.

SCHEME 74

Ph HO
$\overset{+}{Me_2Se}$
I$^-$
$\xrightarrow{\hspace{2cm}}$
Ph O

t-BuOK/DMSO, 20 °C   60%
NaH/DMSO, 20 °C   50%
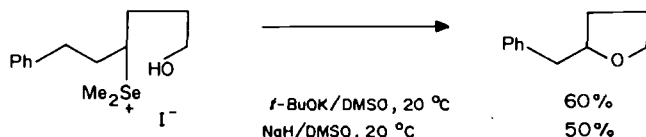
SCHEME 75[106b]

As already pointed out elimination of a hydrogen and a selenyl moiety leads to regio- and stereo-isomeric mixtures of olefins when several topologically different hydrogens are available.

Concomitant elimination of a selenenyl and another heteroatomic moiety in β-heterosubstituted selenides overcomes these problems. Thus β-halogenoselenides are regio- and stereo-selectively transformed to olefins on reaction with selenolate ions[283] or in the presence of an amine[21,131]. The reaction was found to occur by formal *trans* elimination[72,100,130,131,140] of the two heteroatomic moieties. Episeleniiranium salts have been proposed as intermediates in these reactions[72,131]. Attack of the selenolate in the first case and the amine in the second on the charged Se atom of the seleniiranium ion can explain both the reaction and its stereochemical course.

β-Hydroxyselenides are readily available by reaction of α-selenoalkyllithiums with carbonyl compounds[2,4-8,11,67,100,108,126,130,139], by reduction of β-hydroxy-selenoxides[21], by reaction of organometallics on α-selenocarbonyl compounds[39,40,143], by ring-opening of epoxides with selenolates[130,131,284], by reaction of olefins with selenenic acids[231,281,327,337] or related reagents or by hydrolysis of β-halogenoselenides[251]. β-Acetoxy-[226] and trifluoroacetoxy-[285,286] selenides are also found to be valuable precursors of olefins: the reaction takes advantage of the easy transformation of the hydroxyl group to a better leaving group.

Mesyl chloride[21,72,287], thionyl chloride[130], trifluoroacetic anhydride[131,288], phosphorus oxychloride[88,100], diphosphorus tetraiodide[108] or phosphorus triiodide[107,108,269] in the presence of an amine, trimethylsilyl chloride and NaI in MeCN[289] as well as

perchloric or p-toluenesulphonic acids[131] have been successfully used for this purpose. Terminal, α, β-disubstituted, tri- and tetra-substituted olefins have been prepared from the corresponding β-hydroxyselenides (Scheme 76). PI_3 and P_2I_4 were particularly suitable for the synthesis of hindered or strained olefins[107,108] β-Hydroxycyclopropyl selenides are not easily transformed to alkylidene cyclopropanes[8b,107] on reaction with most of the reagents already listed. However, those possessing a secondary hydroxyl lead to alkylidene cyclopropanes on reaction with carbonyl diimidazole at $160\,°C$[8b,107] whereas those bearing a tertiary hydroxyl produce the alkylidene cyclopropanes on reaction with PI_3 already at $20\,°C$[107]. The last conditions have been successfully used for the synthesis of an allene from a β-hydroxyvinyl selenide[185].

Me Cl/NEt$_3$/CH$_2$Cl$_2$ 98%[21]   (a)
HClO$_4$/ether   65%[131]

HexCH(SeMe)CH(OH)Hex $\xrightarrow{\text{SOCl}_2/\text{NEt}_3/\text{CH}_2\text{Cl}_2}$ HexCH=CHHex   (Ref. 130)   (b)
88%

Me$_2$C(SeMe)CH(OH)Dec $\xrightarrow{\text{PI}_3/\text{NEt}_3/\text{CH}_2\text{Cl}_2}$ Me$_2$C=CHDec   (Ref. 144)   (c)
80%

$\xrightarrow{\text{PI}_3/\text{NEt}_3/\text{CH}_2\text{Cl}_2}$ (Ref. 108)   (d)
85%

$\xrightarrow{\text{Im}_2\text{CO}/110\,°C/15\ h}$ =CH—Dec   (Ref. 107)   (e)
58%

$\xrightarrow{\text{PI}_3/\text{NEt}_3/20\,°C/2\ h}$ (Ref. 107)   (f)
75%

$\xrightarrow{\text{POCl}_3/\text{NEt}_3/\text{CH}_2\text{Cl}_2}$
80%
(Ref. 100)   (g)

$\xrightarrow{\text{POCl}_3/\text{NEt}_3/\text{CH}_2\text{Cl}_2}$
81%
(Ref. 100)   (h)

(Ref. 187) (i)

(Ref. 187) (j)

(Ref. 88) (k)

(Ref. 88) (l)

(Ref. 290) (m)
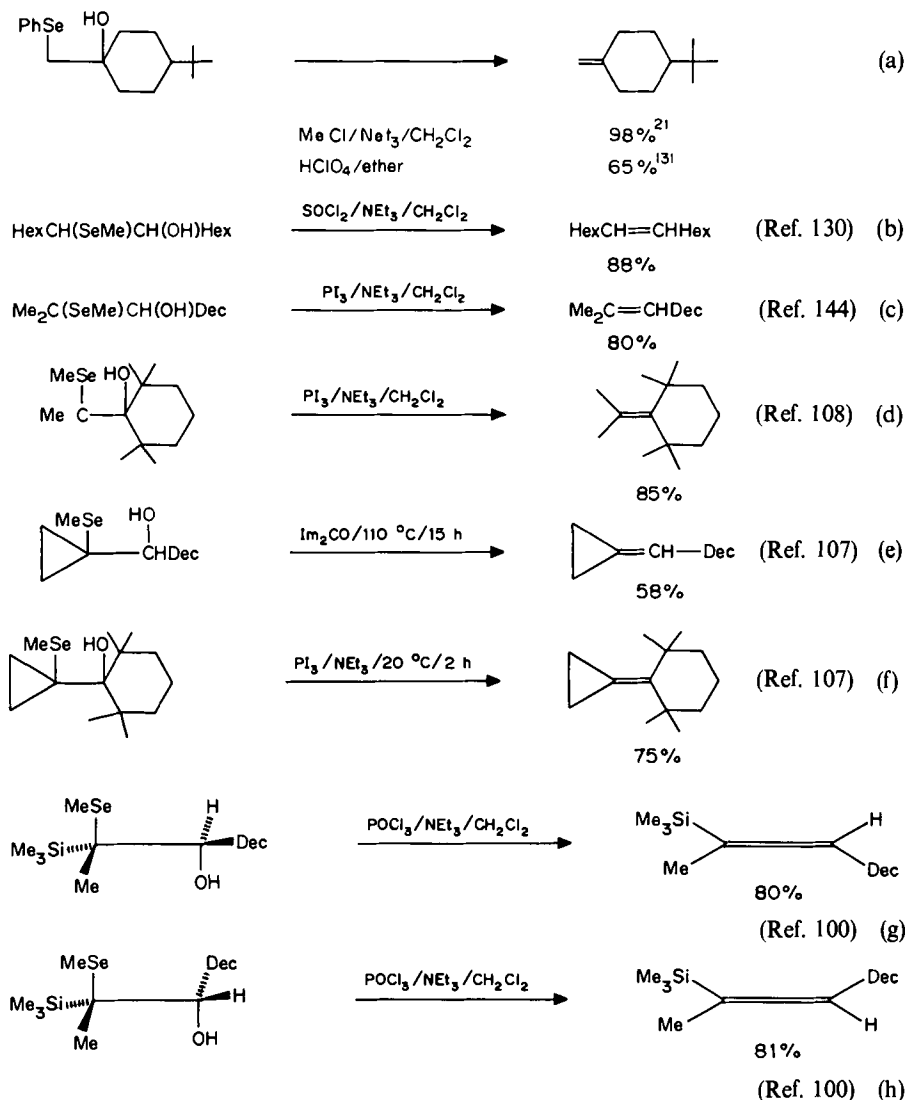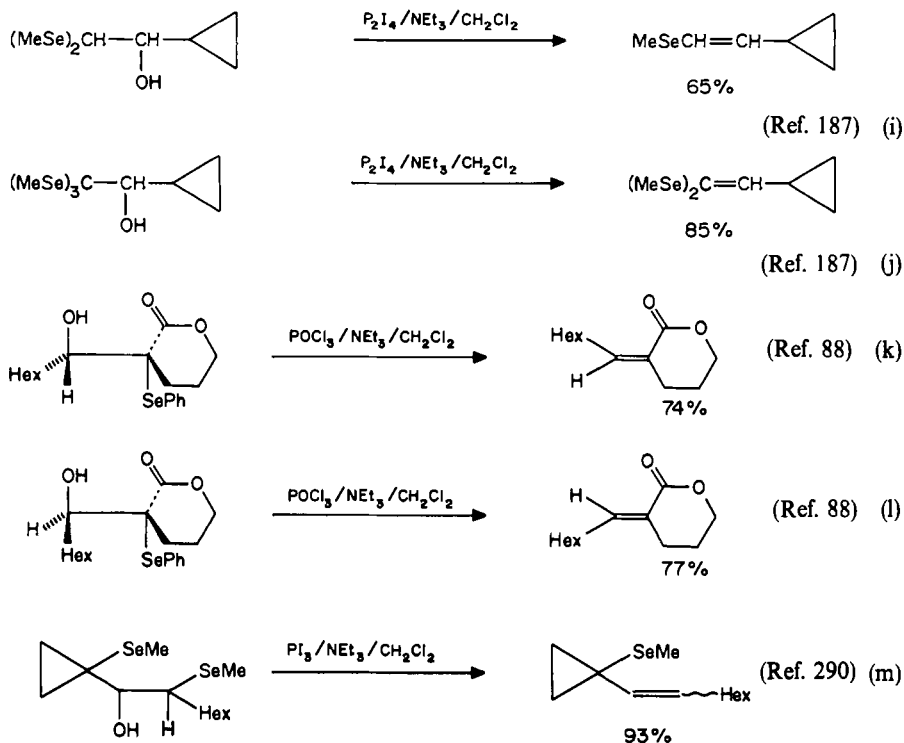
SCHEME 76

b. Synthesis of ketones from β-hydroxyselenides. The presence of two potential leaving groups β to each other makes β-hydroxyselenides valuable candidates for pinacolic-type rearrangements. The selective transformation of each of the two groups to leaving groups has already been described. Usually, transformation of the hydroxyl group to a better leaving group does not lead to carbonyl compounds but to olefins (see above). However, β-hydroxycyclopropyl selenides produce cyclobutanones on reaction with acids[8b,107,109,188] (Scheme 77).

X = MeSe	80 °C/12 h	80%
X = PhSe	80 °C/12 h	70%
X = PhS	40 °C/12 h	50%

(Ref. 109) (a)

(Ref. 115) (b)

Overall yield = 71%   98%   2%
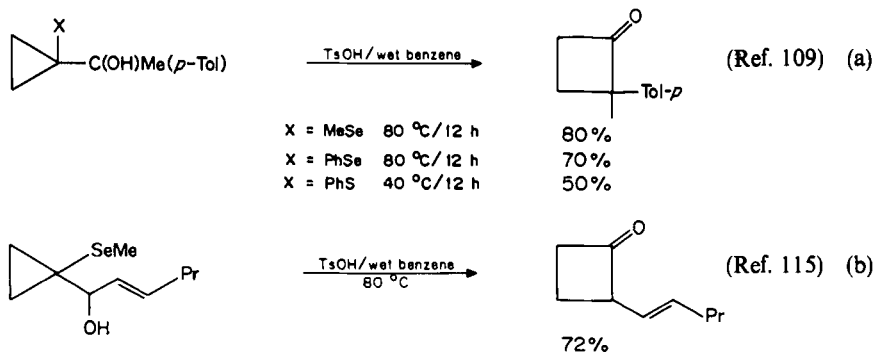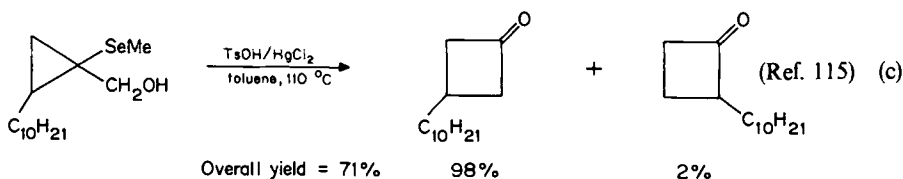
SCHEME 77

The reaction[8b] is similar to the one already described by Trost for thiophenyl analogues[328] but there are some interesting differences. For example in several instances phenylthio derivatives[109] are found to react much faster than methylseleno analogues[109,115] (Scheme 77) and except in rare cases[109] phenylseleno analogues do not react[115].

β-Hydroxyselenides can also react by their selenyl moiety. Their alkylation to β-hydroxyselenonium salts has been already discussed and the rearrangement of those derived from hindered derivatives (Scheme 78) to ketones noted[108,109,135]. However the reaction is not general and for example the selenonium salt **1c** (Scheme 78a) does not rearrange to 2,2-dimethylcycloheptanone (**2c**) even under forced reaction conditions[135] (180 °C, under vacuo).

(1)   **(2)**

a) $R^1 = R^2 = Me$; $M = MgX$ CH_2Cl_2, 20°C   94%[108,135]   (a)
b) $R^1 = H$, $R^2 = Me$; $M = H$ CH_2Cl_2, 20°C   90%[108,135]   (b)
c) $R^1 = R^2 = H$; $M = H$ neat, 180°C   trace[135]   (c)

MeSO₃F/ether
20 °C/1 h

(Ref. 109) (d)

83%
(±)-Cuparenone
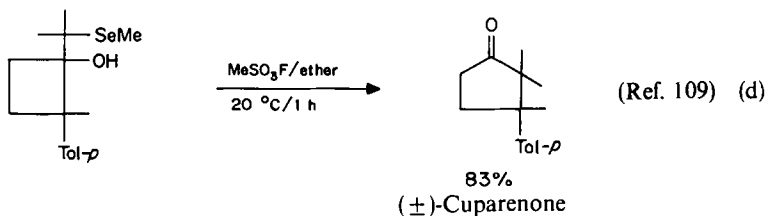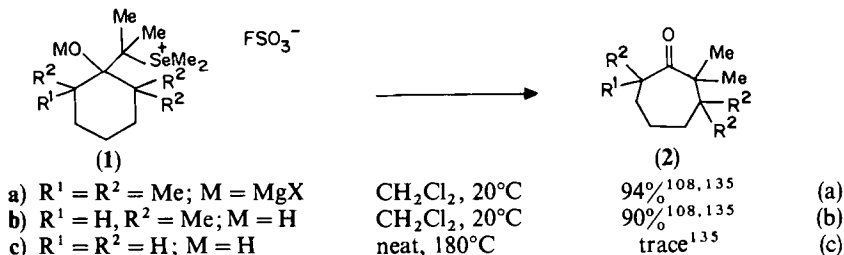
SCHEME 78

The β-hydroxyselenide precursor of the selenonium salt **1c** (Scheme 78a) can in fact be transformed to the desired ketone **2c** on reaction with $AgBF_4$[109,135]. Under these conditions, olefins are also formed, but their formation can be suppressed if the reaction is performed in the presence of basic alumina which removes the acid produced during the process[135] (Scheme 79). This reaction occurs when a β-hydroxyselenide having two alkyl or cycloalkyl groups on the selenenyl-bearing carbon is subjected, in chlorinated solvents, to the reaction of $AgBF_4/Al_2O_3$[109,135]. The reaction is highly regioselective producing α-disubstituted ketones by migration of the more substituted carbon atom. Other metal salts derived from Hg, Ni or Cu are not able to promote this rearrangement. However with thallium ethoxide in $CHCl_3$ or $CHBr_3$ the rearrangement takes place[282,339,340] readily (Scheme 79) with the high regioselectivity already described for the reactions involving $AgBF_4/Al_2O_3$.

R = Me, Ph	$AgBF_4/CHCl_3/40\,°/0.2\,h$	40%	(a)
R = Me	$AgBF_4/Al_2O_3/CHCl_3$	58%	(b)
R = Ph	$AgBF_4/Al_2O_3/CHCl_3$	85%	(c)

$AgBF_4/CHCl_3$, 20 °C/8 h	61%[135]	(d)
$AgBF_4/Al_2O_3/CHCl_3$,20 °C/4 h	62%[135]	(e)
$TlOEt/CHCl_3$, 20 °C/8 h	96%[282]	(f)

72%

$$HeptCH(OH)C(SePh)Me_2 \xrightarrow[\text{TlOEt/CHCl}_3,\ 20°C/15h]{} HCOCHeptMe_2 + HeptCOCHMe_2$$

Overall yield = 70%   60%   40%
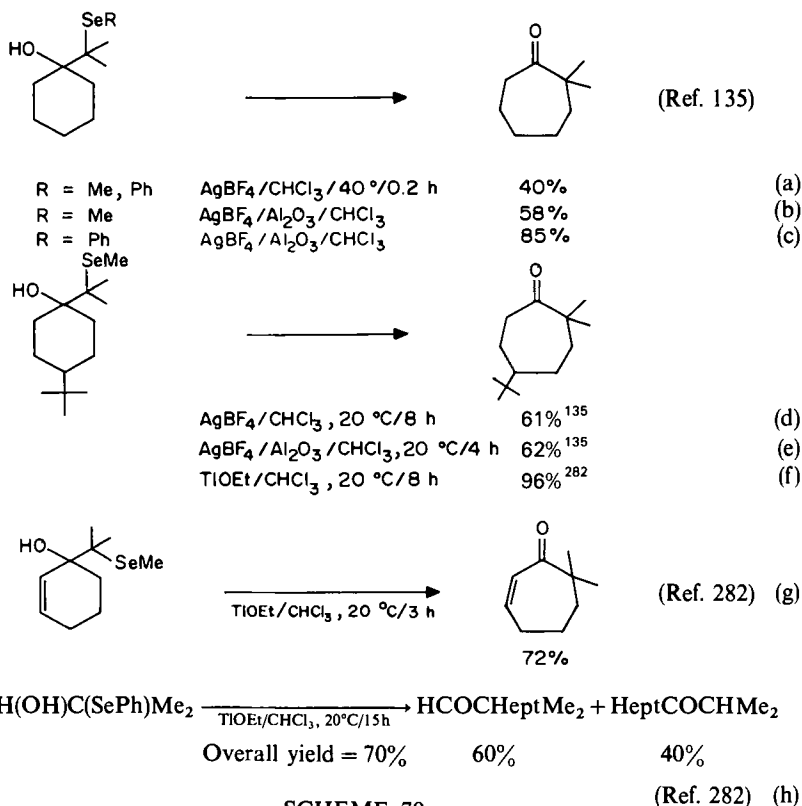
SCHEME 79   (Ref. 282) (h)

Thallium ethoxide also reacts with other β-hydroxyselenides[282]. Those which bear one or two hydrogens on the carbon bearing the selenyl moiety do not lead to rearranged ketones but to epoxides with high stereoselectivity[282] (Scheme 80).

55%   (a)

50%   (b)
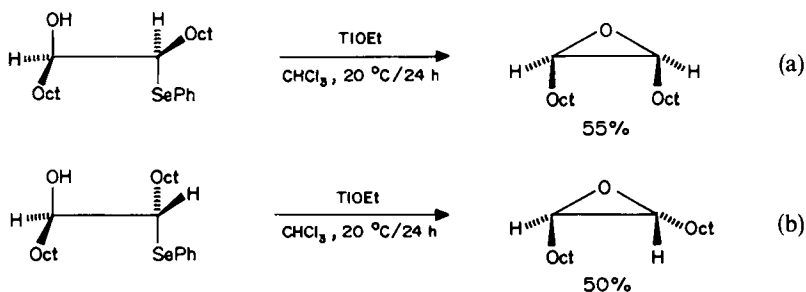
SCHEME 80[282]

Preliminary results seem to indicate the intermediary formation of a carbene by reaction of TlOEt with $CHCl_3$ or $CHBr_3$, one of these being required for the success of the reactions[282]. In fact a similar rearrangement is observed if β-hydroxyselenides are

subjected to the reaction of carbenes prepared by other methods[340] such as by $CHCl_3/t$-BuOK or $CHCl_3/KOH$ under phase-transfer catalysis conditions. The rearrangement takes place also if β-hydroxyselenides are reacted[340] with (bromodichloromethyl)phenylmercury as a carbene source. Other methods which allow the rearrangement of β-hydroxyselenides to ketones involve the use of $AgNO_3$ on celite[329], or the transformation of the selenyl moiety to a selenoxy[153,241] or selenonyl[330] one.

D. Use of Selenoalkylmetals in Organic Synthesis

The α-selenoalkylmetals presented in this review have been prepared by many different routes in which several types of compounds have been used as one of the reaction partners. Among these are carbonyl compounds, alkyl halides and alkyl metals for organometallics possessing a sp^3-hybridized carbanionic centre (Scheme 81) and carbonyl compounds, alkyl halides and olefins for those bearing a sp^2-hybridized carbanionic centre (Schemes 82 and 83).

(a) Carbonyl compounds

$$R^1R^2C{=}O \xrightarrow{a\ *} R^1R^2C(SeR)_2 \xrightarrow{b} R^1R^2CM(SeR) \quad \text{(Refs. 8, 11, 67, 94, 126)}$$

$$R^1CHO \xrightarrow{a} R^1CH(SeR)_2 \xrightarrow{c} R^1CM(SeR)_2 \xrightarrow{d} R^1R^2C(SeR)_2 \xrightarrow{b} R^1R^2CM(SeR)$$

$$R^2 = H, D, \text{alkyl}, SiMe_3 \quad \text{(Refs. 67–72)}$$

(b) Alkyl halides

$$R^1R^2CHX + MSeR \rightarrow R^1R^2CH(SeR)$$

$$\longrightarrow R^1R^2CHSe({=}O)R \xrightarrow{c} R^1R^2CMSe({=}O)R \quad \text{(Refs. 21, 22)}$$

$$\longrightarrow R^1R^2CH(\overset{+}{Se}R_2)\,X^- \xrightarrow{c} R^1R^2CM(\overset{+}{Se}R_2)\,X^- \quad \text{(Ref. 19)}$$

$$R^1R^2CHX + SeR_2 \rightarrow R^1R^2CH(\overset{+}{Se}R_2)\,X^- \xrightarrow{c} R^1R^2CM(\overset{+}{Se}R_2)\,X^- \quad \text{(Ref. 19)}$$

$$R^2X + R^1CM(SeR)_2 \rightarrow R^1R^2C(SeR)_2 \xrightarrow{b} R^1R^2CM(SeR) \quad \text{(Refs. 11, 67, 72, 94, 126)}$$

$$R^2X + MC(SeR)_3 \rightarrow R^2C(SeR)_3 \xrightarrow{b} R^2CM(SeR)_2 \quad \text{(Refs. 67, 68)}$$

(c) Alkyl metals

$$R^1Li + CH_2{=}CHSePh \rightarrow R^1CH_2CHLi(SePh) \quad \text{(Refs. 106b, 21)}$$

$$* \text{ a: RSeH, } ZnCl_2; \text{ b: BuM; c: Base; d: } [R^{2+}]$$

SCHEME 81

Some representative examples of syntheses of important functional groups in which α-selenoalkylmetals have been involved are given below.

1. Alkanes or deuteriated alkanes

a. From aldehydes and ketones. The reaction$({\geq}C{=}O \rightarrow {\geq}CH_2, {\geq}CHD, {\geq}CHR)$· (Schemes 84 and 85a) allows the reduction and the alkylative reduction of the carbonyl group of aldehydes and ketones, but is restricted to the introduction of primary alkyl groups.

The reaction $({\geq}C{=}O \rightarrow {\geq}C{\leq}^{R^1}_{R^2})$ (Scheme 86a) is restricted to aromatic carbonyl compounds. R^1 and R^2 can be primary or secondary alkyl groups. In the case of aromatic aldehydes the following process is even possible:

$$ArCHO \rightarrow ArCR^1R^2R^3 \quad \text{(Scheme 86a)}$$

$R^1CH=CH_2 \xrightarrow{PhSeX} R^1CHXCH_2SePh \xrightarrow[\text{(Ref. 125)}]{t\text{-BuOK/DMSO}}$

$R^1CH_2X + MCH(SePh)_2 \longrightarrow R^1CH_2CH(SePh)_2 \xrightarrow[\text{(Ref. 124)}]{P_2I_4 \text{ or } PI_3}$

$R^1CH=O + MCH(SePh)_2 \longrightarrow R^1CH(OH)CH(SePh)_2 \xrightarrow[\text{(Ref. 187)}]{P_2I_3 \text{ or } PI_3}$

$R^1CH=O + MCH(SePh)SiMe_3 \longrightarrow R^1CH(OH)CH(SePh)SiMe_3 \xrightarrow[\text{(Refs. 71, 181)}]{KH/THF}$

$R^1CH=O + Ph_3\overset{+}{P}CHM(SePh) \xrightarrow{\text{(Refs. 101, 102)}}$

$R^1CH_2CH=O \xrightarrow{PhSeH} R^1CH_2CH(SePh)_2 \xrightarrow[\text{or } P_2I_4 \text{ (Ref. 124)}]{MeI \text{ (Ref. 123)}}$

all leading to:

$R^1CH=CHSePh \xrightarrow{\text{(Ref. 324)}} R^1CH=CM(SeR)$

SCHEME 82

$R^1CH_2X + MC(SeR)_3 \xrightarrow[\text{(Ref. 124)}]{PI_3 \text{ or } P_2I_4} R^1CH_2C(SeR)_3$

$R^1CH=O + MC(SeR)_3 \longrightarrow R^1CH(OH)C(SeR)_3 \xrightarrow[\text{(Ref. 187)}]{PI_3 \text{ or } P_2I_4} R^1CH=C(SeR)_2$

$R^1CH=O + LiC(SePh)_2SiMe_3 \xrightarrow[\text{(Ref. 71)}]{20°C/1h}$

SCHEME 83

$Dec_2C=O \rightarrow Dec_2CLi(SeMe) \xrightarrow{D_2O} Dec_2CD(SeMe) \xrightarrow{Li/EtNH_2} Dec_2CHD$
$\qquad\qquad\qquad\qquad\qquad\qquad 75\% \qquad\qquad\qquad\qquad 87\%$

SCHEME 84[14]

$$\text{HexCH}{=}\text{O} \longrightarrow \text{HexCHLi(SeMe)} \xrightarrow[\text{THF}]{\text{HexBr}} \text{Hex}_2\text{CHSeMe} \xrightarrow[-10°\text{C}]{\text{Li/EtNH}_2} \text{Hex}_2\text{CH}_2 \qquad \text{(Ref. 14)} \qquad \text{(a)}$$

$$77\% \text{ overall} \qquad 74\%$$

$$\xrightarrow[\text{2:BrCH}_2\text{CH}{=}\text{CH}_2]{\text{1:CuI, }-110°\text{C}} \text{HexCH(SeMe)CH}_2\text{CH}{=}\text{CH}_2 \xrightarrow[\text{AIBN}]{\text{Bu}_3\text{SnH}} \text{HexCH}_2\text{CH}_2\text{CH}{=}\text{CH}_2 \quad \text{(Ref. 113)} \quad \text{(b)}$$

$$90\% \qquad 76\%$$

$$\xrightarrow{\text{HexCHO}} \text{HexCH(SeMe)CH(OH)Hex} \xrightarrow{\text{Bu}_3\text{SnH}} \text{HexCH}_2\text{CH(OH)Hex} \qquad \text{(Refs. 108, 144)} \quad \text{(c)}$$

$$70\% \qquad 97\%$$

SCHEME 85

$$\text{PhCH}{=}\text{O} \xrightarrow{1} \text{PhCH(SeMe)}_2 \xrightarrow{2} [\text{PhCK(SeMe)}_2]$$

$$70\% \qquad 70\%$$

$$\xrightarrow{3}$$

$$\text{PhC(O)Me} \xrightarrow[72\%]{1} \text{PhCMe(SeMe)}_2 \xrightarrow{4} [\text{PhCMeLi(SeMe)}] \xrightarrow{5} \text{PhCMe}(i\text{-Pr})(\text{SeMe}) \longrightarrow$$

$$\xrightarrow{4,\ 5} \text{PhCMe}(i\text{-Pr})_2 \qquad \text{(a)}$$

$$97\%$$

$$\text{(Ref. 12)}$$

$$\xrightarrow{4,\ 6} \text{PhCMe}(i\text{-Pr})\text{CH(OH)Ph} \qquad \text{(b)}$$

$$80\%$$

$$\text{EtCHBrMe} + \text{PhSeCHLiCH}{=}\text{CHSePh} \longrightarrow \text{EtCHMeCHSePhCH}{=}\text{CHSePh} \xrightarrow{\text{H}_2\text{O}_2} \text{EtCHMeCH}{=}\text{CHCHO} \qquad \text{(Ref. 321)} \quad \text{(c)}$$

$$75\%$$

1:MeSeH/TiCl$_4$; 2:KDA/THF, $-78°$C/0.2 h; 3:MeI/THF; 4:BuLi/THF, $-78°$C; 5:i-PrI/THF, $-78°$C/0.3 h, 20°C/0.5 h; 6:PhCHO, $-78°$C

$$\triangle\!\!\!\diagdown_O \quad + \quad \text{PhSeCHLiCH}=\text{CHSePh} \quad \xrightarrow{*} \quad \text{MeCH(OAc)CH(SePh)CH}=\text{CHSePh} \quad \xrightarrow{\text{H}_2\text{O}_2} \quad \text{MeCH(OAc)CH}_2\text{CH}=\text{CHCHO} \qquad \text{(Ref. 321)} \quad \text{(d)}$$

$$71\%$$

$$\text{Me}_2\text{CHBr} + \text{PhSeCHLiCH}=\text{C(SePh)SiMe}_3 \rightarrow \text{Me}_2\text{CHCH(SePh)CH}=\text{C(SePh)SiMe}_3 \xrightarrow[\text{2. Et}_2\text{NH}]{\text{1. MeCO}_3\text{H}} \text{Me}_2\text{CHCH}=\text{CHC(O)SiMe}_3 \qquad \text{(Ref. 321)} \quad \text{(e)}$$

$$75\%$$

$$\text{Me}_2\text{C}=\text{O} + \text{PhSeCHLiCH}=\text{C(SePh)SiMe}_3$$

$$\downarrow$$

$$\text{Me}_2\text{C(OH)C(SePh)CH}=\text{CHSePh} \quad \xrightarrow[\text{2. Et}_2\text{NH}]{\text{1. MeCO}_3\text{H}} \quad \text{Me}_2\text{C(OH)CH}=\text{CHC(O)SiMe}_3 \qquad \text{(Ref. 321)} \quad \text{(f)}$$

$$60\%$$

$$\xrightarrow{\text{MeSO}_2\text{Cl/NEt}_3} \text{Me}_2\text{C}=\text{CHCH}=\text{CHSePh}$$

$$80\%$$

SCHEME 86

*then quenching with acetic anhydride

b. From alkyl halides. Schemes 85a and 86a show (C—X → C—R) reactions.

2. Non-functionalized olefins

a. From aldehydes and ketones. This can be achieved (*i*) by their reductive allylation (C(1)=O → C(1)H—C—C=C) (Scheme 85b), (*ii*) by simultaneous formation of σ and π bonds ($\rangle$C(1)=O → $\rangle$C(1)=C$\langle$) by coupling of two identical carbonyl groups (Scheme 87), (*iii*) by simultaneous formation of σ and π bonds (C(1)=O → C(1)=C) from two different carbonyl compounds, one of them being activated as an α-selenoalkyllithium. (Scheme 88) or (*iv*) By simultaneous formation of σ and π bonds from carbonyl compounds and cyclopropane derivatives; this method allows the synthesis of strained alkylidenecycloalkanes (Schemes 89 and 90).

$$t\text{-BuCHO} \rightarrow t\text{-BuCHLi(SeMe)} \xrightarrow[-78 \text{ to } +20°C]{0.5eq.\text{CuI}/\text{Me}_2\text{S/ether}} t\text{-BuCH}=\text{CHBu-}t$$

E isomer exclusively   (b)
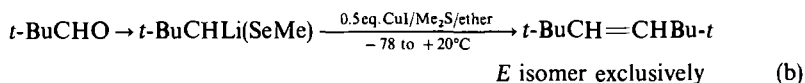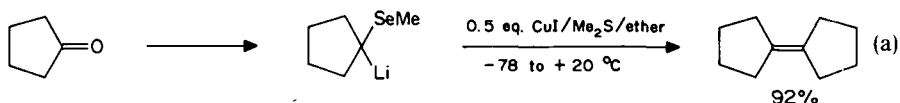
SCHEME 87[117]
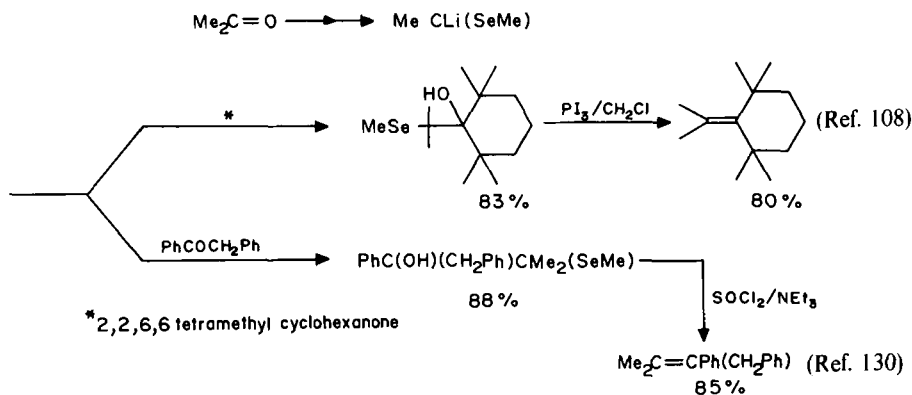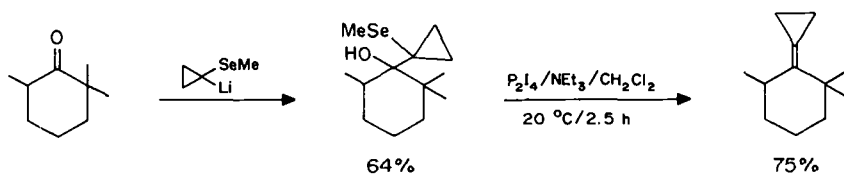
SCHEME 88

SCHEME 89[107]

Reactions (*iii*) and (*iv*) permit the regioselective formation of terminal, di-, tri-, and tetra-substituted olefins as well as alkylidenecycloalkanes including alkylidenecyclobutanes. They have been successfully used for the synthesis of hindered olefins from hindered or easily enolizable carbonyl compounds and although they are completely regioselective they are not usually stereoselective.

b. From alkyl halides. Primary alkyl halides can be used for the preparation of olefins. (C(1)—X → C(1)=C) (Scheme 91). Since the reactions involve at one stage the

HexCH=O $\longrightarrow$ HexCHLi(SeMe) $\xrightarrow{\text{DMF}}$ HexCH(SeMe)CHO $+$ RSe—⊽—Li $\longrightarrow$ HexCH(SeMe)CH(OH)—▽—SeR

80%

R = Me : 71%

R = Ph / R = Me

1. NaIO$_4$/MeOH
2. piperidine/cyclohexane

HexCH(OH)CH=▽

75%

1. MeI/AgBF$_4$
2. t-BuOK/DMSO, 20 °C/15 h

CH$_2$SeMe
HexCH—CH=▽

85%

HexCH=CH—▽—SeR

R = Me : 93%

P$_2$I$_4$/NEt$_3$

SCHEME 90[139,269]

A. Krief

$CH_3(CH_2)_3I + PhC(Se=O)LiPh \rightarrow CH_3(CH_2)_3CPh[Se(Ph)O^-] \rightarrow CH_3(CH_2)_2CH=CHPh$ (Ref. 22) (a)

81% overall

$OctCH_2Br + RSeCH_2Li \xrightarrow[HMPT]{THF} OctCH_2CH_2SeR \xrightarrow{[OctCH_2CH_2Se(R)O-]} OctCH=CH_2$ (Ref. 232) (b)

R = Ph:80%

R = Me:88%

R = Ph:H_2O_2/THF, 20°C/24 h   30%

t-BuO_2H/Al_2O_3/THF, 60°C/3 h   86%

R = Me:H_2O_2/THF, 20°C/24 h   1%

t-BuO_2H/Al_2O_3/THF, 60°C/3 h   83%

$NonCH_2Br + RSeCH_2Li \xrightarrow[HMPT]{THF} NonCH_2CH_2SeR \xrightarrow[2.t\text{-}BuOK/DMSO, 20°C]{1. MeI/AgBF_4} NonCH_2CH_2Se(R)CH_2^- \longrightarrow NonCH=CH_2$ (Refs. 20, 127) (c)

R = Ph:80%

R = Me:88%

R = Ph:71%

R = Me:90%

$OctCH_2Br + $ $\longrightarrow$ $\xrightarrow[2. t\text{-}BuOK/THF, 20 °C]{1. MeSO_3F}$ (Ref. 20) (d)

74%   77%

$PhCH_2Br + PhSeCHLiPh \rightarrow PhCH_2CHLiPh \rightarrow PhCH_2CH(SePh)Ph \xrightarrow{H_2O_2} PhCH=CHPh$ (Ref. 80) (e)

82% overall

SCHEME 91

SeMe—Oct $\xrightarrow{\text{1. MeI/AgBF}_4}$ Oct $\xrightarrow{180\ ^\circ\text{C}}$ $CH_2=C(Oct)CH=CH_2$ (a)
          2. t-BuOK/DMSO   68%*   100%

$\uparrow$ OctBr

SeMe—Li

$\uparrow$

O (cyclobutanone)

$\downarrow$ DecCHO

SeMe—Dec, OH $\xrightarrow[\text{THF, 60 }^\circ\text{C}]{t\text{-BuO}_2\text{H/Al}_2\text{O}_3}$ Dec, OH $\xrightarrow{180\ ^\circ\text{C}}$ Dec—CH(OH)—C(=CH₂)CH=CH₂

90%   70%   75% (b)

*Contains 7% octylidene cyclobutane

SCHEME 92[127]

$BuLi + CH_2{=}CHSePh \xrightarrow[\text{then } H_3O^+]{\text{ether or DME}} BuCH_2CH_2SePh \xrightarrow[\text{THF}]{t\text{-BuO}_2\text{H/Al}_2\text{O}_3} BuCH_2CH_2\overset{+}{S}e(Ph)O^- \rightarrow BuCH{=}CH_2$ (Ref. 121)   (a)

$\phantom{BuLi + CH_2{=}CHSePh}$97%$$74%

$i\text{-}PrLi + CH_2{=}CHSePh \rightarrow [i\text{-}PrCH_2CHLiSePh] \xrightarrow{Me_2C=O} i\text{-}PrCH_2CH(SePh)C(OH)Me_2 \xrightarrow[\text{2. }i\text{-Pr}_2\text{NH/CCl}_4,\ 80\ ^\circ\text{C/0.5 h}]{\text{1. O}_3,\ -78\ ^\circ\text{C/0.1 h}}$ (Ref. 122)   (b)

i-Pr, H / C(OH)Me₂, H (alkene product)

SCHEME 93

$$\text{DecCH=O} + \text{Me}_3\text{SiCLiMe(SeMe)} \rightarrow \text{DecCH(OH)CMe(SeMe)SiMe}_3$$

$$\textbf{A} \quad 50\%$$

$$\textbf{A} \xrightarrow[\text{CH}_2\text{Cl}_2]{\text{POCl}_3/\text{NEt}_3} \text{DecCH=CMeSiMe}_3 \xrightarrow[20°\text{C}/2\text{h}]{\text{Br}_2/\text{CCl}_4} \text{DecCH=CBrMe} \quad \text{(Ref. 100)} \quad \text{(a)}$$

$$83\% \quad * \qquad\qquad 80\%$$

$$\textbf{A} \xrightarrow[\text{THF}/55°\text{C}]{t\text{-BuOK}} \text{DecCH=CMe(SeMe)} \xrightarrow[\text{aq. MeCN}]{\text{HgCl}_2} \text{DecCH}_2\text{C(O)Me} \quad \text{(b)}$$

$$82\%^{100} \qquad\qquad 80\%^{308}$$

SCHEME 94

* Pure Z and pure E isomers are available on reaction with one of the two stereoisomers of A easily purified by SiO_2/thin layer chromatography.

$OctCH_2Br$ + $LiC(SeMe)_3$ $\longrightarrow$ $OctCH_2C(SeMe)_3$

70%

$\xrightarrow{\text{1}}$ $OctCH=C(SeMe)_2$

90%[124]

$\xrightarrow{\text{2}}$

MeI + $OctCH=CLi(SeMe)$ $\longrightarrow$ $OctCH=CH(SeMe)Me$

80%

$\nearrow$ 3 $OctCH=CHMe$

51%[185]

$\rightarrow$ 4 $OctCH=CBrMe$

64%[185]

$\searrow$ 5 $OctCH_2C(O)Me$

77%[185]

$OctCH=C(SeMe)_2$ $\xleftarrow{\text{2}}$

85%[187]

$\xleftarrow{\text{1}}$

$OctCH=O$ $\longrightarrow$ $LiC(SeMe)_3$ $\longrightarrow$ $OctCH(OH)C(SeMe)_3$

60%

1:P_2I_4/NEt_3/CH_2Cl_2, 20°C/1 h; 2:$BuLi$/THF, −78°C; 3:Bu_3SnH/$AIBN$, benzene, 90°C/3 h; 4:Br_2/benzene, 20°C/15 h; 5:Br_2/$EtOH$, 90°C/6 h

SCHEME 95

SCHEME 96

(a) (Ref. 100)

DecCHO + MeCLi(SeMe)SiMe₃ → DecCH(OH)CMe(SeMe)SiMe₃ 50% $\xrightarrow{H_2O_2/THF}$ DecCH(OH)COMe 50%

(b) (Ref. 100)

$\xrightarrow[20°C/12h]{HgCl_2/aq.\ MeCN}$ DecC(O)CH₂Me 75%

(c) (Ref. 101)

PhCH=O→X⁻ Ph₃P⁺CLiMe(SePh) → PhCH=CMe(SePh) 90% $\xrightarrow{HgCl_2/aq.\ MeCN}$ PhCH₂C(O)Me 90%

SCHEME 97

(a) (Ref. 5)

 =O + PhSeCHLi(OMe) →

 (4-tert-butylcyclohexane bearing —C(OH)(OMe)(SePh)) 83% $\xrightarrow[NEt_5]{MeSO_2Cl}$ =CHOMe 62%

(b) (Ref. 21)

i-PrCH=O + (PhSe)₂CHLi → i-PrCH(OH)CH(SePh)₂ $\xrightarrow[NEt_3]{MeSO_2Cl}$ i-PrCH=CHSePh 65%

(c) (Refs. 187, 308)

DecCH=O + (MeSe)₂CLiMe → DecCH(OH)CMe(SeMe)₂ 35% $\xrightarrow[NEt_3]{P_2I_4}$ DecCH=CMe(SeMe) 90% $\xrightarrow[aq.\ MeCN]{HgCl}$ DecCH₂COMe 80%

(d) (Ref. 187)

DecCH=O + (MeSe)₃CLi → DecCH(OH)C(SeMe)₃ 63% $\xrightarrow[NEt_3]{P_2I_4}$ DecCH=C(SeMe)₂ 85%

elimination of the selenyl moiety and one hydrogen they are regioselective, but only in those cases where topologically identical hydrogens are available for that purpose (Scheme 92).

c. From alkyl halides via alkyllithiums. Scheme 93 show $(C(1)—X \to C(1)— M \to C(1)—C≡C)$ reactions. Primary, secondary and tertiary alkyllithiums can be used, but at present only terminal monoalkylated olefins can be prepared by this method, which implies formal vinylation of an organometallic compound.

3. Functionalized olefins

a. α-Heterosubstituted olefins. The reactions have been performed according to $(C(1)= O \to C(1)=C—X)$. Vinyl silanes (Scheme 94a), vinyl selenides (Schemes 94c, 95, 96c and 97b, c) and functionalized vinyl selenides (Scheme 98), vinyl ethers (Scheme 97a), vinyl bromides (Scheme 94a and 95) and ketene selenoacetals (Schemes 97d and 98) are obtained from carbonyl compounds. The transformations are completely regioselective and allow in several instances the synthesis of stereoisomerically pure compounds.

Vinyl selenides (Scheme 95), vinyl bromides (Scheme 95), and ketene selenoacetals (Schemes 95 and 98) can also be obtained from alkyl halides according to the following description $(C(1)—X \to C(1)=C—Y)$.

DecCH$_2$Br + LiC(SeMe)$_3$ ⟶ DecCH$_2$C(SeMe)$_3$

67%[124]

│ 1
▼

DecCH=C(SeMe)$_2$

90%[124]

│ 2
▼

+ DecCH=CLi(SeMe) ⟶ DecCH=CX

           ↑ 2

3 ⟶ **A**, X = H
    80%

A, X = SeMe   (Ref. 185)

78%

DecCH=C(SeMe)$_2$

85%[187]

   ↑ 1

DecCH=O ● LiC(SeMe)$_3$ ⟶ DecCH(OH)C(SeMe)$_3$

63%

1:P$_2$I$_4$/NEt$_3$/CH$_2$Cl$_2$, 20°C/1 h; 2:BuLi/THF, −78°C; 3:Bu$_3$SnH/AIBN, benzene, 80°C/3 h

SCHEME 98

$HexCH=O \rightarrow HexCHLi(SeMe) \xrightarrow[\text{2. BrCH}_2\text{CH}=\text{CH}_2]{\text{1. CuI/ether}} HexCH(SeMe)CH_2CH=CH_2 \xrightarrow[\text{THF, 60°C/4h}]{t\text{-BuO}_2\text{H/Al}_2\text{O}_3} HexCH=CHCH=CH_2$ (a)
$\quad\quad\quad\quad\quad$ 74% $\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ 90% $\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ 90%

$HexCH=CH_2 \xrightarrow[\text{EtOH}]{\text{PhSeBr}} HexCH(OEt)CH_2SePh \xrightarrow[2\,\Delta]{\text{1.NaIO}_4} HexCOCH_2SePh$
$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ (A) $\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ (B)

From (B): $\xrightarrow[\text{2.MeI}]{\text{1.}t\text{-BuOK/}t\text{-BuOH}} HexCOCH(SePh)Me \xrightarrow[2\,\Delta]{\text{1.NaIO}_4} HexCOCH=CH_2$ (b)
$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ 58% overall from **B**

From (B): $\xrightarrow{\text{BrCH}_2\text{CH}=\text{CH}_2} HexCOCH(SePh)CH_2CH=CH_2 \xrightarrow[\text{NEt}_3]{\text{PhSH}} HexCOCH_2CH_2CH=CH_2$
$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ 85% overall from **A**

SCHEME 99[12]

$PhCH=CHCH_2Br \xrightarrow{\text{PhSe(O)CH}_2\text{Li}} [PhCH=CHCH_2CH_2Se(O)Ph] \xrightarrow{20\,°C} PhCH=CHCH=CH_2$ (c)
$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ 75%

SCHEME 100[22]

b. 1, 3-*Dienes*. 1, 3-Dienes can be synthesized:

(*i*) from aldehydes or ketones and allyl halides (C(1)=O → C(1)=C—C=C) (Scheme 99a); interestingly the stereochemistry of the C=C bond of the allyl halide is retained during the process.

(*ii*) from allyl halides (C(1)=C(2)—C(3)—X → C(1)=C(2)—C(3)=C) (Schemes 99a and 100). The last reaction permits an easy synthesis of allylidene cyclopropanes.

(*iii*) from α-enones (C(1)=C(2)—C(3)=O → C(1)=C(2)—C(3)=C) as shown in Scheme 101 or from alkyl halides and cyclobutanone (C(1)—X → C=C—C—(C(1))=C) (Scheme 93). The latter reaction has been extended to the synthesis of functionalized dienes when using epoxides (Scheme 102) or carbonyl compounds (Scheme 93b).

HexCH=O ⟶ HexCHLi(SeMe) + (O= ⬡) ⟶ Hex—C(SeMe)(H)(OH)⬡

64%

PI₃/NEt₃ ⟶ Hex—CH=⬡

79%

SCHEME 101[309]

MeSe ... Li   1. epoxide-CH₂CH₂Pr-*i*   Me₂Se⁺ I⁻ —CH₂CH(OH)CH₂CH₂Pr-*i*
                2. MeI

77%

1. KH/DMSO ⟶ CH₂=C(CH=CH₂)CH₂CH(OH)CH₂CH₂Pr-*i*
2. 180 °C

100% (±)-Ipsenol

SCHEME 102[127]

c. *Allyl alcohols*. (*i*) Consecutive use of two carbonyl compounds enables the preparation of allyl alcohols (HC(1)—C(2)=O + C=O → C(1)=C(2)—COH) (Scheme 103). (*ii*) Preparations of allylic alcohols from one carbonyl compound (C(1)=O → C(1)(OH)—C=C) are included in Schemes 90, 93b, 98, 104 and 105. In these cases the organometallics play the role of vinyl anions. The reaction described in Scheme 98 is particularly suitable for the synthesis of biallylic alcohols. (*iii*) The reaction using alkyllithiums (C(1)—Li → C(1)—C=C—COH) (Scheme 93b) involves the introduction of a vinylic moiety using addition of the alkyllithium across the C=C bond of vinyl selenide which therefore plays the role of a + C=C – synthon. (*iv*) Allyl alcohols have also been prepared from alkyl halides and α-metalloallylselenide and the reaction involves an allylselenoxide → allylseleninate rearrangement (C(1)—X → C(1)—C=C—COH) (Scheme 106).

d. α, β-*Unsaturated aldehydes and ketones*. α, β-Unsaturated aldehydes and ketones are both available by the following methods: (*i*) from two carbonyl compounds, one of them being an aldehyde (C(1)—C(2)=O + CH=O → C(1)=C(2)—C=O) (Scheme 107);

$Me_2C=O \rightarrow Me_2CLi(SeMe) \xrightarrow{NonCH_2CHO} Me_2C(SeMe)CH(OH)CH_2Non \xrightarrow[THF, 80°C]{t-BuO_2H/Al_2O_3} CH_2=CMeCH(OH)CH_2Non$ 65%   (Ref. 144) (a)

92%

$NonCH_2CH=O \rightarrow NonCH_2CHLi(SeMe) \xrightarrow{Me_2CO} Me_2C(OH)CH(SeMe)CH_2Non \xrightarrow[THF, 80°C]{t-BuO_2H/Al_2O_3} Me_2C(OH)CH=CHNon$ 78%   (Ref. 144) (b)

74%

$Me_2C=O \rightarrow Me_2CLi(SePh) \xrightarrow{HexCHO} Me_2C(SePh)CH(OH)Hex \xrightarrow[20°C]{H_2O_2/THF} CH_2=CMeCH(OH)Hex$ 80%   (Ref. 11) (c)

70%

SCHEME 103

55% overall

SCHEME 104[108]

$HexCH=O \rightarrow HexCHLi(SeR) \xrightarrow{DMF} HexCH(SeR)CHO \xrightarrow{CH_2=PPh_3} HexCH(SeR)CH=CH_2$

R = Ph:75%   R = Ph:78%
R = Me:91%   R = Me:85%

$HexCH=CHCH_2OH \xleftarrow[R=Ph]{H_2O_2/CH_2Cl_2-pyridine}$
70% E only

$HexCH(OH)CH=CH_2 \xleftarrow{(O)} HexCH=CHCH_2SeR$

100%
100%

R = Ph:hv, 20°C/0.7 h
R = Me:TsOH, 20°C/3 h

SCHEME 105[290]

$$Ph(CH_2)_3Br \ + \ PhSeCHLiCH=CH_2 \ \longrightarrow \ Ph(CH_2)_3CHCH(SePh)CH=CH_2$$

$$\xrightarrow{H_2O_2}$$

$$Ph(CH_2)_3CH=CHCH_2OH \ \longrightarrow \ \left[Ph(CH_2)_3CH[Se(O)Ph]CH=CH_2\right]$$

SCHEME 106[77]

$$NonCH_2CH=O \ \longrightarrow \ NonCH_2CHLi(SeMe) \ \xrightarrow{HexCHO} \ \left[NonCH_2CH(SeMe)CH(OLi)Hex\right] \ \xrightarrow[THF, 60\ ^{\circ}C/0.5\ h]{CrO_3/H_2SO_4} \ NonCH=CHC(O)Hex$$

50% overall

$$\xrightarrow[CH_2Cl_2, 50\ ^{\circ}C/48\ h]{(Ph)_3BiCO_3}$$

$$76\%^{313} \qquad NonCH_2CH(SeMe)CHC(O)Hex \xrightarrow[3.\ NEt_3]{\substack{1.\ H_3O^+ \\ 2.\ NCIS/Me_2S/benzene,\ 6\ h \\ 3.\ NEt_3}} 70\%^{310-311*}$$

SCHEME 107

*See Ref. 312 for a related transformation.

$$HexCH=O \ \longrightarrow \ HexCHLi(SePh) \ \xrightarrow{\triangle\!\!\!\!\diagup^{Hex}} \ HexCH(SePh)CH_2CH(OH)Hex \ \xrightarrow[acetone,\ 0.3\ h \\ 25\ ^{\circ}C/0.4\ h]{CrO_3/H_2SO_4} \ HexCH=CHC(O)Hex$$

84%   65%

SCHEME 108[174]

$PhCH_2Br + PhSeCHLiCH=CClMe \rightarrow PhCH_2CH(SePh)CH=CClMe \xrightarrow[20°C/0.2h]{H_2O_2/CH_2Cl_2} PhCH_2CH=CHCOMe$ 70% overall

SCHEME 109[77]

+ Me_2CHCHO + $PhSeCHLiC≡CLi$ ⟶

1. Me_2CuLi
2. PhSH
3. HgO

58%

MCPBA, −78 °C
Pyr, 25 °C

X = H, SePh

78% overall

SCHEME 110[314]

(a)

(b)

RCH₂X + PhSeCHLiCOOEt ⟶ RCH₂CH(SePh)COOEt $\xrightarrow[20\,°C]{2\ eq.\ MeCO_3H}$ RCH=CHCOOEt

R = Ph : 65%
R = Me : 60%

SCHEME 111[135]

Ph(CH₂)₂CHO ⟶ Ph(CH₂)₂CHLi(SeMe) ⟶ Ph(CH₂)₂CH(SeMe)CH₂CH(OH)Hex $\xrightarrow[2.\ base]{1.\ MeI}$ PhCH₂CH=CHCH₂CH(OH)Hex

75%

t-BuOK/DMSO, 20 °C   91%
aq. KOH/CH₂Cl₂, adogen 464   73%

SCHEME 112[129]

(*ii*) from one carbonyl compound and an epoxide (C=O + HC(1)—C(2) → C=C(1)—

C(2)=O) (Scheme 108); (*iii*) from alkyl halides (C(1)—X → C(1)—C=C—C=O) (Schemes 109 and 110) and an Se containing reagent which plays the role of an unsaturated homoenolate — C=C—C=O; (*iv*) from olefins (C(1)=C(2) → C=C— C(2)—C(1)=O) (Scheme 99c).

α, β-Unsaturated aldehydes are for their part also available from alkyl halides according to the following equation (C(1)—X → C(1)—C=C—C=O) (Scheme 86c) and γ or δ hydroxy analogues have been prepared when an epoxide or a carbonyl compound is reacted instead of an alkyl halide (Scheme 86d).

e. Ene-4-ones. Ene-4-ones are available from ene-2-ones and α-selenoalkyllithiums which play the role of masked vinyllithiums (O=C(1)—C(2)=C(3) → O=C(1)—C(2)— C(3)—C=C) (Scheme 47). They are also available from allyl halides (C(1)=C(2)— C(3)—X → C(1)=C(2)—C(3)—C=O) and from terminal olefins (C(1)=C(2) → C= C—C—C(2)—C(1)=O) (Scheme 99c).

f. α, β-Unsaturated esters, silyl esters and acids. These are available:
(*i*) from carbonyl compounds through a process which allows the synthesis of pure Z and E enoates (C(1)=O → C(1)=C—C(=O)(OR) (Scheme 76k,l) or according to the following strategy (HC(1)—C(2)=O → C(1)=C(2)—C(=O)OR; R = Me, H) (Scheme 111a).
(*ii*) from alkyl halides (C(1)H—X → C(1)=C—C(=O)OR; R = alky (Scheme 111b) or R = SiMe (Scheme 86f).

g. α-Alkylidene lactones. These have been prepared:
(*i*) from alkyl halides (C(1)—X → C(1)=C—C(=O)—O) (Scheme 8) or
(*ii*) from carbonyl compounds (C(1)=O → C(1)=C—C(=O)—O) in a process which allows the synthesis of pure Z or E isomers (Scheme 76k,l).

h. γ-Functionalized olefins such as homoallyl alcohols. These can be prepared:

(*i*) from epoxides (C(1)—C(2) → HOC(1)—C(2)—C=C) (Scheme 112); or
(*ii*) from carbonyl compounds (C(1)—C(2)=O → C(1)=C(2)—C—COH) (Schemes 102 and 112). In the latter transformation the carbonyl compound plays the role of a masked vinyl anion.

4. Non-functionalized alcohols

Non-functionalized alcohols have been prepared:
(*i*) from two ketones in a reaction which allows the reductive hydroxyalkylation of one of the two carbonyl groups (C(1)=O + C(2)=O → C(1)(H)—COH) (Scheme 85c) or, in the case of aromatic carbonyl compounds, it permits the gem-*ipso* alkylation-hydroxyalkylation of their carbonyl group (C(1)=O + C(2)=O → C(1)(H)—COH) (Scheme 86a).

5. Functionalized alcohols

γ-Halogeno alcohols have been obtained from carbonyl compounds (C(1)=O → Br—

C(1)—C—C—OH)   and   from   epoxides   (C(1)—C(2) → HOC(1)—C(2)—CBr) (Scheme 113).

$MeCH{=}O \longrightarrow MeCHLi(SePh) \xrightarrow[\text{ethanol / } H_2O]{Br_2} PhSeCHMeCH_2CH(OH)Hex \longrightarrow MeCHBrCH_2CH(OH)Hex \xrightarrow[\substack{\text{HMPT} \\ 20-80\ ^\circ C}]{MeMgBr}$

70%   67%   60%

SCHEME 113[106]

$Me_2C{=}O \longrightarrow Me_2CLi(SeMe) \longrightarrow$ 77% $\xrightarrow[\text{2. KOH / ether}]{\text{1. } MeSO_3F}$ 99%

(Ref. 108) (a)

$OctCH{=}O \longrightarrow OctCHLi(SeMe) \xrightarrow{CH_2O} OctCH(SeMe)CH_2OH \xrightarrow[\text{2. aq. KOH / ether}]{\text{1. } MeI}$ 60%

69%

(Ref. 144) (b)

$\longrightarrow CHR(SeMe) \xrightarrow[CHCl_3]{TlOEt} 20^\circ C/4h$

R = H:68%
R = Me:78%
R = t-Bu:54%
R = Ph:43%

80%
80%
60%
65%

(Ref. 282) (c)

SCHEME 114

6. Heterocycles

a. Epoxides. These may be prepared from two carbonyl compounds according to:

$(C(1)=O + C(2)=O \rightarrow$ [epoxide structure] $C(1)—C(2)$) (Scheme 114). The reaction permits the synthesis of terminal, disubstituted, trisubstituted and tetrasubstituted epoxides even from quite hindered and/or enolizable carbonyl compounds. Oxaspiropentanes are however not available by this method. The method involving a carbonyl compound and selenonium

ylides $(C(1)=O \rightarrow$ [structure] $C(1)—C)$ (Scheme 3) is restricted to non-enolizable carbonyl compounds.

b. Oxetanes. These may be prepared:

(*i*) from epoxides and carbonyl compounds, the latter being transformed to an α-

selenoalkyllithium $(C(1)—C(2) + C(3)=O \rightarrow C(1)—C(2)—C(3)$ (Scheme 113). The α-selenoalkyllithium and therefore the carbonyl compound plays the role of a carbene in this transformation.

(*ii*) from an organometallic according to the following equation: $(C(1)—M \rightarrow C(1)—C—C—C)$ (Scheme 115).

$$DecMgBr + ArSeO_2CH=CHCHO \rightarrow ArSeO_2CH=CHCH(OH)Dec$$

$$\xrightarrow[\text{MeONa}]{\text{MeOH}} [ArSeO_2CHNaCH(OMe)CHOHDec] \longrightarrow$$ [oxetane structure with OMe and Dec substituents]

SCHEME 115[293]   78% overall

c. Tetrahydrofurans. These have been synthesized from oxetanes and carbonyl compounds according to $[C(1)—C(2)—C(3) + C(4)=O \rightarrow C(1)—C(2)—C(3)—C(4)]$ (Scheme 116). The set of reactions described in this scheme permit the formal homologization of epoxides to oxetanes and of oxetanes to tetrahydrofurans by regioselective insertion of an alkylidene group arising from an aldehyde or a ketone.

$$HexCH=O \longrightarrow HexCHLi(SeMe) \xrightarrow{\text{oxetone}} MeSeCHHex(CH_2)_3OH \xrightarrow[\text{ethanol / H}_2O]{\text{Br}_2} Hex\text{—[THF ring]}$$

82%   77%

SCHEME 116[106]

7. Alkyl halides

These have been prepared from alkyl halides by one or two carbon homologization reactions. The first process shown in Scheme 117 and schematized as follows $[C(1)—X + C(2)=OC(1)—X + C(2)=O \rightarrow C(1)—C(2)—XC(1)—C(2)—X]$ requires the use of a carbonyl compound whereas the second process, shown in Scheme 118 and schematized as follows $[C(1)—X \rightarrow C(1)—C—C—X]$ involves the transformation of the alkyl halide to an organometallic and its further addition on the $C=C$ bond of a vinyl selenide.

$$NonI + LiCH_2SeR \xrightarrow[\text{1 eq. HMPT}]{\text{THF}} NonCH_2SeR \xrightarrow[\text{DMF/80°C}]{\text{MeI}} NonCH_2I$$

$$R = Me:88\% \qquad 90\%$$
$$R = Ph:80\% \qquad 90\%$$

<p style="text-align:center">SCHEME 117[17]</p>

$$BuX \xrightarrow[65\%]{\text{Li/hexane}} BuLi + CH_2{=}CHSePh \rightarrow BuCH_2CH_2SePh \xrightarrow[\text{MeI/DMF}]{\text{Br}_2/\text{EtOH}} BuCH_2CH_2X$$

$$X = Br:40\%[120]$$
$$X = I:80\%[121]$$

<p style="text-align:center">SCHEME 118</p>

8. Non-functionalized aldehydes and ketones

a. Synthesis from carbonyl compounds. Ketones have been synthesized
(i) from aldehydes and α-silyl-α-selenoalkyllithiums according to the following
[HC(1)=O → C—C(1)(=O)] (Scheme 96b). These, however, are not particularly good
nucleophiles toward carbonyl compounds.

$$PhC(O)Me \rightarrow PhC(O)CH_2Li \xrightarrow{\text{CH}_2{=}\text{CHSe}(=O)\text{Ar}} [PhCOCH_2CH_2CHLiSe(O)Ar]$$

$$\rightarrow [PhCOCHLiCH_2CH_2Se(O)Ar] \rightarrow PhC \longrightarrow PhC \triangle$$

$$t\text{-BuOC(O)CH}_3 \rightarrow t\text{-BuOC(O)CH}_2Li \xrightarrow{\text{DecCH}{\equiv}\text{CHSe}{\equiv}\text{O|Ar}}$$

$$[t\text{-BuOC(O)CH}_2\text{CHDecCHLiSe(O)Ar}] \longrightarrow t\text{-BuO}\overset{O}{\overset{\|}{C}}\text{—}\triangle\text{—Dec}$$

$$Ar = p\text{-Cl-C}_6H_4 \qquad\qquad 52\% \text{ overall}$$

<p style="text-align:center">SCHEME 119[271]</p>

<p style="text-align:center">SCHEME 120</p>

Me_2CLIX , X = SeMe or Se(O)Ph

X = SeMe : 66%

$MeSO_3F/ether$

X = SeMe:82%,[109]
X = Se(O)Ph:39% overall[153]

(Ref. 153)

+ $PhSe(O)CR^1R^2Li$

$R^1 = H$, $R^2 = H$:82% overall
$R^1 = H$, $R^2 = Me$:71% overall
$R^1 = Me$, $R^2 = Me$:63% overall

SCHEME 121

$DecBr$

$\xrightarrow{(PhSe)_2CKMe}$ $DecCMe(SePh)_2$ $\xrightarrow[0.1h]{CuCl_2/CuO}$ $DecC(O)Me$ 85% overall   (a)   (Ref. 69)

$\xrightarrow{(MeSe)_2CLiMe}$ $DecCMe(SeMe)_2$ $\xrightarrow[0.1h]{CuCl_2/CuO}$ $DecC(O)Me$ 72% overall   (b)   (Refs. 68, 266)

$\xrightarrow[-78°C, THF]{Me_3SiCHLi(SeMe)}$ $DecCH(SeMe)SiMe_3$ $\xrightarrow[NaIO_4/EtOH]{H_2O_2/THF \ or}$ $DecCH{=}O$ 77%   (c)   (Ref. 74)

$\xrightarrow[-78°C, THF]{Me_3SiCHLi(SePh)}$ $DecCH(SePh)SiMe_3$ 80% $\xrightarrow{H_2O_2/THF}$ $DecCH{=}O$ 77%   (d)   (Refs. 74, 75)

SCHEME 122

(ii) according to [HC(1)=O → C(1)—C=O] (Schemes 94c, 95, 96c and 97c). The organometallic used in this transformation allows the homologization of the carbonyl compounds.

(iii) in the preparation of a cyclopropyl ketone [HC(1)—C(2)=O → $\overset{C}{\underset{C}{>}}$C(1)—C=O)

Scheme 119). The carbonyl compound plays the role of an α-carbonyl carbene and the alkyl phenyl selenoxide plays the role of an olefin.

(iv) from two ketones according to the following equation [C(1)—C(2)=O + C(3)=O → C(1)—C(3)—C(2)=O]. Schemes 120 and 121 show methods which allow the introduction of a carbon atom bearing two alkyl groups (often prepared from a ketone) between the carbonyl group and usually its more substituted α-carbon atom. The reaction applies also to hindered or strongly enolizable carbonyl compounds.

b. *Synthesis from alkyl halides.* Ketones and aldehydes may be prepared from alkyl halides and α-selenoalkylmetals which play the role of masked acyl anions [C(1)—X + C(2)=O → C(1)—C(2)=O] (Schemes 95, 122 and 123). Among these are the α-selenoalkylmetals bearing an sp³ (Scheme 122) or an sp² (Schemes 95 and 123) carbanionic centre.

$$\text{DecBr} + \text{(PhSe)CLi}=\text{CH}_2 \xrightarrow{\text{THF/HMPT}} \underset{70\%}{\text{DecC(SePh)}=\text{CH}_2} \xrightarrow{\text{H}_2\text{SO}_4/\text{H}_2\text{O}} \underset{80\%}{\text{DecC(O)Me}}$$

SCHEME 123[121]

$$\text{BuLi} + \text{CH}_2=\text{CHSePh} \rightarrow [\text{BuCH}_2\text{CH(SePh)Li}] \xrightarrow{\text{PhSeBr}} \underset{80\%[120]}{\text{BuCH}_2\text{CH(SePh)}_2}$$

$$\xrightarrow[\text{acetone 1\%}]{\text{CuCl}_2/\text{CuO}} \underset{70\%[266]}{\text{BuCH}_2\text{CH}=\text{O}} \qquad (a)$$

$$i\text{-PrLi} + \text{CH}_2 = \text{CHSePh} \rightarrow [i\text{-PrCH}_2\text{CH(SePh)Li}] \xrightarrow{\text{Me}_3\text{SiCl}} \underset{86\%[122]}{i\text{-PrCH}_2\text{CH(SePh)SiMe}_3}$$

$$\xrightarrow{\text{H}_2\text{O}_2/\text{THF}} \underset{70\text{-}80\%[75]}{i\text{-PrCH}_2\text{CH}=\text{O}} \qquad (b)$$

SCHEME 124

73%   81%

(Ref. 115)   (a)

61%   70%

(Refs. 107, 115)   (b)

SCHEME 125

SCHEME 126[110]

(Ref. 69) (a)

72 %

CuCl₂/CuO

HO CMe(SePh)₂

76%

MeCK(SePh)₂/THF

(b)

+

HO Me

51%(Refs. 117, 148)
85%(Refs. 117, 148)

O Me

SeMe

36%
0%

1.1 eq.CuCl₂/4 eq.CuO/1% H₂O in acetone, 20 °C
1. as before, then 2. NaIO₄/MeOH–H₂O,20 °C

HO CMe(SeMe)₂

78%

MeCLi(SeMe)₂/ether

(c)

O Me

82%

(Refs. 117, 148)

1. CuCl₂/4 CuO
2. acetone/H₂O 1%, 20 °C/0.2 h

CMe(SeMe)₂

78%

MeCLi(SeMe)₂/THF/HMPT

SCHEME 127[117,148,157]

Me

O Me

70%

(Refs. 117, 148)

1.1 eq. CuCl₂/4 eq. CuO/1%
H₂O in acetone, 20 °C
2. HgCl₂/MeCN, 85 °C/2 h

Me

CMe(SeMe)₂

70%

1. (MeSe)₂CMeLi; THF/HMPT, –78 °C
2. MeI, THF/HMPT

SCHEME 128[117]

Particularly valuable are the α-metallosilyl selenides, since after reaction the alkylsilyl selenides are transformed to aldehydes or ketones under very mild oxidative conditions (Schemes 122c, d and 124b). The 1-potassio-1,1-bis(phenylseleno) alkanes required in Scheme 122(a) are themselves readily available from aldehydes [e.g. $CH_3CHO \rightarrow (PhSe)_2CKMe$].

c. Synthesis from alkylmetals. Ketones and aldehydes may be prepared according to the following equation $[C(1)M \rightarrow C(1)-C-C=O]$ (Scheme 124). The preparation of aldehydes according to this scheme is directly related to the addition of an enolate to an alkyl halide but involves a reversed polarization $(C(1)^- + C^+ - C=O)$.

Other reactions are more specific to cyclic ketones. This is particularly the case of:

(i) cyclobutanones which are available according to the following equation $[C(1)=O \rightarrow \overline{C(1)-C-C-C}=O]$ (Schemes 78, 125 and 126). The α-methylselenocyclopropyllithiums used as a coreagent bring the three missing carbon units and are much better for that purpose than their phenylseleno analogues.

(ii) cyclopentanones which are available from cyclobutanones and another carbonyl compound. This carbonyl compound is inserted at the α- or β-position of the carbonyl group of the cyclopentanone $[C(1)=O + \overline{C(2)-C(3)-C(4)-C(5)}=O \rightarrow \overline{C(1)-C(2)-C(3)-C(4)-C(5)}=O]$ or $[C(1)=O \rightarrow \overline{C(2)-C(1)-C(3)-C(4)-C(5)} = O]$ as shown in Scheme 126.

9. Functionalized aldehydes and ketones

a. α-Hydroxycarbonyl compounds. α-Hydroxycarbonyl compounds, including the β, γ-unsaturated ones, are available from two carbonyl compounds, one of them being transformed to 1, 1-bis(seleno)alkyllithiums or to 1-lithio-1-silyl alkyl selenides $[C(2)=O + HC(1)=O \rightarrow HOC(2)-C(1)=O]$ (Schemes 42 and 96a) or $[C(1)=C(3)-C(2)=O + H_2C(4)=O \rightarrow C(4)=C(3)-C(2)(OH)-C(1)=O]$ (Scheme 127a,b). Best results are obtained in the second case when 1, 1-bis(methylseleno)alkyllithiums are used instead of their phenylseleno analogues and ether was found to be the most suitable solvent to selectively introduce the masked acyl anion equivalent at the $C(1)$ site of the enone.

b. 1,4-Diketones. 1,4-Diketones can be synthesized from enones according to the following equation $[O=C(1)-C(2)=C(3) + HC(4)=O \rightarrow O=C(1)-C(2)-C(3)-C(4)=O]$ (Schemes 127c and 128). The saturated carbonyl compound is transformed to 1-lithio-1, 1-bis(seleno) alkane and plays the role of an acyl anion equivalent which selectively adds at the $C(3)$ site of the enone if the reaction is performed in the presence of HMPT used as a cosolvent. The hydrolysis of the 4-oxo-selenoacetal to the 1,4-diketone can be conveniently achieved by using one molar equivalent of $CuCl_2$ in wet acetone. In some cases (Scheme 128) the selenoacetal moiety is transformed to a vinyl selenide instead of to a ketone. The vinyl selenide can, however, in turn be hydrolysed to the desired ketone.

10. Carboxylic acids and esters

Carboxylic acids and esters have been synthesized

(a) from alkyl halides and α-metalloorthoseleno esters which play the role of a masked carbonic ester anion $[C(1)-X \rightarrow C(1)-C(=O)OH]$ (Scheme 129).

(b) from ester by formal dialkylation on the α-carbon atom according to the following equation $[H_2C(1)-C(2)(=O)OC \rightarrow \underline{C-C-C(1)}-C(2)(=O)-O-C(3)]$ (Scheme 119b).

$$\text{HexBr} + (\text{MeSe})_3\text{CLi} \xrightarrow{-78°\text{C/THF}} \text{HexC(SeMe)}_3 \xrightarrow{\text{H}_2\text{O}_2\text{/THF}} \text{HexCO}_2\text{H}$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad 80\% \qquad\qquad\qquad\qquad 82\%$$

SCHEME 129[74]

II. α-TELLUROORGANOMETALLICS: SYNTHESIS AND SYNTHETIC USEFULNESS

A. Synthesis of α-Telluroorganometallics

Telluroalkylmetals are much less well known that their seleno analogues. The first description of such compounds appeared in 1970 when Lloyd and coworkers described the first telluronium ylide[295] (Scheme 130) as a rather unstable compound[295,302].

SCHEME 130[295]

Since that date other stabilized telluronium ylides have been synthesized[304,306,316-317] and some of them have been used in synthesis[316,317]. For example dialkyltelluronium carbethoxymethylides are reported[316] to produce α,β-unsaturated esters on reaction with carbonyl compounds whereas dialkyl telluronium allylides[317] lead to the formation of allyl epoxides on reaction with the same derivatives (Scheme 131).

PhCH=O

$\xrightarrow{\text{Me}_2\text{Te}=\text{CHCO}_2\text{Et}}$ PhCH=CHCO$_2$Et   (Ref. 316)

75% (E/Z = 50/50)

$\xrightarrow{\text{Me}_2\text{Te}=\text{CH}-\text{CH}=\text{CH}_2}$ PhCH—CH—CH=CH$_2$ (Ref. 317)

65% (cis/trans = 17/83)

SCHEME 131

The synthetic methods used for the synthesis of these ylides[295,302,304-306] are similar to those used for the Se analogues and imply the reaction of diazo compounds with tellurides[295,302], or the reaction of active methylene derivatives with dihalogenotellurides.

Dialkyltelluronium carbethoxymethylides and dialkyl telluronium allylides are prepared[316,317] on reaction of the corresponding telluronium salts with t-BuOK in THF at −20° and −78 °C, respectively. Whereas dialkyltelluronium allylides are quantitatively formed by reaction with t-BuOK in THF on the corresponding telluronium salts, diphenyltelluronium analogues do not produce the ylide but instead produce diphenyl telluride and allyl bromides.

On the other hand telluromethyllithium has been synthesized by Seebach[294] from 1,1-bis(phenyltelluro)methane and methyllithium, butyllithium or t-butyllithium. The reaction takes advantage of the cleavage of the C—Te bond (Scheme 132). The reaction seems to be easier than the related C—Se bond cleavage in selenoacetals already

described in this review. Phenyltelluromethyllithium is surprisingly found to be thermally stable[34,294] and does not rearrange even after 12 h at 20 °C.

$$(PhTe)_2CH_2 \longrightarrow \begin{array}{l} \xrightarrow[-78°C]{LDA/THF} (PhTe)_2CHLi \xrightarrow{PhCH_2Br} (PhTe)_2CHCH_2Ph \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad 100\% \\[2em] \xrightarrow[-PhTeMe]{MeLi} PhTeCH_2Li \xrightarrow{PhCHO} PhTeCH_2CH(OH)Ph \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad 60\% \end{array}$$

SCHEME 132[294]

The presence of two heteroatomic moieties greatly favours the metalation of the telluro compounds. Thus bis(phenyltelluro)methane[297] (Scheme 132) and (diphenyl-phosphino)methyl phenyl telluride[299] have been metalated with LDA (Scheme 133).

$$Ph_2P(O)CH_2TePh \xrightarrow[-78°C]{LDA/THF} Ph_2P(O)CHLiTePh \xrightarrow[-78°C]{PhCHO}$$

$$Ph_2P(O)CH{=}CHPh(trans)$$

$$41\%$$

SCHEME 133[299]

Vinyl phenyl telluride has also been metalated [34,297] (Scheme 134). The best results are obtained when lithium dicyclohexylamide is used. BuLi[297] also permits the metalation of vinyl phenyl telluride, but the yield is poor (10%) due to competing Te/Li exchange.

$$CH_2{=}CH(TePh) \longrightarrow \begin{array}{l} \xrightarrow{BuLi} CH_2{=}CLi(TePh) + Te/Li\ exchange \\ \qquad\qquad\qquad 10\% \\[2em] \xrightarrow{LiN(C-C_6H_{11})_2} CH_2{=}CLi(TePh) \xrightarrow{PhCHO} CH_2{=}C(TePh)CH(OH)Ph \\ \qquad\qquad\qquad 51\% \qquad\qquad\qquad\qquad 88\% \end{array}$$

SCHEME 134[297]

It has been noticed[34] that the telluryl moiety stabilizes an α-carbanion better than a selenyl moiety. Such results have been obtained from competitive metalation experiments between differently substituted tellurides and selenides[34].

B. Reactivity of α-Telluroorganometallics

Little is known about the reactivity of these organometallics towards electrophiles.

C. Reactivity of Tellurides and Functionalized Tellurides[319]

Similarly to selenides[221] alkyl phenyl and alkyl methyl tellurides are reduced to the corresponding alkane on reaction with triphenyltin hydride[221]. As expected the reaction is

usually faster with tellurides than with selenides (Scheme 135). The reduction is even faster if dichlorotelluronium salts (Scheme 135) are used in place of the telluride[221].

$C_{12}H_{25}X$ $\longrightarrow$ $C_{12}H_{26}$

X = SePh	2.5 mol eq. Ph_3SnH, 120°C/2.5 h	73%
X = TePh	2.4 mol eq. Ph_3SnH, 20°C/5 h	87%
X = TeCl$_2$	3.5 mol eq. Ph_3SnH, 20°C/2 h	70%

C_8H_{17}—CH—CH$_2$TePh $\longrightarrow$ C_8H_{17}—CH—CH$_3$
          | |
         OR   OR

R = H	2.2 mol eq. Ph_3SnH, 80°C/1.5 h	88%
R = Ac	2 mol eq. Ph_3SnH, 80°C/0.7 h	71%

SCHEME 135[221]

$$\text{DecCH}_2\text{TePh} \xrightarrow{\ Y-X\ } \left[\text{DecCH}_2\overset{\overset{\displaystyle X}{|}}{\underset{\underset{\displaystyle Y}{|}}{\text{TePh}}} \right] \longrightarrow \text{DecCH}_2X$$

Y—X	Conditions	Yields
Cl—Cl	DMF, 160°C	89%
Br—Br	DMF or ethanol, 70°C	93%
I—I	CH$_3$CN or THF, 85°C	71%
Me—I	DMF or THF, 55°C	88%

SCHEME 136[322]

Phenyltelluroalkanes react with sulphuryl chloride[322], bromine[217,322] and iodine[322] and produce the corresponding telluronium dihalides in quantitative yield. These telluronium derivatives subsequently heated at 70–100 °C afford alkyl halides smoothly (Scheme 136). Although the pyrolysis is expected to occur via a 1,2-halogen shift, the yields are much improved[322] by the addition of alkali metal halides or ammonium halides[322,297].

1,1-Bis(phenyltelluro)alkanes also react[322] with Br$_2$ and lead to 1,1-dibromoalkanes (Scheme 137); on the other hand the same treatment with NaI and I$_2$ produces aldehydes (Scheme 137). Closely related reactions have already been described for selenoanalogues[18].

UndecCH(TePh)$_2$

$\xrightarrow{\text{Br}_2/\text{DMF, 70°C}}$ UndecCHBr$_2$
                        82%

$\xrightarrow[\text{20°C/1 h or 69°C/0.3 h}]{\text{I}_2/\text{NaI}}$ UndecCH=O
                        86%

SCHEME 137[322]

SCHEME 138

Tellurides lead to olefins on reaction with *t*-butyl hydroperoxide in benzene (Scheme 138): a telluroxide is proposed as a n intermediate[2]. The yield of olefin is rather low (35%) probably due to a side-reaction involving a rearrangement of the telluroxide which produces an alcohol (Scheme 138c)[2,318]. The mechanism of the reaction has been described by Sharpless[2] and involves, as in the case of sulphoxides and selenoxides, a *syn* elimination reaction. Finally if different hydrogens are available for the elimination reaction, those leading to the less substituted olefins are the more prone to be eliminated. More recently a facile elimination of some telluroxides, leading to olefins[332], allylic alcohols[332] and allylic ethers[331,332] has been described (Scheme 138d).

Phenyl alkyl tellurides are transformed to alkyl methyl ethers when reacted with excess perbenzoic acid in methanol (Scheme 139) and, although not isolated, tellurones[333] have been postulated as intermediates in this transformation. However when a Ph group is vicinal to the Te moiety (Scheme 139c), the replacement of the Te moiety by the MeO group is accompanied by Ph migration[331], whereas cyclic compounds bearing a MeO and

a telluryl group in the β-position readily afford the dimethyl acetals of the ring-contracted cyclic aldehydes[331].

$$DecCH_2CH_2TePh \xrightarrow[20°C/1\ h,\ 50\%\ yield]{4\ mCPBA/MeOH} DecCH_2CH_2OMe \qquad (a)$$

1. Br_2/CCl_4, 0°C
2. 0.5 N aq. NaOH, 20°C/0.1 h

$$\longrightarrow DecCH_2CH_2Te(O)Ph \xrightarrow[20°C/1\ h,\ 95\%\ yield]{2\ m\text{-}CPBA/MeOH}$$

$$PhCH(Me)CH_2TePh \xrightarrow[20°C/1\ h]{3\ m\text{-}CPBA/MeOH} MeOCH(Me)CH_2Ph \qquad (b)$$
$$90\%$$

$$PhCH(OMe)CH_2TePh \xrightarrow[20°C/1\ h]{2\ m\text{-}CPBA/MeOH} (MeO)_2CHCH_2Ph \qquad (c)$$
$$90\%$$

SCHEME 139[331]

On the other hand, β-hydroxytellurides are not prone to elimination of the two heteroatomic moieties[301] and under conditions where β-hydroxyselenides are transformed in high yield to olefin[4-6,8], the telluro analogues only lead to a very low yield[301] of the olefins (Scheme 140).

$$PhTeCH_2CH(OH)Ph \xrightarrow[110°C]{toluene} CH_2\!=\!CHPh$$
$$15\%$$

SCHEME 140[301]

Despite the results just reported, Kauffman has found[299] that 1-diphenyl-phosphino-1-phenyltelluromethyllithium reacts with benzaldehyde and immediately loses the telluryl and hydroxyl moieties (Scheme 133).

III. REFERENCES

1. H. Rheinboldt (Ed.), *Methoden zur Herstellung und Umwandlung organischer Selenium und Tellur Verbindungen: Methoden der Organischen Chemie IX*, Georg Thieme Verlag, Stuttgart, 1955, p. 916
2. K. B. Sharpless, K. M. Gordon, R. F. Lauer, D. W. Patrick, S. P. Singer and M. W. Young, *Chem. Scripta*, 8A, 9 (1975).
3. D. L. Klayman and W. H. H. Gunther (Eds.), *Organic Selenium Compounds: Their Chemistry and Biology*, John Wiley and Sons, New York, 1973.
4. D. L. J. Clive, *Tetrahedron*, 34, 1049 (1978).
5. H. J. Reich, *Acc. Chem. Res.*, 22 (1979).
6. H. J. Reich, in *Oxidation in Organic Chemistry, Part* C (Ed. W. S. Trahanovsky), *Organic Chemistry: A series of Monographs*, Vol. 5C, Academic Press, New York, 1978.
7. Ref. 6, p. 11.
8. (a) A. Krief, *Tetrahedron*, 36, 2531 (1980).
8. (b) A. Krief, *Synthesis and Synthetic Applications of 1-Metallid-1-selenocyclopropanes and Cyclobutanes and related 1-Metallo-1-silylcyclopropanes*. *Topics Curr. Chem.*, Vol. 135, 1 (1986).
9. G. Avrey, D. Barnard and D. T. Woodbridge, *J. Chem. Soc.* 2089 (1962).
10. H. Gilman and F. J. Webb, *J. Amer. Chem. Soc.*, 71, 4062 (1949).
11. W. Dumont, P. Bayet and A. Krief. *Angew. Chem. Int. Ed.*, 13, 804 (1974).
12. (a) M. Clarembeau and A. Krief, *Tetrahedron Letters*, 26, 1093 (1985); (b) M. Clarembeau and

A. Krief, unpublished results; (c) M. Clarembeau and A. Krief, *Tetrahedron Letters*, **27**, 1719 (1986); (d) M. Clarembeau and A. Krief, *Tetrahedron Letters*, **27**, 1723 (1986); (e) A. Krief. M. Clarembeau, *J.C.S. Chem. Commun*, 688 (1986).
13. Ref. 8, p. 2608.
14. M. Sevrin, D. Van Ende and A. Krief. *Tetrahedron Letters*, 2643 (1976).
15. D. L. J. Clive, G. Chittattu and C. K. Wong, *J. Chem. Soc. Chem. Commun.*, 41 (1978).
16. D. L. J. Clive, G. J. Chittattu, V. Farina, W. A. Kiel, S. M. Menchen, C. G. Russell, A. Singh, C. K. Wong and N. J. Curtis, *Proceedings of the Third International Symposium on Organic Selenium and Tellurium Compounds* (Metz, 9–12 July 1979).
17. M. Sevrin, W. Dumont, L. Hevesi and A. Krief, *Tetrahedron Letters*, 2647 (1976).
18. M. Sevrin and A. Krief, *J. Chem. Soc., Chem. Commun.*, 656 (1980).
19. W. Dumont, P. Bayet and A. Krief, *Angew. Chem. Int. Ed.*, **13**, 274 (1974).
20. S. Halazy and A. Krief. *Tetrahedron Letters*, 4233 (1979).
21. H. J. Reich and F. Chow, *J. Chem. Soc., Chem. Commun.*, 790 (1975).
22. H. J. Reich and S. K. Shah, *J. Amer. Chem. Soc.*, **97**, 3250 (1975).
23. L. Hevesi, M. Sevrin and A. Krief, *Tetrahedron Letters*, 2651 (1976).
24. A. Krief, *Proceedings of the Third International Symposium on Organic Selenium and Tellurium Compounds*, (Metz, 9–12 July 1979).
25. A. Krief, W. Dumont, A. Cravador, J. N. Denis, S. Halazy, L. Hevesi, D. Labar, J. Lucchetti, J. Rémion, M. Sevrin and D. Van Ende, *Bull. Soc. Chim. Fr. II*, 519 (1980).
26. D. N. Jones, D. Mundy and R. D. Whitehouse, *J. Chem. Soc., Chem. Commun.*, 86 (1970).
27. K. B. Sharpless, M. W. Young and R. F. Lauer, *Tetrahedron Letters*, 1979 (1973).
28. P. A. Grieco and M. Miyashita, *J. Org. Chem.*, **39**, 120 (1974).
29. C. A. Kingsbury and D. J. Cram, *J. Amer. Chem. Soc.*, **82**, 1810 (1960).
30. B. J. Wakefield, *The Chemistry of Organolithium Compounds*, Pergamon Press, Oxford, 1974.
31. D. Seebach and K. H. Geiss, in *New Applications of Organometallic Reagents in Organic Synthesis* (Ed. D. Seyferth), Elsevier, Amsterdam, 1976.
32. D. J. Cram, *Fundamentals of Carbanion Chemistry—Organic Chemistry: A Series of Monographs*, Vol. 4, Academic Press, New York, 1965.
33. D. J. Peterson, *Organomet. Chem. Rev.*, **A7**, 295 (1972).
34. (a) T. Kauffmann, *Top. Curr. Chem.*, **92**, 109 (1980).
    (b) T. Kauffmann, *Angew. Chem. Int. Ed.*, **21**, 410 (1982).
35. U. Schöllkopf, *Angew. Chem. Int. Ed.*, **10**, 763 (1970).
36. (a) U. Schöllkopf, in *Methoden der Organischen Chemie XIII/1*, Georg Thieme Verlag, Stuttgart, 1970, p. 87.
    (b) K. Nutzel, H. Gilman and G. F. Wright, in *Methoden der Organischen Chemie XIII/2a*, Georg Thieme Verlag, Stuttgart, 1973, p. 53.
37. D. Seebach, *Angew. Chem. Int. Ed.*, **8**, 639 (1969).
38. O. W. Lever, *Tetrahedron*, **32**, 1943 (1976).
39. A. W. Johnson, *Ylid Chemistry*, Academic Press, New York (1966).
40. P. Beak and D. B. Reitz, *Chem. Rev.*, **78**, 275 (1978).
41. D. Seebach and D. Enders, *Angew. Chem. Int. Ed.*, **14**, 15 (1975).
42. (a) D. Hoppe, *Angew. Chem. Int. Ed.*, **13**, 789 (1974).
    (b) U. Schöllkopf, *Angew. Chem. Int. Ed.*, **16**, 339 (1977).
43. H. Ahlbrecht, *Chimia*, **31**, 391 (1977).
44. T. H. Chan, *Acc. Chem. Res.*, **10**, 442 (1977).
45. E. W. Colvin, *Chem. Soc. Rev.*, 7, 15, (1978).
46. W. S. Wadsworth, *Organic Reactions*, **25**, 73 (1977)
47. J. Boutagy and R. Thomas, *Chem. Rev.* **74**, 87 (1974) and references cited therein.
48. A. Maercker, *Organic Reactions*, **14**, 270 (1965).
49. U. Schöllkopf, *Newer Methods of Preparative Organic Chemistry*, Vol. 3, Academic Press, New York, 1964, p. 111; *Angew. Chem.*, **71**, 260 (1959).
50. L. D. Bergelson and M. M. Shemyakin, *Angew. Chem. Int. Ed.*, **3**, 250 (1964).
51. H. J. Bestmann, Newer Methods of Preparative Organic Chemistry, Vol 5, Academic Press, New York, 1968, p. 1; *Angew. Chem. Int. Ed.*, **4**, 583, 645, 830 (1965).
52. H. Pommer, *Angew. Chem. Int. Ed.*, **16**; 423 (1977) and references cited therein.
53. E. Block, *Reaction of Organosulfur Compounds—Organic Chemistry: A Series of Monographs*, Vol. 37, Academic Press, New York, 1978.

54. D. Seebach, *Synthesis*, 17 (1969).
55. B. T. Gröbel and D. Seebach, *Synthesis*, 357 (1977).
56. L. A. Paquette, *Acc. Chem. Res.*, **1**, 209 (1968).
57. P. D. Magnus, *Tetrahedron*, **33**, 2019 (1977).
58. B. M. Trost and L. S. Melvin, *Sulfur Ylides Emerging Synthetic Intermediates—Organic Chemistry: A Series of Monographs*, Vol. 31, Academic Press, New York, 1975, and references cited therein.
59. G. Köbrich, *Angew. Chem. Int. Ed.*, **6**, 41 (1967).
60. G. Köbrich, *Bull. Soc. Chim. Fr.*, 2712 (1969).
61. J. Villieras, *Organomet. Chem. Rev.*, **A7**, 81, (1971).
62. M. S. Newman and B. J. Magerlein, *Organic Reactions*, **5**, 413 (1949).
63. M. Ballester, *Chem. Rev.*, **55**, 283 (1955).
64. J. Hine, *Divalent Carbon*, Ronald Press, New York, 1964.
65. W. Kirmse, *Carbene Chemistry—Organic Chemistry: A Series of Monographs*, Vol. 1, Academic Press, New York, 1971.
66. M. Jones and R. A. Moss, *Carbenes* (Ed. R. A. Moss) Vols 1 and 11, Wiley-Interscience, New York, 1973.
67. (a) D. Seebach and N. Peleties, *Angew. Chem. Int. Ed.*, **8**, 450 (1969).
    (b) D. Seebach and N. Peleties, *Chem. Ber.*, **105**, 511 (1972).
68. D. Van Ende, A. Cravador and A. Krief, *J. Organometal. Chem.*, **1**, 177 (1979).
69. S. Raucher and G. A. Koolpe, *J. Org. Chem.*, **43**, 3794 (1978).
70. H. J. Reich, W. W. Willis and P. D. Clark, *J. Org. Chem.*, **46**, 2775 (1981).
71. B. T. Gröbel and D. Seebach, *Chem. Ber.*, **110**, 852 (1977).
72. H. J. Reich, F. Chow and S. K. Shah, *J. Amer. Chem. Soc.*, **101**, 6638 (1979).
73. P. Bouhy, *Mémoire de Licence*, Namur, June 1980.
74. D. Van Ende, W. Dumont and A. Krief, *J. Organometal Chem.*, **C10**, 149, (1978).
75. K. Sachdev and H. S. Sachdev, *Tetrahedron Letters*, 4223 (1976).
76. H. J. Reich and S. K. Shah, *J. Org. Chem.*, **42**, 1773 (1977).
77. H. J. Reich, *J. Org. Chem.*, **40**, 2570 (1975).
78. M. Clarembeau, unpublished results.
79. M. R. Binns, R. K. Haynes, T. L. Houston and W. R. Jackson, *Tetrahedron Letters*, 573 (1980).
80. R. H. Mitchell, *J. Chem. Soc., Chem. Commun.*, 990 (1974).
81. H. J. Reich and S. K. Shah, *J. Amer. Chem. Soc.*, **99**, 263 (1977).
82. In one case however selenoxide *syn* elimination exclusively occurred, see Ref. 4 in our Ref. 81.
83. F. Zutterman and A. Krief, unpublished results.
84. D. Liotta, M. Saindane and D. Brothers, *J. Org. Chem.*, **47**, 1598 (1982).
85. H. J. Reich and M. L. Cohen, *J. Amer. Chem. Soc.*, **101**, 1307 (1979).
86. F. G. Bordwell, J. E. Bares, J. E. Bartmess, G. E. Drucker, J. Gerhold, G. J. Mc Collum, M. Van Der Puy, N. R. Vanier and W. S. Matthews, *J. Org. Chem.*, **42**, 326 (1977).
87. K. B. Sharpless, R. F. Lauer and A. Y. Teranishi, *J. Amer. Chem. Soc.* **95**, 6137 (1973).
88. (a) J. Lucchetti and A. Krief, *Tetrahedron Letters*, 2693 (1978).
    (b) J. Lucchetti and A. Krief, *Tetrahedron Letters*, 2697 (1978).
89. J. Lucchetti and A. Krief, *J. Chem. Soc., Chem. Commun.*, 127 (1982).
90. N. Petragnani and H. M. C. Ferraz, *Synthesis*, 476 (1978).
91. P. A. Grieco, *Synthesis*, 67 (1975) and references cited therein.
92. P. A. Grieco and Y. Yokoyama, *J. Amer. Chem. Soc.*, **99**, 5210 (1977).
93. Y. Masuyama, Y. Ueno and M. Okawara, *Chem. Letters*, 835 (1977).
94. D. Van Ende, W. Dumont and A. Krief, *Angew. Chem. Int. Ed.*, **14**, 700 (1975).
95. W. Dumont and A. Krief, *Angew. Chem. Int. Ed.*, **16**, 540 (1977).
96. A. Cravador, A. Krief and L. Hevesi, *J. Chem. Soc., Chem. Commun.*, 451 (1980).
97. J. Lucchetti and A. Krief, *Compt. Rend., Ser. C*, **289**, 287 (1979).
98. (a) D. L. J. Clive and S. M. Menchen, *J. Chem. Soc., Chem. Commun.*, 356 (1978).
    (b) D. L. J. Clive and S. M. Menchen, *J. Org. Chem.*, **44**, 1883 (1979).
99. A. Cravador and A. Krief, *Compt. Rend., Ser. C*, **289**, 267 (1979).
100. W. Dumont, D. Van Ende and A. Krief, *Tetrahedron Letters*, 485 (1979).
101. N. Petragnani, R. Rodrigues and J. V. Comassetto, *J. Organomet. Chem.*, **114**, 281 (1976).
102. J. V. Comassetto and C. A. Brandt, *J. Chem. Res. (S)*, 56 (1982).
103. T. Sakakibara, S. Ikuta and R. Sudoh, *Synthesis*, 261 (1982).

104. Ref. 8, p. 2605.
105. H. M. J. Gillissen, P. Schipper, P. J. J. M. van Ool and H. M. Buck, *J. Org. Chem.*, **45**, 319 (1980).
106. (a) M. Sevrin and A. Krief, *Tetrahedron Letters*, 585 (1980).
     (b) M. Sevrin, Ph.D. *Thesis*, Namur, October 1980.
107. S. Halazy and A. Krief, *J. Chem. Soc., Chem. Commun.*, 1136 (1979).
108. D. Labar and A. Krief, *J. Chem. Soc., Chem. Commun.*, 564 (1982).
109. S. Halazy, F. Zutterman and A. Krief, *Tetrahedron Letters*, 4385 (1982).
110. S. Halazy and A. Krief, *J. Chem. Soc., Chem. Commun.*, 1200 (1982).
111. W. Dumont and A. Krief, *Société Chimique de France, Journée d'automne, Palaiseau*, September 1981.
112. J. Lucchetti, J. Remion and A. Krief, *Compt. Rend., Ser. C*, **288**, 553 (1979).
113. J. L. Bertrand, *Mémoire de Licence*, Namur, June 1983.
114. M. Clarembeau and J. L. Bertrand and A. Krief, *Israel J. Chem.*, **24**, 125 (1984).
115. S. Halazy, *Ph.D. Thesis*, Namur, December 1982.
116. F. Zutterman and A. Krief, *J. Org. Chem.*, **48**, 1135 (1983).
117. J. Lucchetti, *Ph.D. Thesis*, Namur, March 1983.
118. W. Dumont, M. Sevrin and A. Krief, *Angew. Chem. Int. Ed.*, **16**, 541 (1977).
119. Ref. 22, footnote 13.
120. Th. Kauffmann, H. Ahlers, H.J. Tilhard and A. Woltermann, *Angew. Chem. Int. Ed.*, **16**, 710 (1977).
121. M. Sevrin, J. N. Denis and A. Krief, *Angew. Chem. Int. Ed.*, **17**, 526 (1978).
122. S. Raucher and G. A. Koolpe, *J. Org. Chem.*, **43**, 4252 (1978).
123. M. Sevrin, W. Dumont and A. Krief, *Tetrahedron Letters*, 3835 (1977) and references cited therein.
124. J. N. Denis and A. Krief, *Tetrahedron Letters*, 3407 (1982) and references cited therein.
125. S. Raucher, *J. Org. Chem.*, **43**, 2950 (1977).
126. (a) D. Seebach and A. K. beck, *Angew. Chem. Int. Ed.*, **13**, 806 (1974).
     (b) D. Seebach, N. Meyer and A. K. Beck, *Liebigs Ann. Chem.*, 846 (1977).
127. S. Halazy and A. Krief, *Tetrahedron Letters*, 1997 (1980).
128. W. Dumont, A. Cravador and A. Krief, unpublished results
129. M. Sevrin and A. Krief, *Tetrahedron Letters*, 187 (1978).
130. J. Remion and A. Krief, *Tetrahedron Letters*, 3743 (1976).
131. J. Remion, W. Dumont and A. Krief, *Tetrahedron Letters*, 1385 (1976).
132. D. Labar, W. Dumont, L. Hevesi and A. Krief, *Tetrahedron Letters*, 1145 (1978).
133. S. Halazy, J. Lucchetti and A. Krief, *Tetrahedron Letters*, 3971 (1978).
134. S. Halazy and A. Krief, *Tetrahedron Letters*, 1829 (1981).
135. D. Labar, J. L. Laboureur and A. Krief, *Tetrahedron Letters*, 983 (1982).
136. J. N. Denis, W. Dumont and A. Krief, *Tetrahedron Letters*, 453 (1976).
137. W. Dumont and A. Krief, *Angew. Chem. Int. Ed.*, **14**, 350 (1975).
138. D. Van Ende and A. Krief, *Tetrahedron Letters*, 457 (1976).
139. S. Halazy and A. Krief, *Tetrahedron Letters*, 1833 (1981).
140. A. M. Leonard-Coppens and A. Krief, *Tetrahedron Letters*, 3227 (1976).
141. A. Anciaux, A. Eman, W. Dumont, D. Van Ende and A. Krief, *Tetrahedron Letters*, 1613 (1975).
142. W. Dumont and A. Krief, *Angew. Chem. Int. Ed.*, **15**, 161 (1976).
143. S. Halazy, W. Dumont and A. Krief, *Tetrahedron Letters*, 4737 (1981).
144. D. Labar and A. Krief, unpublished results.
145. F. Zutterman, unpublished results.
146. J. Lucchetti, W. Dumont and A. Krief, *Tetrahedron Letters*, 2695 (1979).
147. J. D. White, M. C. Kang and B. G. Sheldon, *Tetrahedron Letters*, 4539 (1983).
148. J. Lucchetti and A. Krief, *Tetrahedron Letters*, 1623 (1981).
149. J. Lucchetti, W. Dumont and A. Krief, *Tetrahedron Letters*, 2695 (1979).
150. J. Lucchetti and A. Krief, *J. Organometal. Chem.*, **C49**, 194 (1980).
151. L. Fitjer, H. J. Shauerman and D. Wehle, *Tetrahedron Letters*, **25**, 2329 (1984).
152. 2,2,6,6-Tetraphenylcyclohexanone was kindly provided by prof. D. H. R. Barton, Institut des Substances Naturelles, Gif-sur-Yvette, France.
153. R. C. Gadwood, *J. Org. Chem.*, **48**, 2098 (1983).

154. D. Van Ende, *Ph.D. Thesis*, Namur, 1976.
155. L. Wartski, M. El Bouz, J. Seyden-Penne, W. Dumont and A. Krief, *Tetrahedron Letters*, 1543 (1979).
156. W. Dumont, J. Lucchetti and A. Krief, *J. Chem. Soc., Chem. Commun.*, 66 (1983).
157. J. Lucchetti and A. Krief, *Synth. Commun.*, **14**, 1153 (1983).
158. H. J. Reich, S. K. Shah and F. Chow, *J. Amer. Chem. Soc.*, **101**, 6648 (1979).
159. J. N. Denis and A. Krief, *Tetrahedron Letters*, 3995 (1979).
160. J. N. Denis and A. Krief, *J. Chem. Soc., Chem. Commun.*, 544 (1980).
161. N. N. Magdesieva, R. A. Kandgeteyan and A. A. Ibragimov, *J. Organometal. Chem.*, **42**, 399 (1972) and references cited therein.
162. K. H. Wei, I. C. Paul, M.-M. Y. Chang and J. I. Musher, *J. Amer. Chem. Soc.*, **96**, 4099 (1974).
163. E. Ernstbrunner and D. Lloyd, *Liebigs Ann. Chem.*, **753**, 196 (1971).
164. (a) D. Lloyd and M. I. C. Singer, *J. Chem. Soc., Chem. Commun.*, 390 (1967).
    (b) E. D. Hughes and K. I. Kuriyan, *J. Chem. Soc.*, 1609 (1935).
165. W. W. Lotz and J. Gosselck, *Tetrahedron*, **29**, 917 (1973).
166. (a) Recently a report from Negoro appeared (Ref. 166b), 8 years after our own paper and seems to be incorrect. We have tried without success to repeat the reactions therein described. Moreover the ¹H-NMR published in this paper do not refer to epoxides as proposed but to the starting carbonyl compound.
    (b) K. Negoro, K. Takaki and M. Yasumura, *Angew. Chem. Int. Ed.*, **20**, 671 (1981).
167. E. G. Kataev and V. N. Petrov, *J. Gen. Chem. USSR*, **32**, 3626 (1962).
168. H. J. Reich and J. M. Renga, *J. Org. Chem.*, **40**, 3313 (1975).
169. W. Hölzle and W. Jenny, *Helv. Chim. Acta*, **41**, 593 (1958).
170. E. G. Kataev, T. G. Maunafov, E. A. Berdnikov and O. A. Komarovskaya, *J. Org. Chem. USSR*, **9**, 1998 (1973).
171. T. A. Hase and P. Kukk'ola, *Synth. Commun.*, **10**, 451 (1980).
172. A. E. Feiring, *J. Org. Chem.*, **45**, 1958, 1962 (1980).
173. I. Kuwajima and M. Shimizu, *Tetrahedron Letters*, 1277 (1978).
174. M. Sevrin, W. Dumont and A. Krief, *Tetrahedron Letters*, 183 (1978).
175. D. J. Buckley, S. Kulkowit and A. McKervey, *J. Chem. Soc., Chem. Commun.*, 506 (1980).
176. H. J. Reich and M. L. Cohen, *J. Amer. Chem. Soc.*, **101**, 1307 (1979).
177. J. Hooz and R. Mortimer, *Tetrahedron Letters*, 805 (1976).
178. B. Harirchian and P. Magnus, *J. Chem. Soc., Chem. Commun.*, 522 (1977).
179. Y. Okamoto, R. Homsany and T. Yano, *Tetrahedron Letters*, 2529 (1972).
180. S. Raucher, *J. Org. Chem.*, **43**, 4885 (1978).
181. W. Dumont, D. Van Ende and A. Krief, *Tetrahedron Letters*, 485 (1979).
182. H. J. Reich and J. M. Renga, *J. Org. Chem.*, **40**, 3313 (1975).
183. H. J. Reich, J. M. Renga and J. E. Trend, *Tetrahedron Letters*, 2217 (1976).
184. E. G. Kataev, T. G. Mannafov and Y. Y. Samitov, *Zh. Org. Khim.*, **11**, 2324 (1975).
185. J. N. Denis and A. Krief, *Tetrahedron Letters*, 3411 (1982).
186. B. T. H. Gröbel and D. Seebach, *Chem. Ber.*, **110**, 867 (1977).
187. J. N. Denis, S. Desauvage, L. Hevesi and A. Krief, *Tetrahedron Letters*, 4009 (1981).
188. S. Halazy and A. Krief, *Tetrahedron Letters*, 4341 (1981).
189. D. Seyferth (Ed.) *New Applications of Organometallic Reagents in Organic Synthesis* Elsevier, Amsterdam, 1976.
190. D. Seyferth and M. A. Weiner, *J. Org. Chem.*, **26**, 4797 (1961).
191. R. M. Magid and J. G. Welch, *J. Amer. Chem. Soc.*, **90**, 5211 (1968).
192. D. E. Applequist and E. G. Saurborn, *J. Org. Chem.*, **37**, 1676 (1972).
193. A. H. Haubein and H. Gilman, *J. Amer. Chem. Soc.*, **66**, 1515 (1944).
194. P. Miginiac and C. Bouchoule, *Bull. Soc. Chim. Fr.*, 4156 (1968).
195. J. J. Eisch and A. M. Jacobs, *J. Org. Chem.*, **28**, 2145 (1963).
196. H. A. McNinch and H. Gilman, *J. Org. Chem.*, **26**, 3723 (1961).
197. D. Seyferth and M. A. Weiner, *J. Org. Chem.*, **24**, 1395 (1959).
198. M. Micha-Screttas and C. G. Screttas, *J. Org. Chem.*, **44**, 713 (1979).
199. M. A. Weiner and D. Seyferth, *Organic Synthesis*, **41**, 30 (1961).
200. D. Seyferth, R. Suzuki, C. J. Murphy and C. R. Sabet, *J. Organometal. Chem.*, 431 (1964).
201. D. F. Hoeg and D. I. Lusk, *J. Amer. Chem. Soc.*, **86**, 928 (1964).
202. D. J. Peterson, *J. Org. Chem.*, **32**, 1717 (1967) and references cited therein.

203. E. J. Corey and D. Seebach, *J. Org. Chem.*, **31**, 4097 (1966).
204. W. E. Parham and R. F. Motter, *J. Amer. Chem. Soc.*, **81**, 2146 (1959).
205. W. E. Parham, M. A. Kalnins and D. R. Theissen, *J. Org. Chem.*, **27**, 2698 (1962).
206. T. M. Dolak and T. A. Bryson, *Tetrahedron Letters*, 1961 (1977).
207. W. Dumont, A. Anciaux, A. Eman, J. N. Denis and A. Krief, to be published.
208. A. Anciaux, A. Eman, W. Dumont and A. Krief, *Tetrahedron Letters*, 1617 (1975).
209. J. N. Denis, W. Dumont and A. Krief, *Tetrahedron Letters*, 4111 (1979).
210. W. Dumont and A. Krief, *J. Chem. Soc., Chem. Commun.*, 673 (1980).
211. W. Dumont and A. Krief, *Angew. Chem. Int. Ed.*, **15**, 161 (1976).
212. D. J. Peterson, *J. Organometal. Chem.*, **9**, 373 (1967).
213. G. A. Gornowicz and R. West, *J. Amer. Chem. Soc.*, **90**, 4478 (1968).
214. A. G. Brook, J. M. Duff and D. G. Anderson, *Can. J. Chem.*, **48**, 561 (1970).
215. T. Hiyama, A. Kanakura, Y. Morizawa and H. Nozaki, *Tetrahedron Letters*, 1279 (1982).
216. (a) L. A. Paquette, K. A. Horn and G. J. Wells, *Tetrahedron Letters*, 259 (1982).
    (b) T. J. Cohen, personal communication, 1981.
217. L. F. Cason and H. G. Brooks, *J. Org. Chem.*, **19**, 1278 (1954).
218. G. R. Buell, R. Corriu, G. Guerin and L. Spialter, *J. Amer. Chem. Soc.*, **92**, 7424 (1970).
219. T. H. Chan and E. Chang, *J. Org. Chem.*, **39**, 3264 (1974).
220. K. C. Nicolaou and Z. Lysenko, *J. Amer. Chem. Soc.*, **99**, 3185 (1977).
221. D. L. J. Clive, G. J. Chittattu, V. Farina, W. A. Kiel, S. M. Menchen, C. G. Russell, A. Singh, C. K. Wong and N. J. Curtis, *J. Amer. Chem. Soc.*, **102**, 4438 (1980).
222. S. Halazy, unpublished results.
223. J. N. Denis and A. Krief, *J. Chem. Soc., Chem. Commun.*, 229 (1983).
224. P. A. Grieco, S. Gilman and M. Nishizawa, *J. Org. Chem.*, **41**, 1485 (1976).
225. G. Hölzle and W. Jenny, *Helv. Chim. Acta*, **89**, 712 (1958).
226. K. B. Sharpless and R. F. Lauer, *J. Org. Chem.*, **39**, 429 (1974).
227. H. J. Reich, J. M. Renga and I. L. Reich, *J. Amer. Chem. Soc.*, **97**, 5434 (1975).
228. W. G. Salmond, The Upjohn Company. *U. S. Patent*, No. 3,970,676 (1976)
229. K. B. Sharpless, R. F. Lauer and A. Y. Teranishi, *J. Amer. Chem. Soc.*, **95**, 6137 (1973).
230. T. Minami, H. Sako, T. Ikehira, T. Hanamoto and I. Hirao, *J. Org. Chem.*, **48**, 2569 (1983).
231. T. Hori and K. B. Sharpless, *J. Org. Chem.*, **43**, 1689 (1978).
232. D. Labar, L. Hevesi, W. Dumont and A. Krief, *Tetrahedron Letters*, 1141 (1978).
233. K. B. Sharpless and M. W. Young, *J. Org. Chem.*, **40**, 947 (1975).
234. R. D. Clark and C. H. Heathcock, *J. Org. Chem.*, **41**, 1396 (1976).
235. L. D. Kwart, A. G. Horgan and H. Kwart, *J. Amer. Chem. Soc.*, **103**, 1232 (1981).
236. K. Torssell, *Tetrahedron Letters*, 623 (1974).
237. Y. Tsuda, T. Sano, J. Taga, K. Isobe, J. Toda, H. Irie, H. Tanaka, S. Takagi, M. Yamaki and M. Murata, *J. Chem. Soc., Chem. Commun.*, 933 (1975).
238. S. David, A. Lubineau and J. M. Vatele, *J. Chem. Soc., Chem. Commun.*, 701 (1975); *J. Chem. Soc. Perkin Trans. 1*, 1831 (1976).
239. L. A. Paquette, C. C. Liao, R. L. Burson, R. E. Wingard, Jr., C. N. Shih, J. Fayos and J. Clardy, *J. Amer. Chem. Soc.*, **99**, 6935 (1977).
240. L. A. Paquette, C. C. Liao, D. C. Liotta and W. E. Fristad, *J. Amer. Chem. Soc.*, **98**, 6412 (1976).
241. B. M. Trost and P. H. Scudder, *J. Amer. Chem. Soc.*, **99**, 7601 (1977).
242. H. J. Reich, *J. Org. Chem.*, **39**, 428 (1974).
243. K. Isobe, J. Taga and Y. Tsuda, *Tetrahedron Letters*, 2331 (1976).
244. K. C. Nicolaou and W. E. Barnette, *J. Chem. Soc., Chem. Commun.*, 331 (1977).
245. K. C. Nicolaou and Z. Lysenko, *Tetrahedron Letters*, 1257 (1977).
246. E. J. Corey, G. E. Keck and I. Szekely, *J. Amer. Chem. Soc.*, **99**, 2006 (1977).
247. D. L. J. Clive, G. Chittattu, N. J. Curtis, W. A. Kiel and C. K. Wong, *J. Chem. Soc., Chem. Commun.*, 725 (1977).
248. A. G. Gonzalez, C. Betancor, C. G. Francisco, R. Hernandez, J. A. Salazar and E. Suarez, *Tetrahedron Letters*, 2959 (1977).
249. D. Liotta and G. Zima, *J. Org. Chem.*, **45**, 2551 (1980).
250. A. Toshimitsu, H. Owada, T. Aoai, S. Uemura and M. Okano, *J. Chem. Soc., Chem. Commun.*, 546 (1981).
251. J. N. Denis, J. Vicens and A. Krief, *Tetrahedron Letters*, 2697 (1979).

252. P. S. Liu, V. E. Marquez, J. A. Kelley, and J. S. Driscoll, *J. Org. Chem.*, **45**, 5225 (1980).
253. F. M. Dean and B. K. Park, *J. Chem. Soc., Chem. Commun.*, 142 (1975).
254. S. H. Korzeniowski, D. P. Vanderbilt and L. B. Hendry, *Org. Prep. Proc. Int.*, **8**, 81 (1976).
255. J. Schwartz and Y. Hayasi, *Tetrahedron Letters*, 1497 (1980).
256. J. Tsuji, K. Masaoka and T. Takahashi, *Tetrahedron Letters*, 2267 (1977).
257. J. Tsuji, K. Masaoka, T. Takahashi, A. Suzuki and N. Miyaura, *Bull. Chem. Soc. Japan*, **50**, 2507 (1977).
258. P. A. Grieco and M. Miyashita, *J. Org. Chem.*, **39**, 120 (1974).
259. P. A. Grieco and M. Nishizawa, *J. Chem. Soc., Chem. Commun.*, 582 (1976).
260. P. A. Zoretic and R. Soja, *J. Org. Chem.*, **41**, 3587 (1976); *J. Heterocycl. Chem.*, **14**, 681 (1977).
261. D. N. Brattesani and C. H. Heathcock, *Tetrahedron Letters*, 2279 (1974); *J. Org. Chem.*, **40**, 2165 (1975).
262. T. Sakakibara, I. Takai, E. Omara and R. Sudoh, *J. Chem. Commun.*, 261 (1981).
263. A. Toshimitsu, H. Owada, S. Uemura and M. Okano, *Tetrahedron Letters*, 2105 (1982).
264. H. J. Reich and W. W. Willis, *J. Amer. Chem. Soc.*, **102**, 5967 (1980).
265. T. G. Back and S. Collins, *Tetrahedron Letters*, 5111 (1981).
266. A. Burton, L. Hevesi, W. Dumont, A. Cravador and A. Krief, *Synthesis*, 877 (1979).
267. W. G. Salmond, M. A. Barta, A. M. Cain and M. C. Sobala, *Tetrahedron Letters*, 1683 (1977).
268. S. K. Shah, *Ph. D. Thesis*, University of Wisconsin, Madison, 1977.
269. S. Halazy and A. Krief, *Tetrahedron Letters*, 2135 (1981).
270. Diphosphorus tetraiodide (P_2I_4) a powerful deoxygenator, Aldrich, Technical Information 191, 1980, Product No. 21865–0.
271. M. Shimizu and I. Kuwajima, *J. Org. Chem.*, **45**, 2921 (1980).
272. F. Ogura, H. Yamaguchi, T. Otsubo and H. Tanaka, *Bull. Chem. Soc. Japan*, **55**, 641 (1982).
273. D. Barnard and D. T. Woodbridge, *Chem. Ind. (London)*, 1603 (1959).
274. K. Balenovic, R. Lazic, V. Polak and P. Stern, *Bull. Sci. Cons. Acad. Sci. Arts RSF Yougosl. Sect. A17*, 147 (1972); *Chem. Abstr.*, **77**, 139499j (1972).
275. N. Bregant, I. Perina and K. Balenovic, *Bull. Sci. Cons. Acad. Sci. Arts RSF Yougosl. Sect. A17*, 148 (1972); *Chem. Abstr.*, **77**, 152092j (1972).
276. I. Perina, N. Bregant and K. Balenovic, *Bull. Sci. Cons. Acad. Sci. Arts RSF Yougosl. Sect. A18*, 4 (1973); *Chem. Abstr.*, **78**, 160007w (1973).
277. M. Poje and K. Balenovic, *Bull. Sci. Cons. Acad. Sci. Arts RSF Yougosl. Sect. A20*, 1 (1975); *Chem. Abstr.*, **83**, 43558u (1975).
278. I. Perina, N. Bregant and K. Balenovic, *Bull. Sci. Cons. Acad. Sci. Arts RSF Yougosl. Sect. A18*, 3 (1973); *Chem. Abstr.*, **79**, 5096b (1973).
279. K. Balenovic, N. Bregant and I. Perina, *Synthesis*, 172 (1973).
280. A. Cravador and A. Krief, *Tetrahedron Letters*, 2491 (1981).
281. D. Labar, A. Krief and L. Hevesi, *Tetrahedron Letters*, 3967 (1978).
282. J. L. Laboureur and A. Krief, *Tetrahedron Letters*, **25**, 4569 (1984).
283. M. Sevrin, J. N. Denis and A. Krief, *Tetrahedron Letters*, 1877 (1980).
284. K. B. Sharpless and R. F. Lauer, *J. Amer. Chem. Soc.*, **95**, 2697 (1973).
285. D. L. J. Clive, *J. Chem. Soc., Chem. Commun.*, 100 (1974).
286. K. B. Sharpless and R. F. Lauer, *J. Org. Chem.*, **39**, 428 (1974).
287. D. L. J. Clive, C. G. Russell and S. C. Suri, *J. Org. Chem.*, **47**, 1632 (1982).
288. C. J. Kowalski and J. S. Dung, *J. Amer. Chem. Soc.*, **102**, 7951 (1980).
289. D. L. J. Clive and V. N. Kale, *J. Org. Chem.*, **46**, 231 (1981).
290. T. Di Giamberardino, S. Halazy, W. Dumont and A. Krief, *Tetrahedron Letters*, 3413 (1983).
291. (a) D. J. Cram and F. A. Abd. Elhafez, *J. Amer. Chem. Soc.*, **74**, 5828 (1952).
     (b) T. J. Leitereg and D. J. Cram, *J. Amer. Chem. Soc.*, **90**, 4011, 4019 (1968).
292. (a) M. Cherest, H. Felkin and N. Prudent, *Tetrahedron Letters*, 2199 (1968).
     (b) M. Cherest and H. Felkin, *Tetrahedron Letters*, 2205 (1968).
293. M. Shimizu and I. Kuwajima, *J. Org. Chem.*, **45**, 4063 (1980).
294. D. Seebach and A. K. Beck, *Chem. Ber.*, **108**, 314 (1975).
295. (a) B. H. Freeman and D. Lloyd, *J. Chem. Soc., Chem. Commun.*, 924 (1970).
     (b) B. H. Freeman, D. Lloyd and M. I. C. Singer, *Tetrahedron*, **28**, 343 (1972).
296. E. J. Corey and M. Jautelat, *Tetrahedron Letters*, 5787 (1968).
297. Ref. 34b, p. 417.
298. Ref. 34b, p. 426.

299. Ref. 34b, p. 427.
300. Ref. 34b, p. 427.
301. T. Kauffmann, H. Ahlers, R. Joussen, R. Kriegsmann, A. Vahrenhorst and R. Woltermann, *Tetrahedron Letters*, 4399 (1978).
302. D. Lloyd, *Chem. Scripta*, **8a**, 14 (1975).
303. N. S. Zefirov, *Chem. Scripta*, **8a**, 20 (1975).
304. N. N. Magdesieva, R. A. Kyandzhetsian and O. A. Rakitin, *Zh. Org. Khim.*, **11**, 2562 (1975).
305. N. N. Magdesieva, R. A. Kyandzhetsian and O. A. Rakitin, *Zh. Org. Khim.*, **12**, 36 (1976).
306. I. D. Sadekov, A. I. Usachev, A. A. Maksimenko and V. I. Minkin, *Zh. Obshch. Khim.*, **45**, 2562 (1975).
307. M. Sevrin, unpublished results.
308. (a) A. Burton, *Mémoire de Licence*, Namur, June 1978.
    (b) A. Burton, L. Hevesi and A. Krief, unpublished results.
309. S. Spreutel, *Mémoire de Licence*, Namur, June 1979.
310. J. Lucchetti and A. Krief, *Compt. Rend., Ser. C*, **288**, 537 (1979).
311. R. Baudat and M. Petrzilka, *Helv. Chim. Acta*, **62**, 1406 (1979).
312. G. H. Posner and M. J. Chapdelaine, *Tetrahedron Letters*, 3227 (1977).
313. D. H. R. Barton, D. J. Lester, W. B. Motherwell and M. T. Barros Papoula, *J. Chem. Soc., Chem. Commun.*, 246 (1980).
314. H. J. Reich, P. M. Gold and F. Chow, *Tetrahedron Letters*, 4433 (1979).
315. I. D. Sadekov, A. I. Usachev, A. A. Maksimenko and A. I. Minkin, *Zh. Obsch. Khim.*, **48**, 934 (1974).
316. A. Osuka, Y. Mori, H. Shimizu and H. Suzuki, *Tetrahedron Letters*, 2599 (1983).
317. A. Osuka and H. Suzuki, *Tetrahedron Letters*, 5109 (1983).
318. S. Uemura and S. Fukuzawa, *Tetrahedron Letters*, 4347 (1983).
319. For some synthetic methods based on tellurium chemistry see the references cited in our Ref. 318.
320. L. Hevesi and A. Krief, *Angew. Chem. Int. Ed.*, **15**, 381 (1976).
321. H. J. Reich, M. C. Clark and W. W. Willis, *J. Org. Chem.*, **47**, 1618 (1982).
322. K. Chikamatsu, T. Otsubo, F. Ogura, H. Yamaguchi, *Chem. Letters*, 1081 (1982).
323. T. Otsubo, F. Ogura, H. Yamaguchi, H. Higuchi, Y. Sakata and S. Misumi, *Chem. Letters*, 447 (1981).
324. J. V. Comasseto, *J. Organometal. Chem.*, **253**, 131 (1983).
325. D. H. R. Barton, G. Bashiardes and J. L. Fourrey, *Tetrahedron Letters*, **25**, 1287 (1984).
326. M. Clarembeau and A. Krief, *Tetrahedron Letters*, **25**, 3629 (1984).
327. H. J. Reich, S. Wollowitz, J. E. Trend, F. Chow and D. F. Wandelborn, *J. Org. Chem.*, **43**, 1697 (1978).
328. B. M. Trost, D. E. Keeley, H. C. Ardnt and M. J. Bogdanowicz, *J. Amer. Chem. Soc.*, **99**, 3088 (1977).
329. H. Nishuyama, T. Kitajima, A. Yamamoto and K. Itho, *J. Chem. Soc., Chem. Commun.*, 1232 (1982).
330. J. N. Denis, J. L. Laboureur and A. Krief, unpublished results.
331. S. Uemura and S. Fukuzawa, *Tetrahedron Letters*, 4347 (1983).
332. S. Uemura and S. Fukuzawa, *J. Amer. Chem. Soc.*, **105**, 2748 (1983).
333. H. Lee and M. P. Cava, *J. Chem. Soc., Chem. Commun.*, 277 (1981).
334. A. Krief, W. Dumont, J. N. Denis, G. Evrard and B. Norberg, *J. Chem. Soc. Chem. Commun.*, 569 (1985).
335. A. Krief, W. Dumont and J. N. Denis, *J. Chem. Soc. Chem. Commun.*, 570 (1985).
336. M. Clarembeau, A. Cravadoi, W. Dumont, L. Hevesi, A. Krief, J. Lucchetti and D. Van Ende, *Tetrahedron*, in press.
337. D. Labar and A. Krief, *Bull. Soc. Chem. Belg.*, **93**, 1005 (1984) and references cited.
338. D. Labar, PhD thesis, Namur, March 1985.
339. (a) J. L. Laboureur and A. Krief, *Tetrahedron Letters*, **25**, 2713 (1984).
    (b) A. Krief and J. L. Laboureur, *J. C. S., Chem. Commun.*, 702 (1986).
    (c) Schmit, S. Sahroui-Taleb, E. Differding, G. G. Dehasse, S. De Lombaert and L. Ghosez, *Tetrahedron Letters*, **25**, 5043 (1984).
340. A. Krief, J. L. Laboureur and W. Dumont, *Tetrahedron Letters*, **28**, 1549 (1987).
    (b) A. Krief and J. L. Laboureur, *Tetrahedron Letters*, **28**, 1545 (1987).

CHAPTER **18**

Selenium and tellurium derivatives of carbohydrates and nucleoside analogs

ZBIGNIEW J. WITCZAK

Whistler Center For Carbohydrate Research, Purdue University, Smith Hall, West Lafayette, Indiana 47907, USA

I. INTRODUCTION

The chemistry of organic selenium compounds has developed rapidly over the past 15 years and has acquired new dimensions[1-8] especially in the area of the synthesis of natural products[9], selenocarbohydrates[10-16], selenonucleosides[17] and other selenium-containing molecules of biological interest[18,19]. Various aspects of biologically important organic selenium compounds have been extensively studied and reviewed[20]. The biomedical and biochemical aspects are treated in three books[21-23].

In carbohydrate chemistry, the first article[24] reporting on the introduction of selenium into a sugar moiety was published in 1917, since when a number of reports dealing with the synthesis of many natural products[9] through organoselenium intermediates have been published. This chapter collates information on the synthesis and reactivity of organoselenium and organotellurium intermediates and illustrates some of the chemical properties that have contributed to the synthesis of selenocarbohydrates and selenonucleosides.

Knowledge of selenium intermediates, seleno sugars and selenonucleosides is growing steadily and they now constitute key intermediates in routes to various heterocyclic derivatives of sugars and to free sugars.

II. SELENOGLYCOSIDES AND OTHER SELENIUM DERIVATIVES OF CARBOHYDRATES: SYNTHESIS AND REACTIONS

Bonner and Robinson[13] synthesized several selenoglycosides using the approach previously adopted by Schneider and Wrede[24]. The reaction sequence starts with α-D-glycopyranosyl bromide (equation 1) and proceeds with Walden inversion at $C_{(1)}$. The same methodology was used by Wagner and Lehmann[14] for the synthesis of the various substituted selenoglycosides (equation 2).

$$\text{(scheme, equation 1): } \text{glycopyranosyl bromide tetraacetate} \xrightarrow[\text{CHCl}_3, \text{EtOH}]{\text{PhSeH, KOH}} \text{SePh derivative} \xrightarrow{\text{NH}_3, \text{MeOH}} \text{deacetylated SePh glycoside}$$

(1)

$$\text{(scheme, equation 2): } \xrightarrow[\text{Me}_2\text{CO}]{\text{R}^3\text{C}_6\text{H}_4\text{SeK}} \text{O-SeC}_6\text{H}_4\text{R}^3 \text{ derivative}$$

$$R^1 = H, R^2 = OAc$$
$$R^1 = OAc, R^2 = H$$

$$R^3 = H, 4\text{-Me}, 4\text{-Cl}, 2\text{-Me}$$

(2)
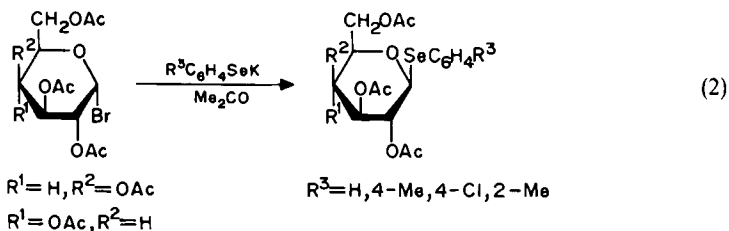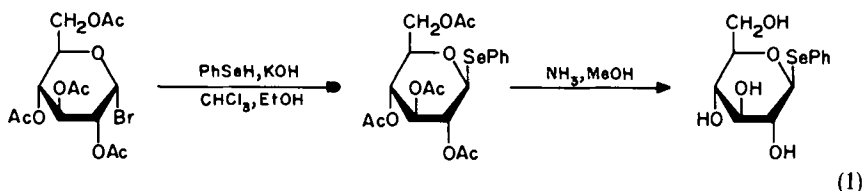
A similar approach was employed for the preparation of the sodium salt of 1-seleno-D-glucose[16]. This sequence proceeded by treatment of α-D-glucosyl bromide with PhCOSeK, followed by methanolysis (equation 3). This sodium salt of 1-seleno-D-glucose was an excellent precursor in the synthesis of selenoglycosides and sugar diselenides, as reported by Wagner and Nühn[25]. However, they proceeded by treatment of α-D-glucosyl bromide with selenourea, followed by basic hydrolysis of the intermediate 2,3,4,6-tetra-O-acetyl-1-selenopseudourea-β-D-glucopyranose hydrobromide, with formation of the sodium salt of 1-seleno-D-glucose (equation 4).

$$\text{(scheme, equation 3): } \text{glucosyl bromide tetraacetate} \xrightarrow[\text{Me}_2\text{CO, H}_2\text{O}]{\text{PhCOSeK}} \text{SeCOPh derivative} \xrightarrow[\text{MeOH}]{\text{MeONa}} \text{SeNa glucose}$$

(3)

$$\text{(scheme, equation 4): } \text{glucosyl bromide tetraacetate} \xrightarrow[\text{Me}_2\text{CO}]{\overset{\text{Se}}{\underset{}{\text{H}_2\text{NCNH}_2}}} \text{SeC(NH}_2\text{)=NH}_2^+ \text{Br}^- \text{ derivative} \xrightarrow[\text{MeOH}]{\text{NaOMe}} \text{SeNa glucose}$$

(4)
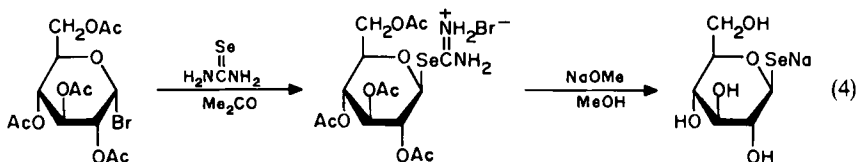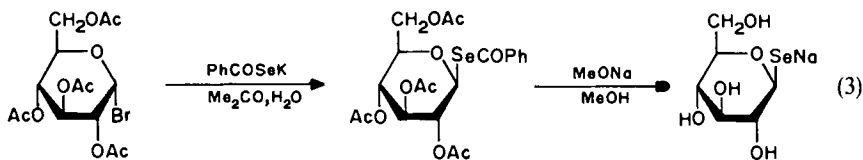
Other interesting examples of the application of similar procedures have appeared in the literature[26].

All of the above-mentioned methods of synthesis of selenoglycosides lead preferentially to the formation of β-anomers, which are probably thermodynamically more stable than the α-anomers. However, Frenzel and coworkers[26] found that the formation of both anomers of selenoglycosides occurs during opening of the epoxide ring of Brigl's anhydride (3, 4, 6-tri-O-acetyl-1, 2-anhydro-α-D-glucopyranose) with benzeneselenol (equation 5). The anomeric products were separated by thin-layer chromatography and the purity, configuration and conformation of the glycosides were confirmed by ^{1}H NMR spectroscopy. It is noteworthy that the protons *cis* to the aglycone are shifted to lower field in comparison with O- and S-series of glycosides.

$$\text{(5)}$$
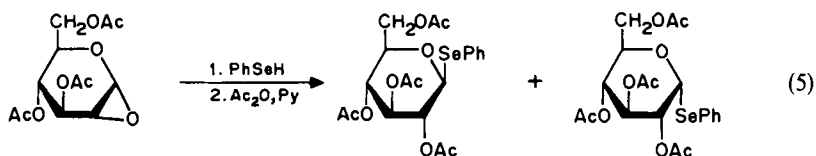
Another interesting example of the application of Brigl's anhydride in selenoorganic chemistry is its reaction with the triethylammonium salt of 2-oxo-2-seleno-5, 5-dimethyl-1, 3, 2-dioxaphosphorinane, with the formation of 3, 4, 6-tri-O-acetyl-D-glucal and a diselenide[27] (equation 6).

$$\text{(6)}$$
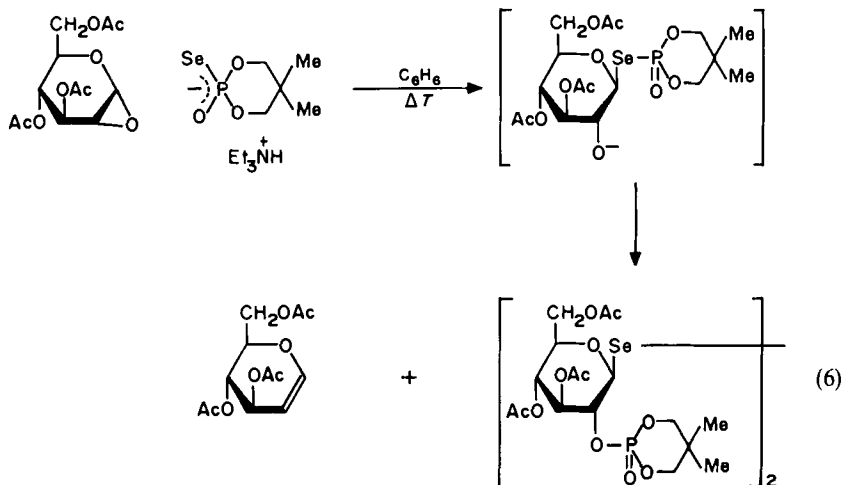
The reaction of the triethylammonium salt of 2-thio-2-seleno-5, 5-dimethyl-1, 3, 2-dioxaphosphorinane with 2, 3, 4, 6-tetra-O-acetyl-α-D-glucopyranosyl bromide and 2, 3, 4, 6-tetra-O-acetyl-α-D-galactopyranosyl bromide gave both seleno- and thioglycosides (equation 7). Analogous reactions of α-D-glucosyl bromides with triethylammonium salts of seleno acids of phosphorus have been reported[28]. Interesting transformations involving selenoglycosides have also been reported[29]. The first is anomerization of a selenoglucoside (equation 8) on heating in boiling xylene for 12 h, and the second is a selenono–selenolo rearrangement of a selenous ester to yield a selenoglycoside (equation 9).

$$(7)$$

$$R^1 = H, R^2 = OAc$$
$$R^1 = OAc, R^2 = H$$

$$(8)$$

$$(9)$$
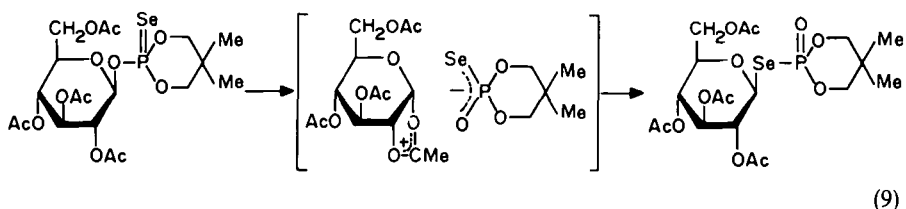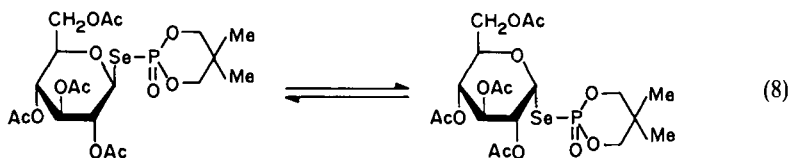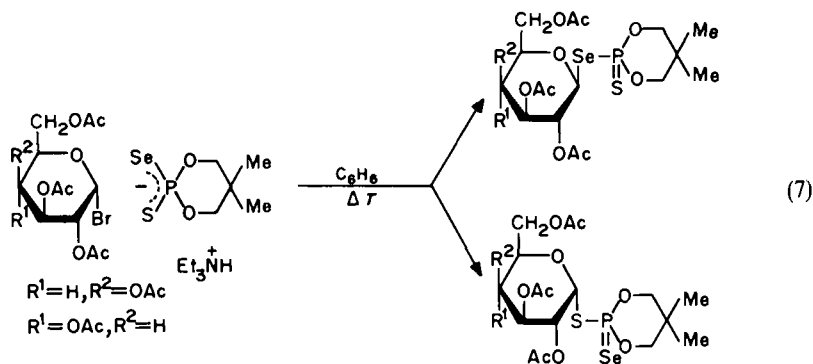
Zingaro's group reported the synthesis of selenoglucose esters of diorganyl groups, including those containing phosphorus, arsenic and antimony[12,30,31]. A 1-selenodimethylarsino derivative has been synthesized as depicted in equation 10. Dialkylphosphinous esters of β-seleno-D-glucose have been prepared through the reactions of symmetrical tetraalkyldiphosphines with 6-bis(2,3,4,6-tetra-O-benzoyl)-β-D-glucopyranosyl diselenide[32] (equation 11).

$$(10)$$

$$R = alkyl \tag{11}$$
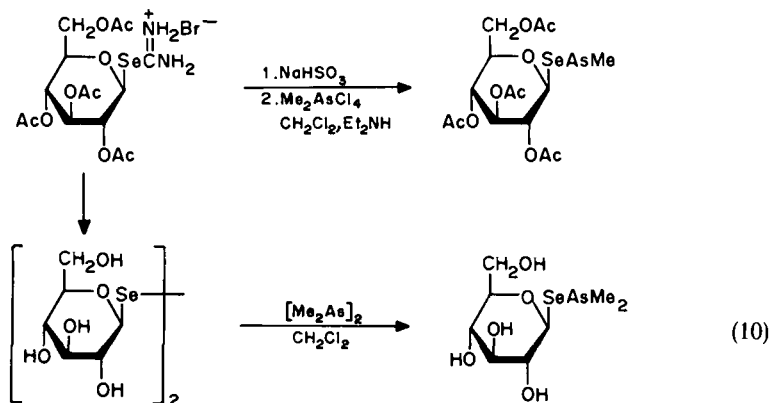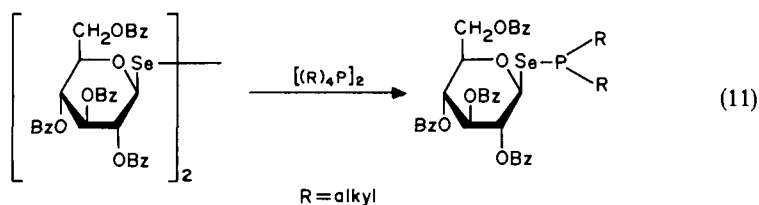
The antimony analogues are prepared by the use of an analogous series of reactions. However, the use of dimethylstibine halides in the two-phase water–dichloromethane reaction is obviated by the extreme hydrolytic instability of the antimony—halogen bond. Therefore, these derivatives were prepared exclusively by the addition of tetramethyl-stibine to the diselenide[33]. Zingaro[12] and Daniel and Zingaro[34] also reported the synthesis of dimethylarsinous acid esters of 1-seleno-D-galactose, as shown in equation 12.

$$R = H, Me \tag{12}$$
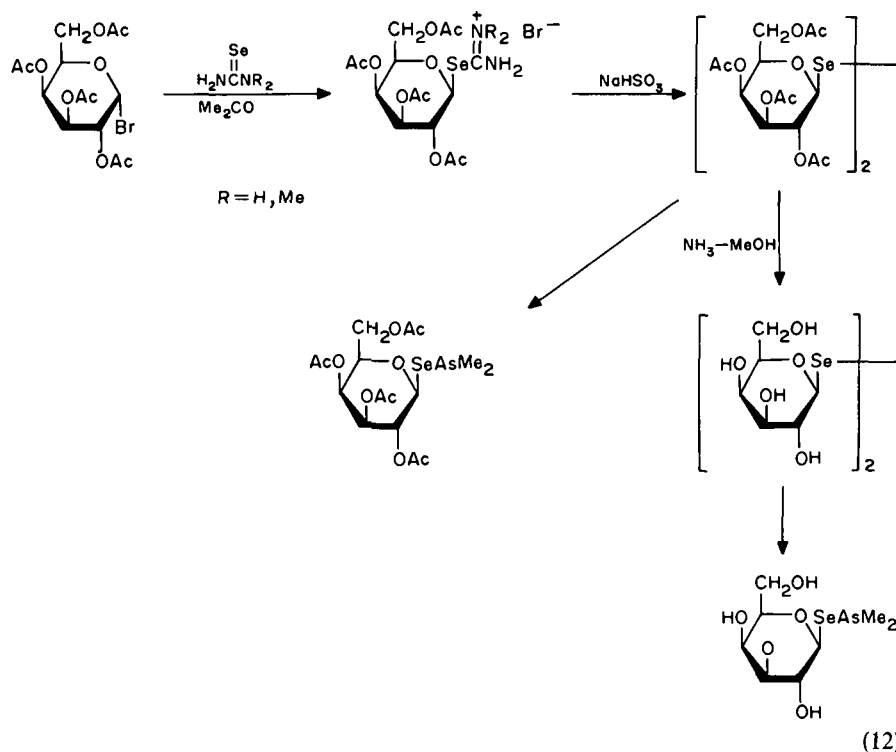
The synthesis of 1-selenodimethylarsin-2-acetamido-2-deoxy-α-D-glucopyranose has been reported by Chen and coworkers[35]. Reaction with dimethylselenourea is followed by reduction of the intermediate selenoureide with sodium hydrogen sulfite to the diselenide and subsequent condensation with dimethylarsine (equation 13). Interestingly, the coupling constant and chemical shift of the anomeric proton ($J_{1,2} = 4\,Hz$, $\delta = 5.38\,ppm$) of the intermediate diselenide is indicative of α-D-anomeric configuration, in contrast to a previous report of a similar reaction of 1-halogeno sugars with selenourea[16] and with the selenophenolate ion[25].

$$(13)$$
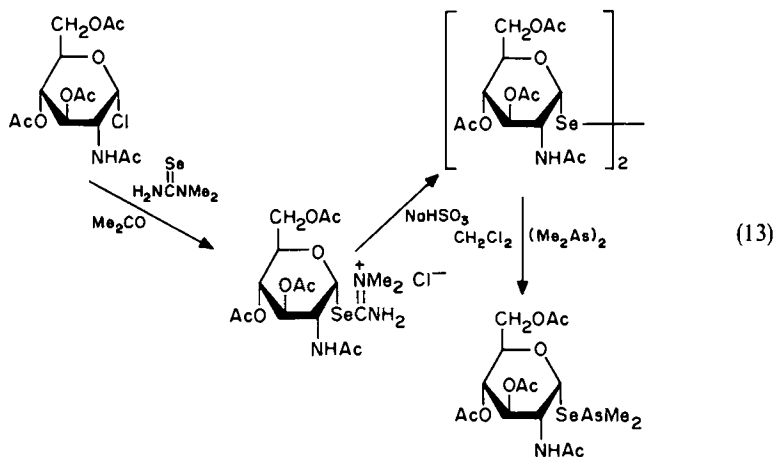
D-Glucosyl selenophosphates are readily synthesized[36] by the action of dicyclohexyl-ammonium O, O-di-*tert*-butyl phosphoroselenate with a glycosyl halide at low temperature, because of thermal instability of the synthesized product. Dealkylation of the intermediate was effected with boiling toluene or by the catalytic influence of trifluoroacetic acid (TFA) in benzene for 24 h at room temperature (equation 14).

$$(14)$$
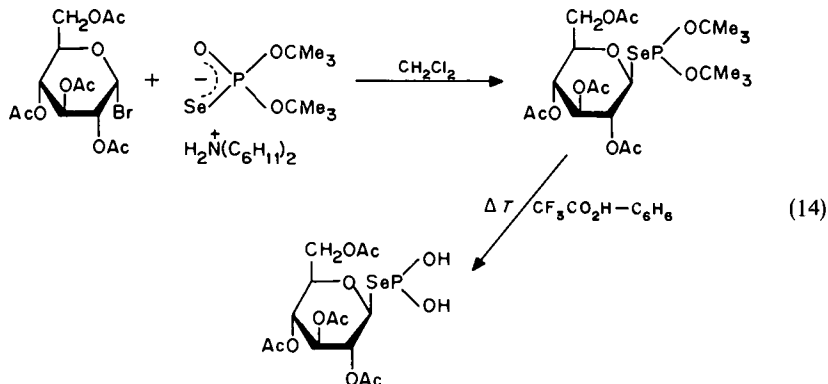
An interesting synthetic approach to 2′-deoxydisaccharides has been published by Jaurand and coworkers[37]. This reaction proceeds through stereoselective glycosyloxy-selenation of 3, 4, 6-tri-O-benzyl-D-glucal, followed by reductive removal of the phenyl-seleno group with tributyltin hydride, with excellent yields (90–95%) (equation 15).

Introduction of the arylseleno residue into the sugar moiety has been accomplished with phenylselenyl halides[38,39], using methods based on the Current and Sharpless[39] procedure of addition of ArSeX to olefins. Examples of ArSeX addition to olefins involving cyclization through reactions with internal nucleophiles have also been reported[40–45]. Another method of introduction of the arylseleno residue is the opening of the oxirane ring of sugars with PhSeH, which has been reported by many workers[46–52]. These methods of converting epoxides into phenyl selenides which were intermediates to unsaturated derivatives of sugars are based on the Sharpless and Lauer method of synthesis of allylic alcohols from epoxides[53–57].

$$(15)$$

$$R =$$
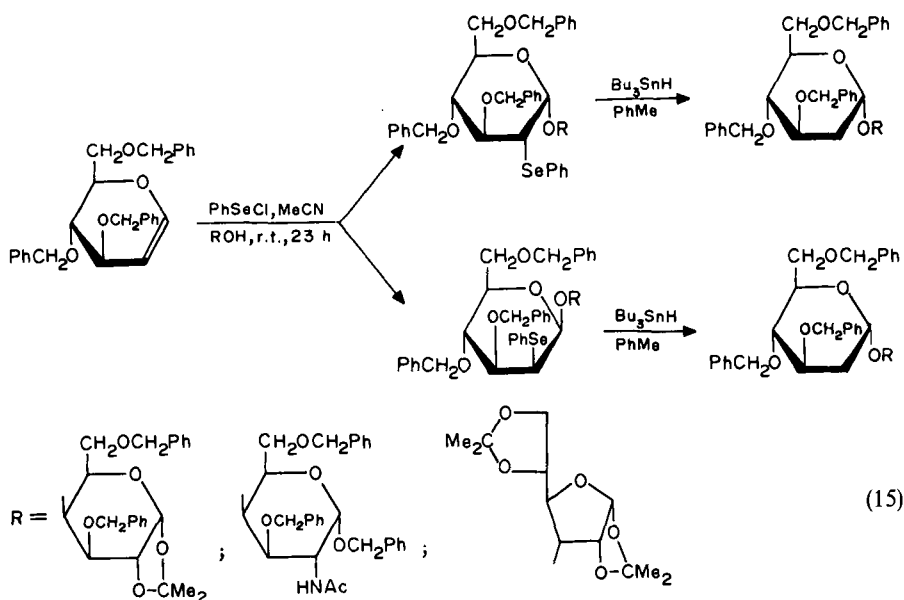
Paulsen and coworkers[58] successfully employed 2-methyl-2-selenoxo-1,3-benzothiazole (MSBT) the conversion of various anhydro sugars into unsaturated derivatives. The conversion proceeds in 5–10 h at room temperature with high yields and, usually, a high degree of purity of the product (equation 16). Under these conditions the 1,6-anhydro ring of 1,6:3,4- or 1,6:2,3-dianhydro sugars is unreactive and cleavage of only the 2,3- or 3,4-anhydro ring is observed[58]. This selectivity of the reaction constitutes a new entry to the rare class of unsaturated 1,6-anhydro sugars (equation 17).

$$(16)$$

$$R^I = H, Me$$

$$R = OCH_2Ph, N_3$$

$$(17)$$
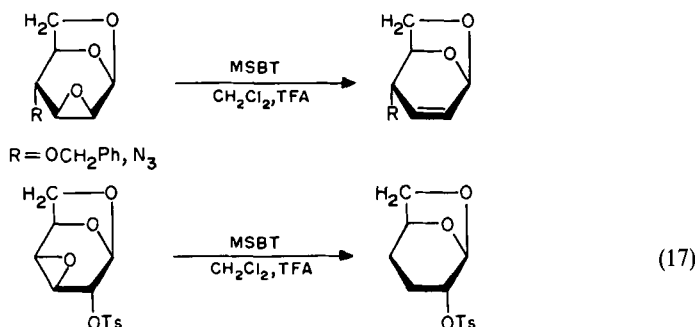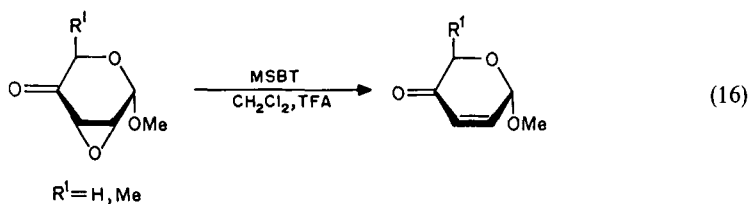
Another example is the reaction of phenylselenyl chloride with a sugar precursor to yield a cyclic intermediate from which the unsaturated derivative was obtained by oxidation with MCPBA (equation 18)[59].

(18)
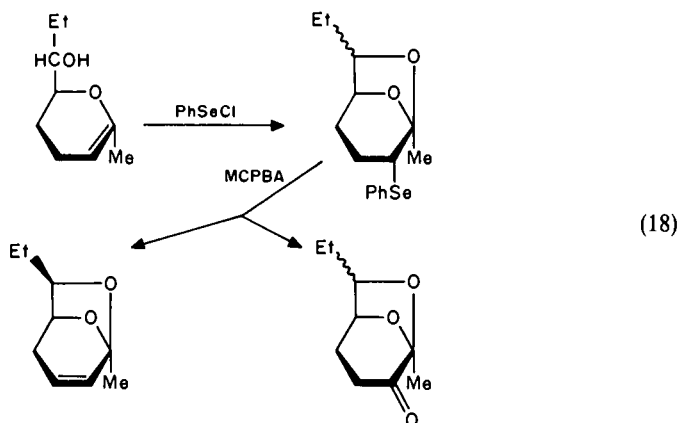
Another interesting application of organoselenium reagents is the formation of unsaturated sugars in the reaction employing the *N*-phenylselenophthalimide (N-PSP)–tributylphosphine system[60]. This reaction sequence proceeds by treatment of an appropriately protected methyl α-D-glucoside with N-PSP–Bu₃P in oxolane, followed by oxyselenation with hydrogen peroxide (equation 19).

(19)
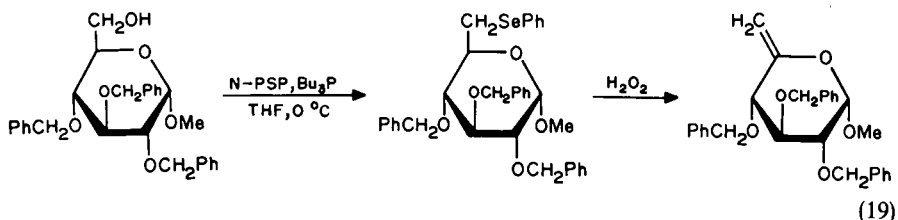
Cyclization of unsaturated sugars mediated by phenylselenyl chloride led exclusively to *C*-glycosyl derivatives[61]. This synthetic strategy involved stereoselective *C*-functionalization of the anomeric site of the carbohydrate using derivatives of an acyclic precursor, 6-*O*-benzyl-1,2-dideoxy-3,4-*O*-isopropylidene-D-ribohex-1-enitol (equation 20).

(20)
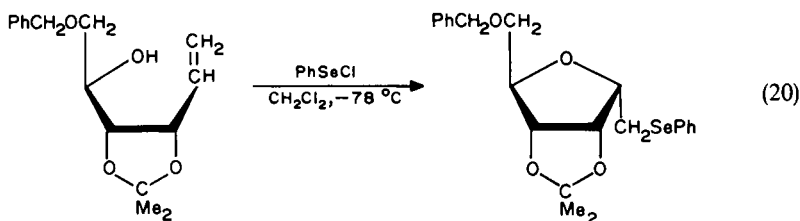
Another route to *C*-glycosyl derivatives through selenium intermediates involves the generation and trapping of the $C_{(1)}$ glucosyl radical with acrylic ester[62] (equation 21). This concept is based on the procedure of Geise and coworkers[63–66] of coupling glucosyl

bromide with acrylonitrile or with methyl acrylate with axial arrangement of the substituents in $C_{(1)}$.

(21)
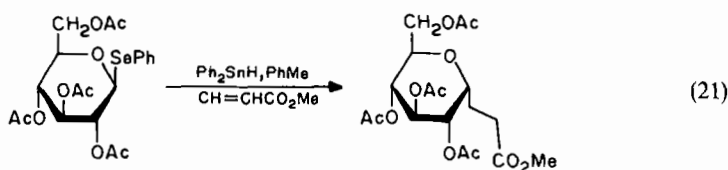
An interesting synthetic approach to 3-C-substituted glycals has been reported by Rollin and coworkers[67]. The reaction sequence starts from 3,4,6-tri-O-acetyl-D-glucal and proceeds by formation of a vinyl glycoside, which by thermal rearrangement forms a 3-C-substituted glycal (equation 22).

(22)
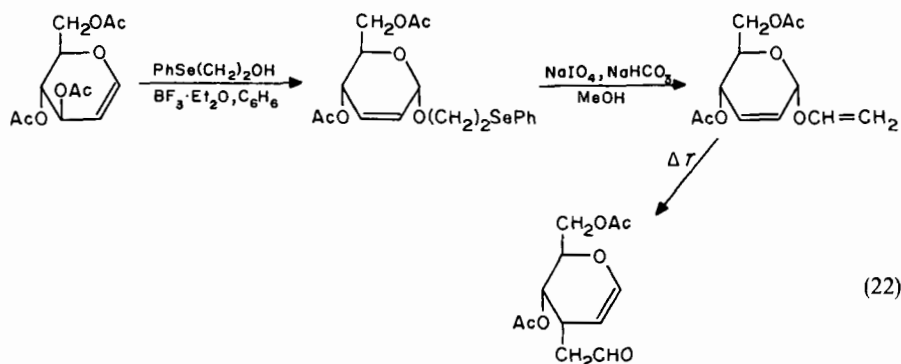
The previously mentioned phenylselenyl chloride-mediated cyclization of unsaturated sugars (equation 20) developed by Nicolaou and coworkers[41,68] and commonly called phenylselenolactonization has also been employed in the synthesis of butenolides[69] and is illustrated in equation 23.

$R = Me, Et, Ph$

(23)
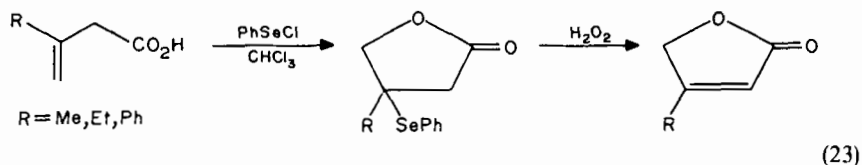
The phenylselenyl group in a sugar moiety may undergo the interesting photorearrangement[70] depicted in equation 24.

(24)
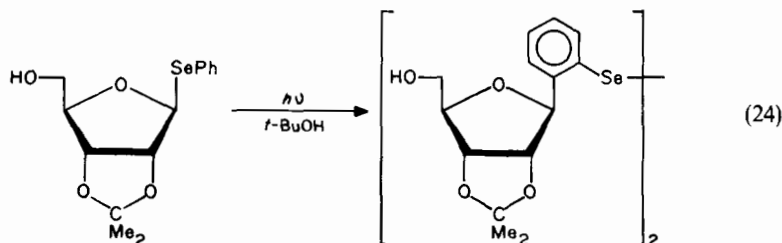
The very reactive o-nitrophenylselenyl group undergoes eliminative oxidation by treatment with hydrogen peroxide much more easily than other arylselenyl groups and is therefore employed in the synthesis of unsaturated sugars[71] (equation 25).

$$
\text{(25)}
$$
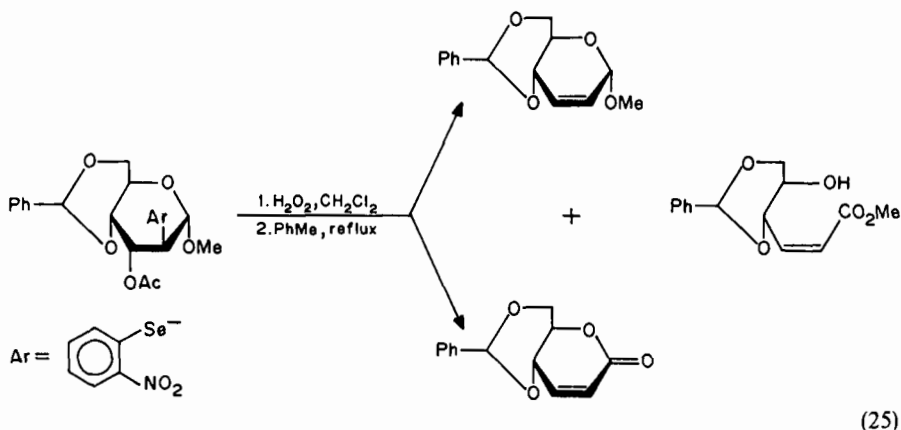
The reaction of nitro sugars with phenylselenyl bromide proceeds with the formation of an intermediate phenylseleno nitro derivative, which on oxidative elimination provides the corresponding saturated nitro sugar[72] (equation 26).

$$
\text{(26)}
$$
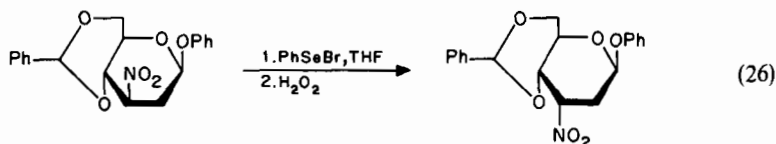
The o-nitrophenyl selenocyanate–tributylphosphine system developed by Grieco and coworkers[73,74] has been employed in the synthesis of the antibiotic calcimycin[74] (equation 27).

$$
\text{(27)}
$$

Calcimycin
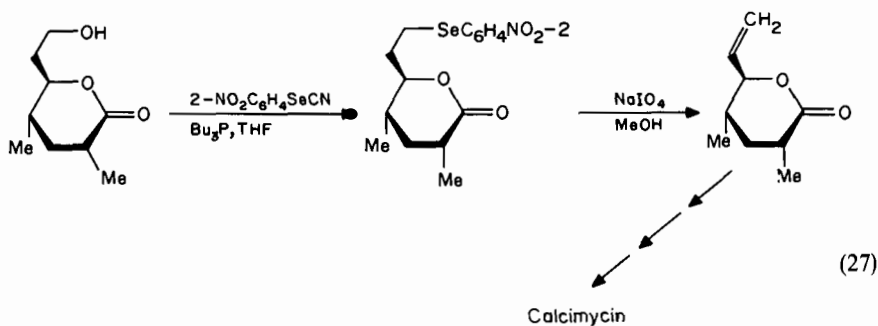
Sugar isoselenocyanates[11] were obtained in a reaction employing monosaccharide isocyanides[75]. This approach proceeds by treatment of appropriately protected isocyanides with elemental selenium under the catalytic influence of triethylamine (equation 28).

$$\text{(28)}$$

R¹=H, R²=R³=OAc

R¹=R³=OAc, R²=H

R¹=OAc, R²=H, R³=NHAc
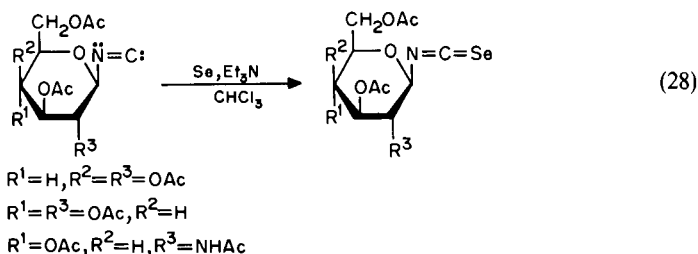
III. SUGARS WITH SELENIUM IN THE SUGAR RING

The introduction of sulfur[76], nitrogen[77,78] and phosphorus atoms[79-81] into furanose and pyranose rings of simple monosaccharides is successful and well known, but the introduction of selenium has usually failed or is very difficult[82-86]. Blumberg and coworkers[82] reported the first successful introduction of a selenium atom as the sugar ring heteroatom into L-arabinose, D-ribose, and D-xylose. The synthesis of benzyl 1,5-diseleno-L-arabinopyranoside is illustrated in equation 29.

$$\text{(29)}$$
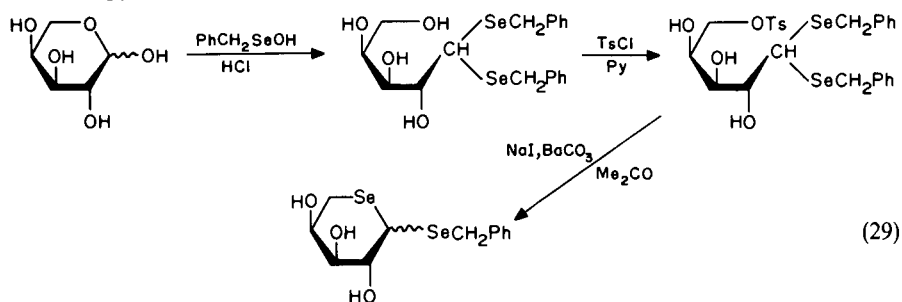
A similar approach has been employed for the synthesis of the benzyl 2,3,4-tri-O-acetyl-1,5-diseleno-D-xylopyranoside and benzyl 2,3,4-tri-O-benzyl-1,5-diseleno-D-xylopyranoside, using as the starting material 1,2-O-isopropylidene-5-O-p-tolylsulfonyl-α-D-xylofuranose (equation 30). Analogously, the benzyl 2,3,4-tri-O-acetyl-1,5-diseleno-D-ribopyranoside has been prepared from methyl 2,3-O-isopropylidene-5-O-p-toluenesulfonyl-β-D-ribofuranoside (equation 31).

$$\text{(30)}$$
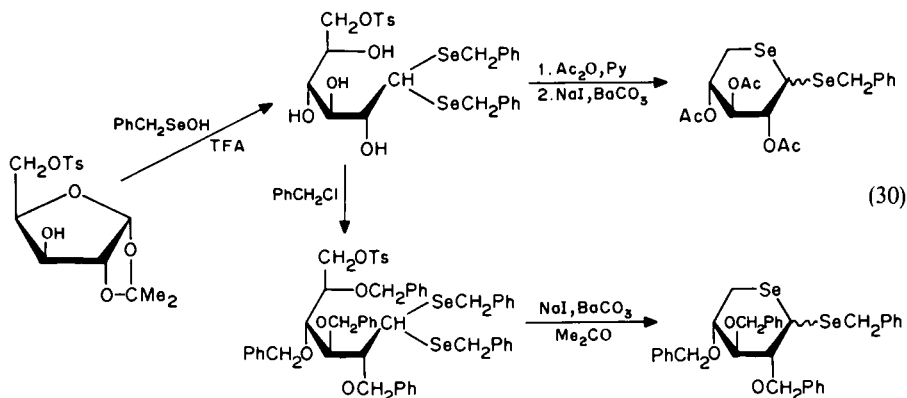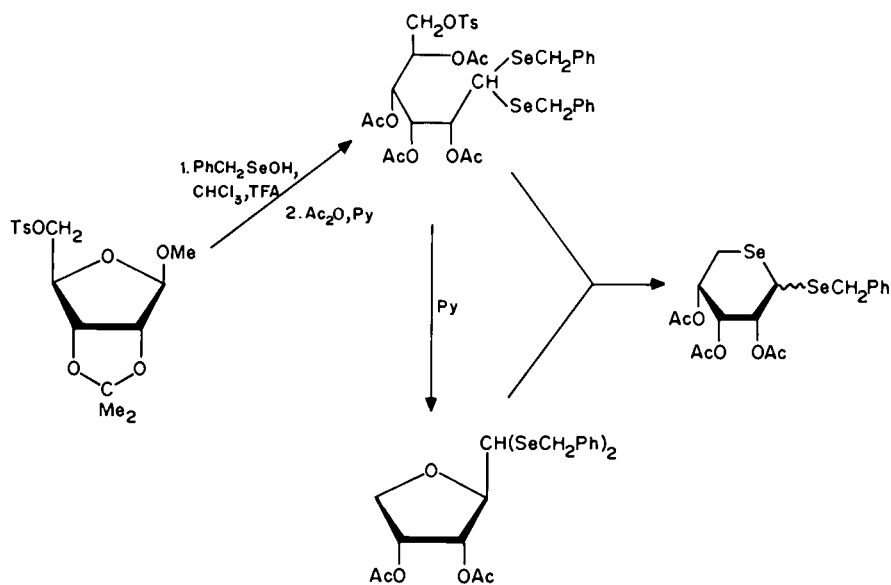
(31)

Interestingly, the glycosidic benzylseleno group from benzyl 2,3,4-tri-*O*-acetyl-1,5-diseleno-D-xylopyranoside can be smoothly removed with a mixture of mercury(II) acetate and acetic acid, whereas cleavage with mercury(II) chloride and cadmium carbonate in methanol give 2,3,4-tri-*O*-acetyl-5-selenobenzyl-5-seleno-D-xylose dimethyl acetal instead of the expected corresponding methyl glycoside (equation 32).
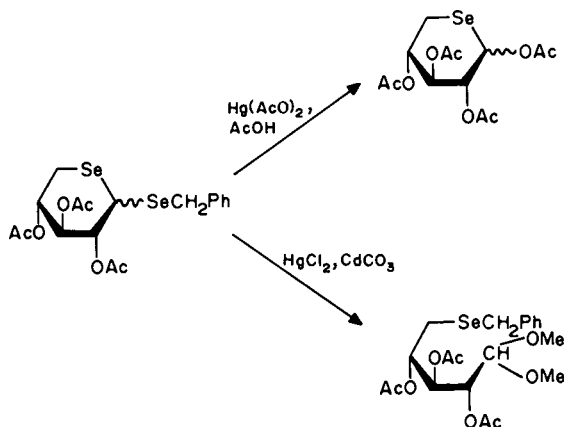
(32)

The introduction of a selenium atom into the furanose ring has been accomplished by application of the toluenesulfonyl derivative, on treatment with iodide ions in the presence of barium carbonate (equation 33). This is the first example of the synthesis of a selenoglycoside with a selenium atom in the furanose ring.

(33)
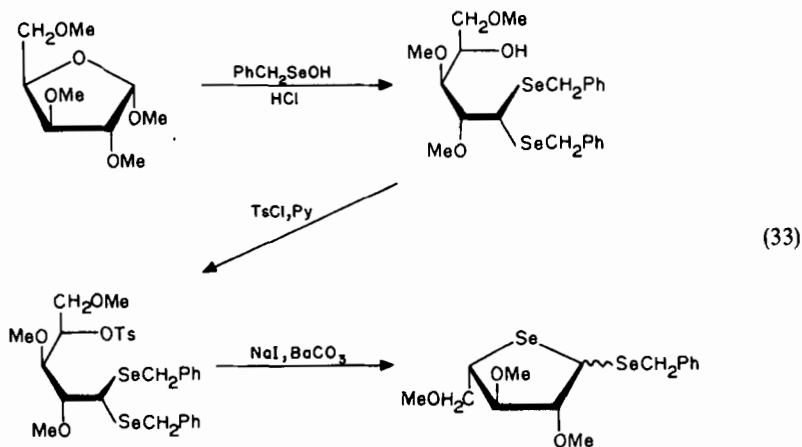
Van Es and Whistler[83] also reported a synthesis of the sodium salt of 5-deoxy-5-seleno-D-xylose, a convenient precursor to the 3,4-dihydroxy-2,3,4,5-tetrahydro-D-*threo*-2-selenophene-2-carbaldehyde dimethyl acetal (equation 34). The same acetal can also be obtained by removing the benzylseleno group from benzyl 2,3,4-tri-*O*-acetyl-1,5-diseleno-D-xylopyranose with mercury(II) acetate in acetic acid, followed by methanolysis with sodium methoxide, as reported by Blumberg and coworkers[82] (equation 35).

(34)

$$(35)$$
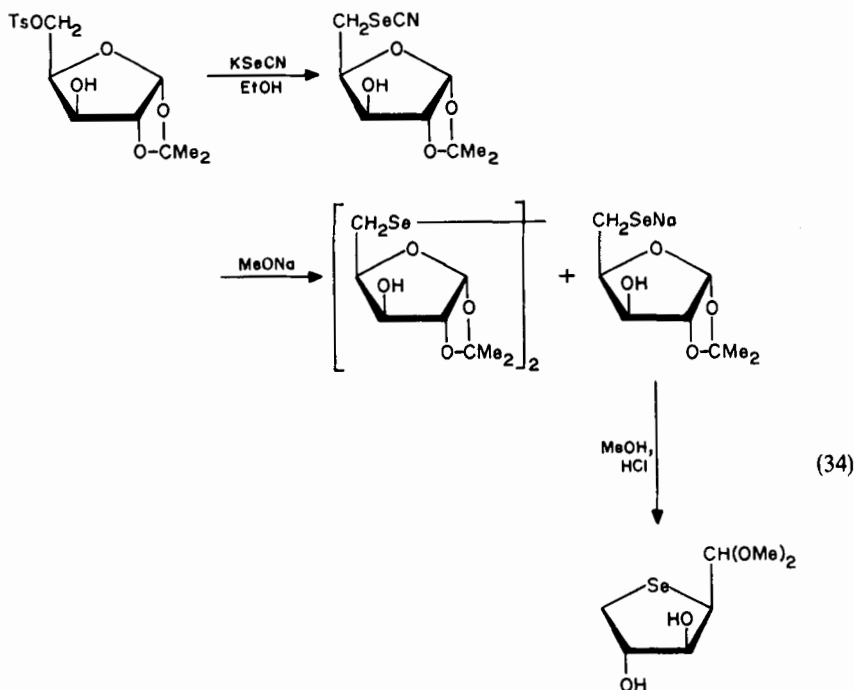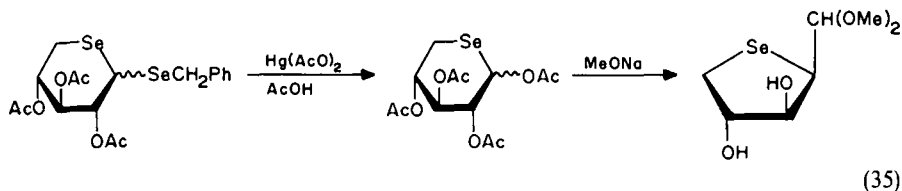
IV. SELENONUCLEOSIDE ANALOGS: SYNTHESIS AND REACTIONS

The antitumor and antiviral activity[87] of nucleoside analogs[88,89] is well known. These properties have prompted a major search for a new synthetic methodology for introducing sulfur or selenium into purine or pyrimidine bases. The first successful introduction of selenium into nucleosides was reported in 1960 by Jaffe and Mautner[90,91]. However, the 6-selenopurine-9-β-D-ribonucleoside was highly unstable[90] under neutral and basic conditions. Under the same conditions 6-selenoguanosine[92] has been found to be stable.

Townsend and Milne[92,93], Chu[94] and Shine and Chu[95] independently described the synthesis of 6-selenoguanosine (equation 36), which with methyl iodide under basic conditions afforded 6-methylselenoguanosine (equation 37). Similarly, 6-methyl-selenoinosine has been synthesized.

$$(36)$$

$$(37)$$
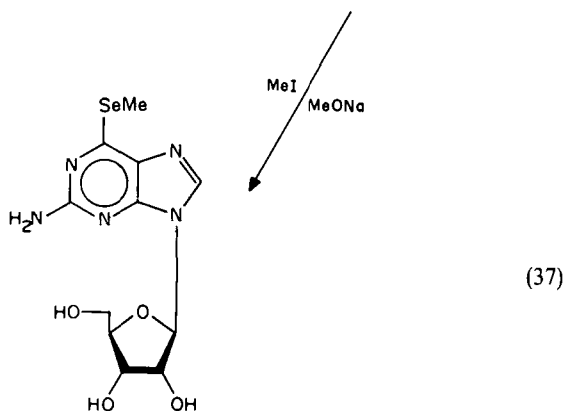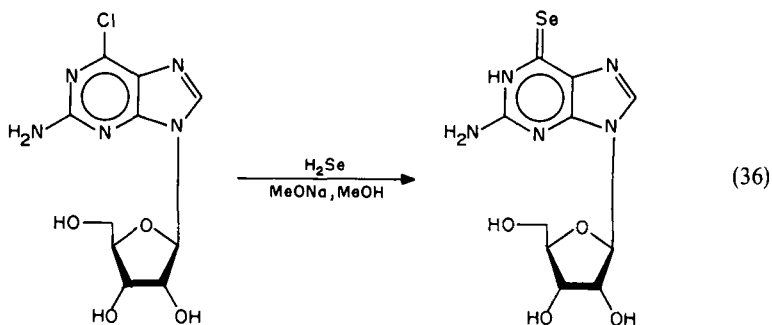
Milne and Townsend[96,97] and Chu and Davidson[98] independently reported the synthesis of both α-and β-anomers of 2'-deoxy-6-selenoguanosine (equation 38). However,

these derivatives are unstable in aqueous solution and decompose at room temperature after 24 h.

$$R = C_6H_4Me$$

(38)
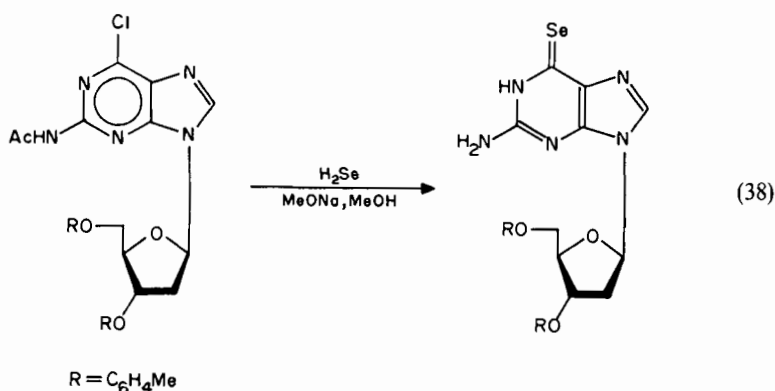
The synthesis of 7-selenoxo-3-(β-D-ribofuranosyl)pyrazolo[4, 3-d]pyrimidine (selenoformicin B) has also been reported by Milne and Townsend[99]. The synthesis involves a simple nucleophilic displacement of the chlorine with selenourea in ethanol at reflux temperature (equation 39).

$$R = ribofuranosyl$$

(39)
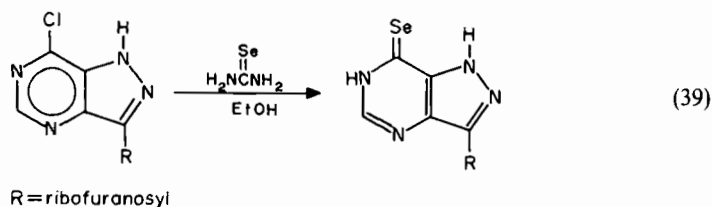
Wise and Townsend[100,101] also reported the synthesis of 2- and 4-selenouridine. The synthetic sequence begins with silylation of 2-selenouracil, followed by condensation with 2, 3, 5-tri-O-benzoyl-1-O-acetyl-α-D-ribofuranose. Deprotection of the condensation product with sodium methoxide in methanol produced 2-selenouridine in 30% yield (equation 40). The synthetic approach to 4-selenouridine starts from 4-chloro-1-(2, 3, 5-tri-O-benzoyl-β-D-ribofuranosyl)pyrimidin-2-one, which on treatment with selenourea in methanol, and subsequent debenzoylation, affords 4-selenouridine. However, the seleno group in both 2-seleno- and 4-selenouridine is very labile[100,101].

(40)
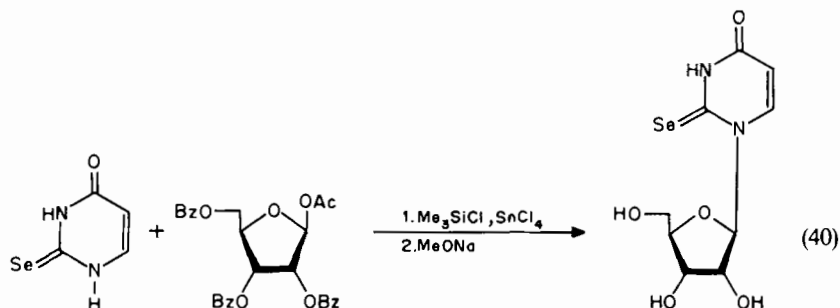
Chu and coworkers[102] reported the synthesis of some 8-substituted cyclic selenonucleo-
tides by treatment of 8-bromoadenosine 3′,5′-cyclic monophosphate with sodium
hydrogen selenide in refluxing methanol and subsequent alkylation (equation 41).

$$R = Me, Et, CH_2Ph$$
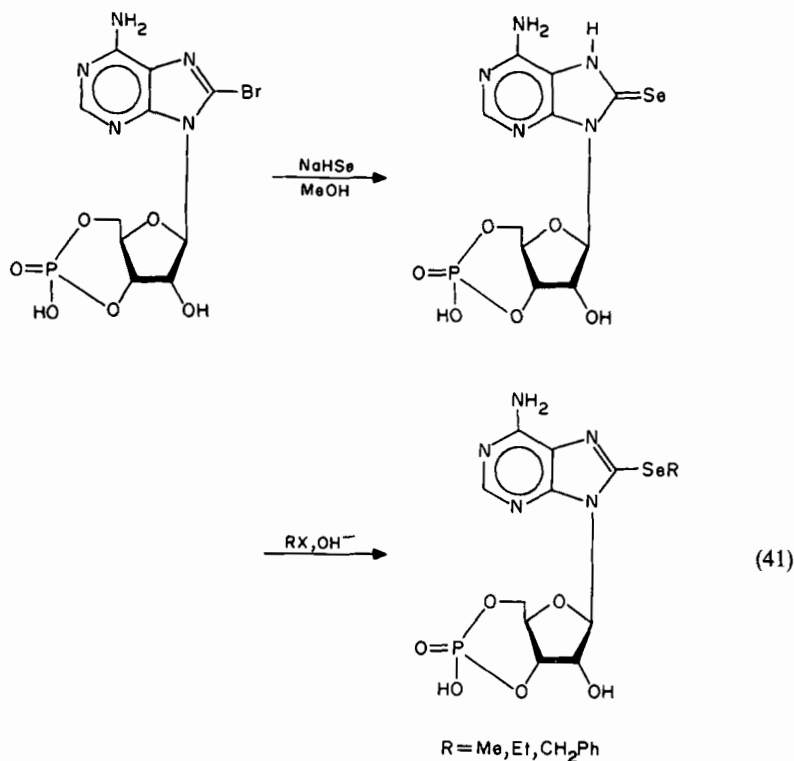
An interesting approach has been developed for the synthesis of 6-selenoxo-9-(β-D-
ribofuranosyl)purine 3′,5′-cyclic phosphate[103] using as a starting material the 6-amino
precursor. The proposed mechanism of this displacement involves amine to imine,
tautomerization, followed by addition of hydrogen selenide and then elimination of
ammonia with formation of the nucleotide (equation 42).

$$\text{(42)}$$
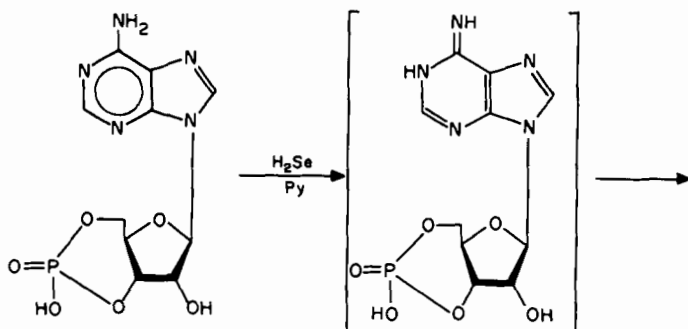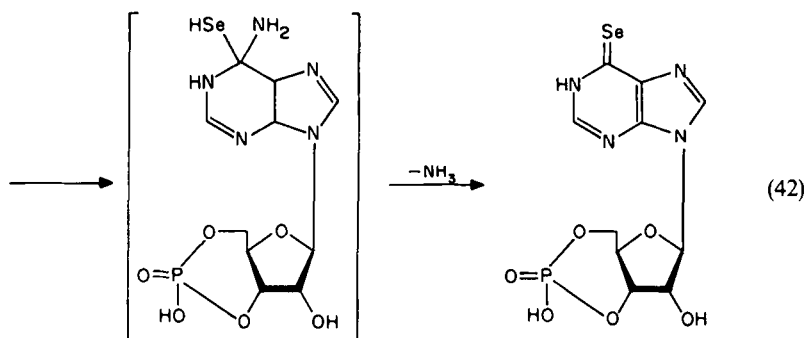
Alkylation, chlorination and seleno–thiono conversion have also been reported (equation 43).

$$R = Me, CH_2C_6H_4NO_2\text{-}p$$

$$\text{(43)}$$
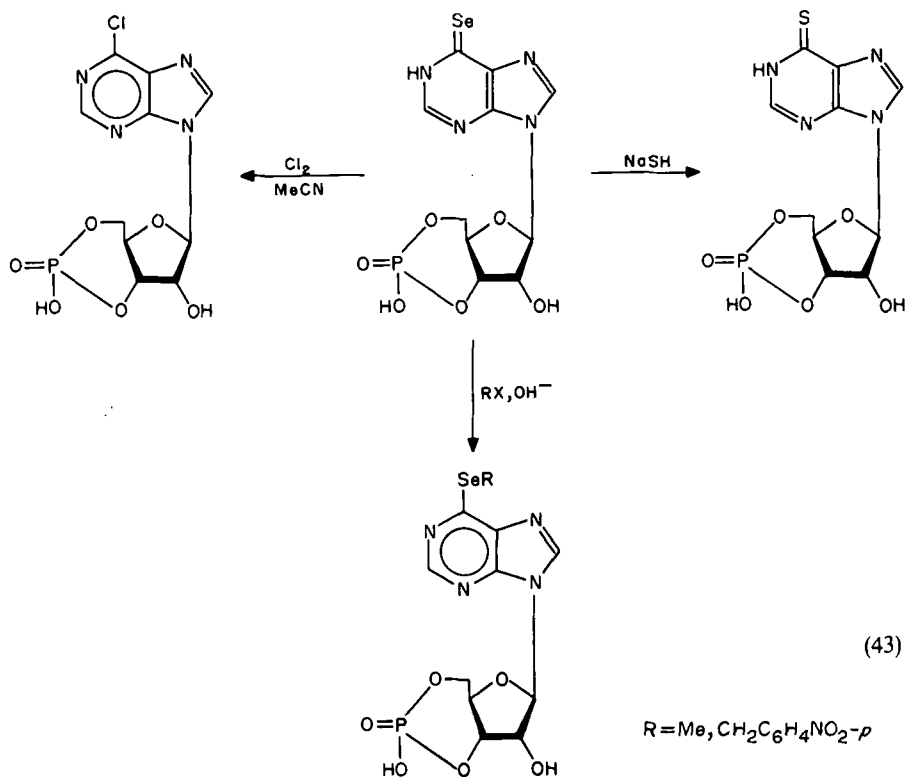
8-Seleno derivatives of guanosine 3',5'-cyclic phosphate (cGMP) have also been prepared[104] using as a starting material cGMP, which by direct bromination gave 8-bromo-cGMP. Treatment with selenourea gave the isoselenouronium hydrobromide intermediate, which on alkylation yielded the required nucleotides (equation 44). 8-Substituted selenoguanosine 5'-monophosphates and selenoguanosines were prepared similarly[104].

$$R = Me, Et, Pr, i\text{-}Pr, CH_2Ph,$$
$$CH_2C_6H_4NO_2\text{-}p$$

(44)
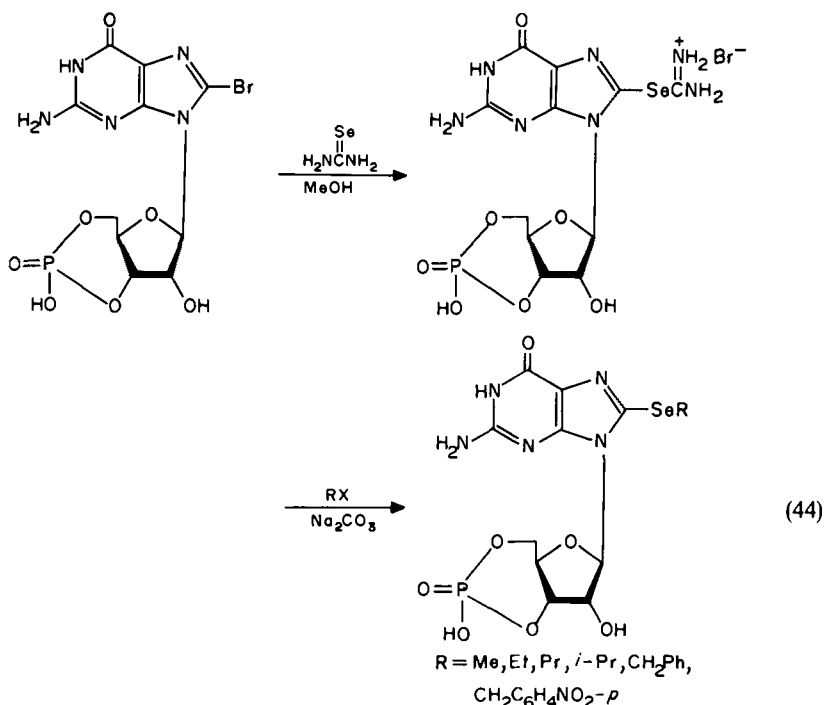
Chu and coworkers[105] also synthesized and tested a series of 6-substituted 6-selenopurine arabinosides, employing the methodology previously described[99-104]. In a subsequent report[106] they also described a new and efficient synthesis of 6-seleno-substituted nucleosides, nucleotides and cyclic nucleotides in 22–75% yields by displacement of the amino group in the heterocycle with hydrogen selenide in aqueous pyridine (at 68 °C in a sealed tube). This modification requires no prior protection of the sugar moiety and also gives higher yields than conventional procedures.

Milne and Townsend[107] have accomplished the synthesis of 4-seleno-5-cyano-7-(β-D-ribofuranosyl)pyrrolo[2,3-d]pyrimidines as shown in equation 45, and 7-(β-D-ribofuranosyl)pyrrolo[2,3-d]pyrimidin-4-selone[108] has been prepared similarly.

$$R = Me, CH_2CH = CH_2,$$
$$CH_2C_6H_4NO_2\text{-}p$$

(45)
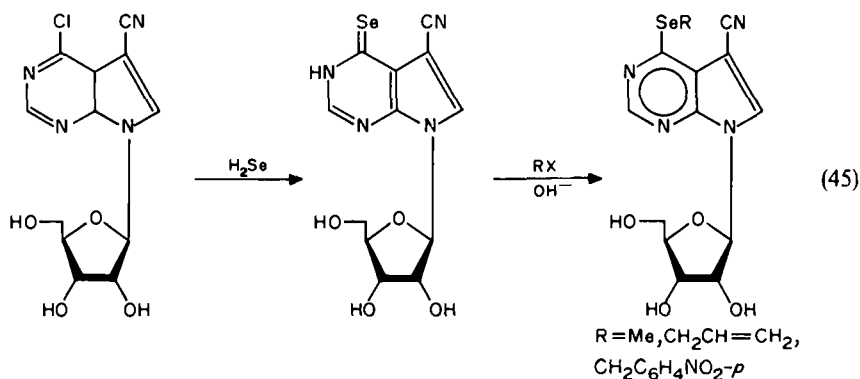
Interesting results on the reactivity of the 4-substituted seleno group and the 5-cyano group in both nucleosides towards nucleophilic reagents such as hydrazine and hydroxylamine have been reported[107] (equation 46). The configuration (Z or E) of the products has not been established.

(46)
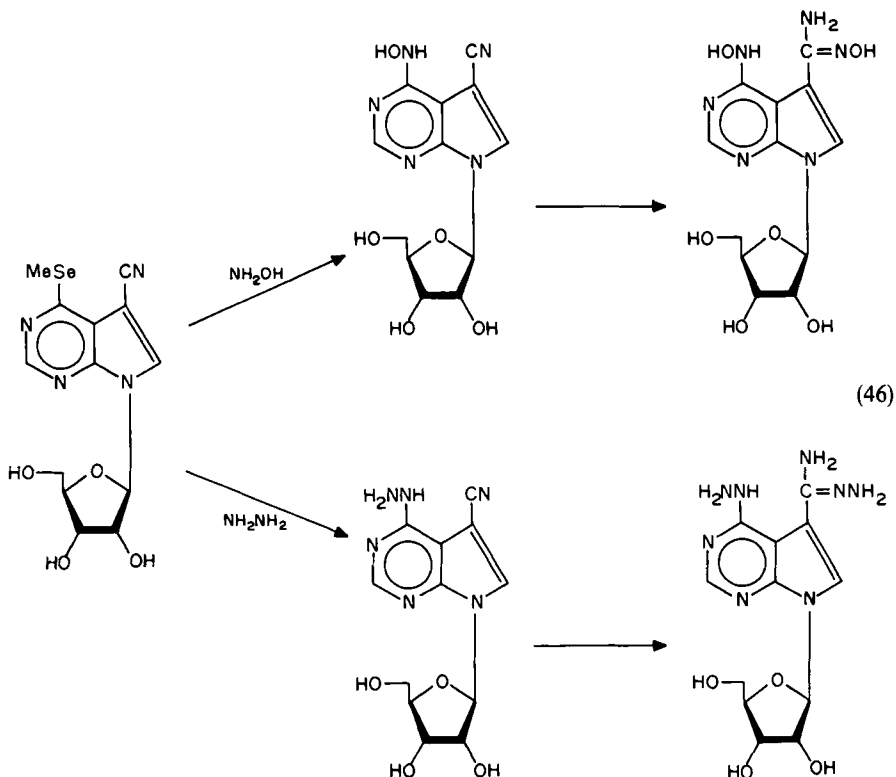
An interesting report on the effects of exocyclic atoms (O, S and Se) in nucleosides on the chemical shifts of the anomeric proton in the sugar moieties and protons at $C_{(5)}$ and $C_{(6)}$ positions of the hetero ring has been published by Wise and Townsend[109]. They also reported[110] the first synthesis of a selenium-bridged cyclonucleoside, Se,2'-cyclo-2-selenocytidine, using 2-selenocytosine as a starting material.

The synthesis of the first cyclic selenopurine uncleotide was also reported by Wise and coworkers[111]. Treatment of 8-bromoadenosine with selenourea, followed by subsequent reaction with 2-acetoxyisobutyryl chloride(AIBC), furnished Se[8],2'-cyclo-8-seleno-β-D-arabinofuranosyladenine in 54% yield (equation 47).

Tributylphosphine combined with diphenyl diselenide in acetonitrile has been reported[112] to yield new types of selenonucleotides, e.g. 3'-O-acetylthymidine-Se-phenyl 5'-phosphoroselenoate is obtained from the monopyridinium salt of 3'-acetylthymidine 5'-phosphate (equation 48).

Treatment of thymidine 5'-phosphate with bis(trimethylsilyl)acetamide (BSA) in dimethylformamide solution with selenium powder afforded a mixture of two products (equation 49), thymidine 5'-phosphoroselenoate and its autooxidized product having an Se—Se bond. Alkylation of this mixture afforded Se-ethylthymidine 5'-phosphoroselenoate.

(47)

(48)

(49)
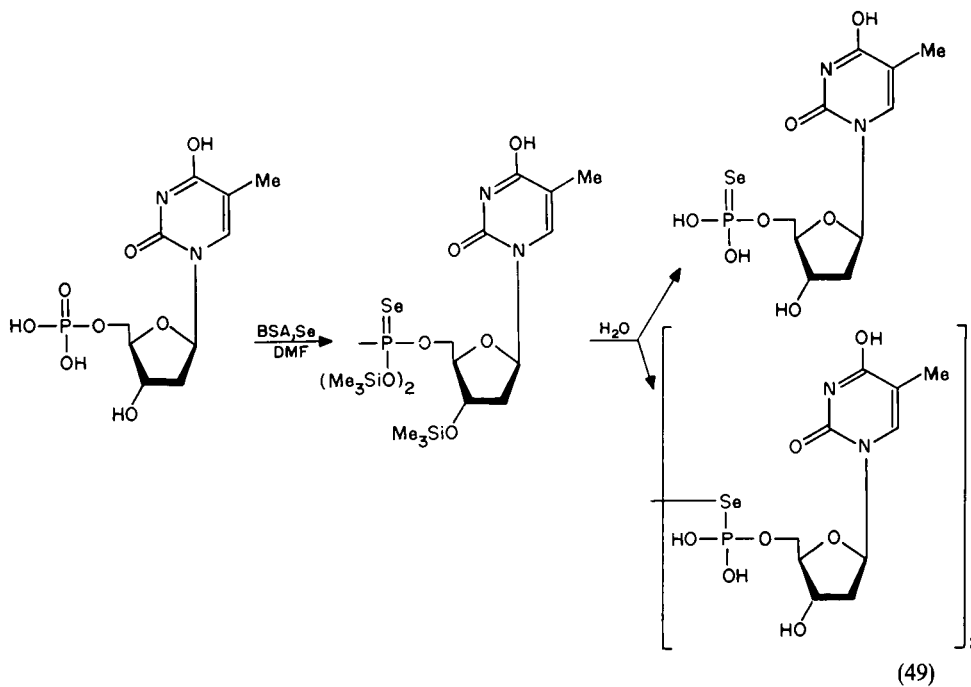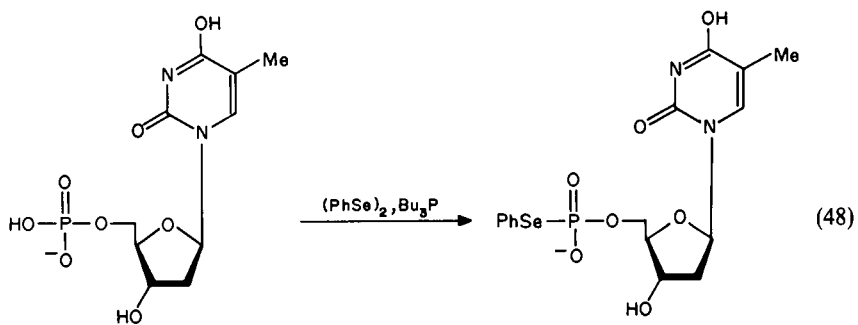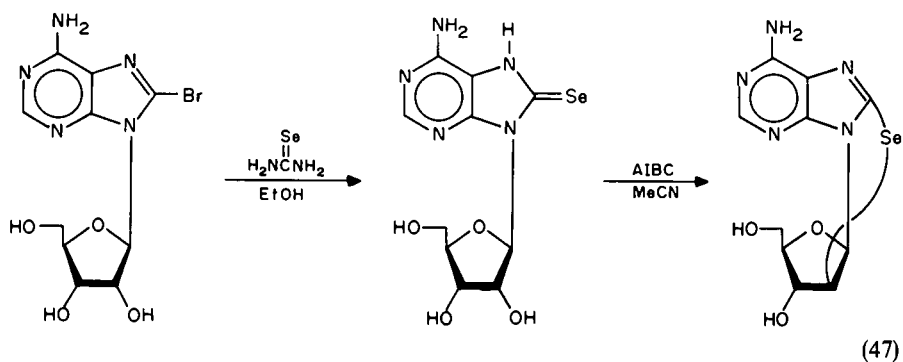
Takaku and coworkers[113] reported the synthesis of 5'-Se-(2-nitrophenyl)-5'-selenoxyadenosine as an excellent precursor to 9-(5'-deoxy-β-D-erythro-pent-4-enofuranosyl)adenine (equation 50).

$$2\text{-}O_2NC_6H_4SeCN, Bu_3P$$
Py

$$H_2O_2$$

$$Et_3N, Py$$

(50)
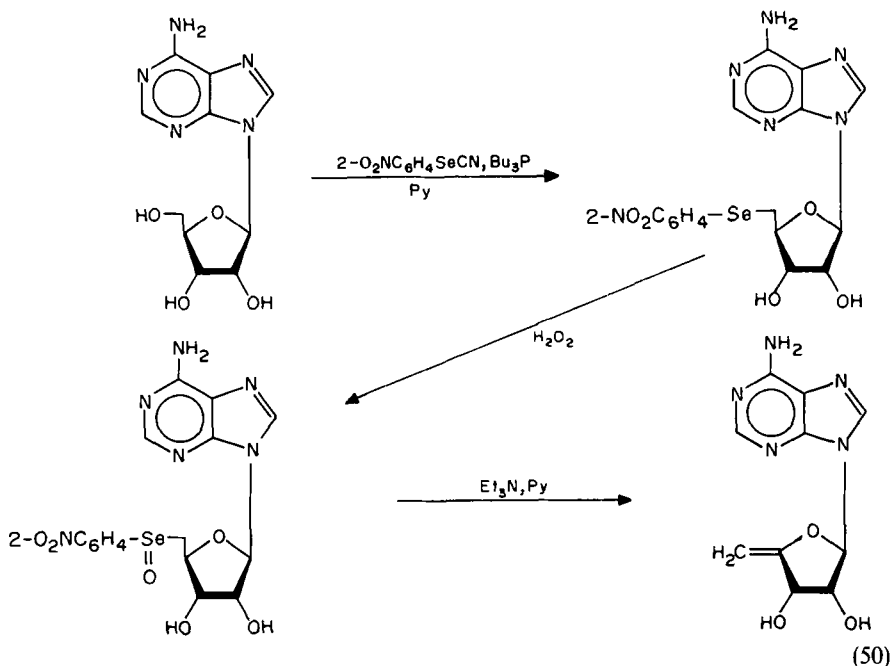
Treatment of adenosine with 2-nitrophenyl selenocyanate and tributylphosphine gave an intermediate selenide, which on oxidation, followed by treatment with triethylamine in pyridine, yielded an unsaturated nucleoside. Triethylamine promotes *syn* elimination of the selenoxide group and hydrogen at the 4'-position, similarly to the results previously reported by Zylber and coworkers[114]. However, a recent report by Boullais and coworkers[115] showed that triethylamine in dimethyl sulfoxide promotes elimination effectively and with higher yields. Alternatively, the elimination of the selenoxide group with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in toluene solution is also very effective (equation 51).

$$DBu, PhMe$$

(51)
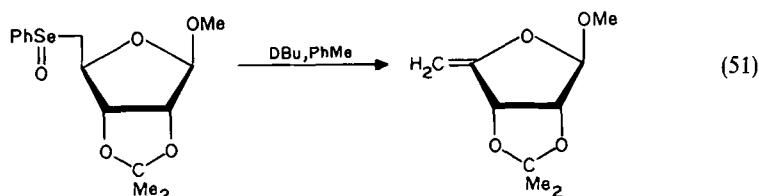
The first introduction of selenazole as a base in nucleosides was reported in 1983 by Srivastava and Robins[116]. The synthetic approach started with 2,3,5-tri-O-benzoyl-β-D-ribofuranosyl-1-carbonitrile, which on treatment with hydrogen selenide in the presence of 4-(dimethylamino)pyridine as catalyst afforded the intermediate selenoamide. Subsequent condensation with ethyl bromopyruvate provided an anomeric mixture of ethyl 2-(2,3,5-tri-O-benzoyl-D-ribofuranosyl)selenazole-4-carboxylate, which after separation

and deprotection afforded selenazofurin in moderate yield (equation 52). Two novel convenient syntheses[117,118] of selenazofurin have been published recently (equation 53).
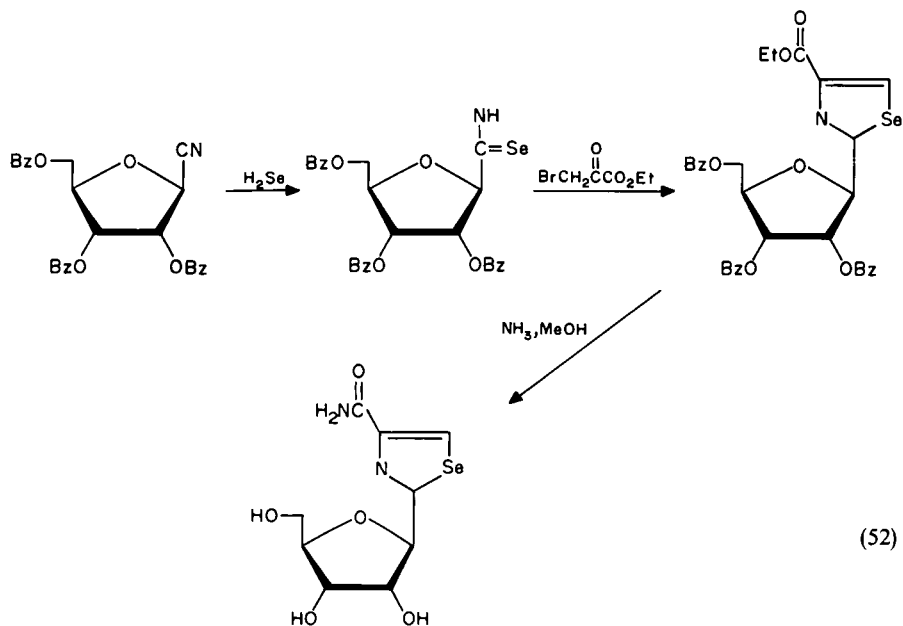
(52)
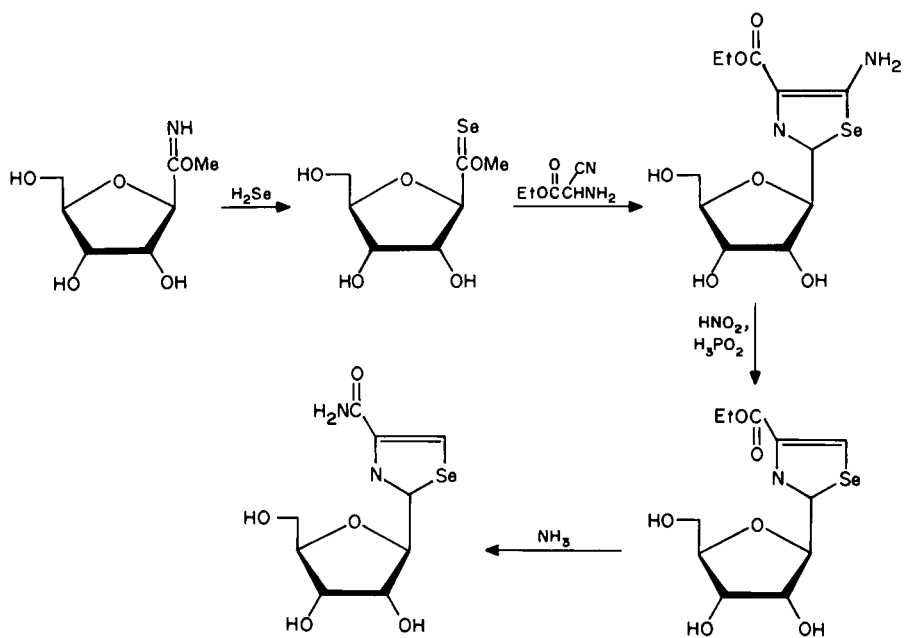
(53)

Pyrazolo[4, 3-*d*]pyrimidine nucleosides continue to be of considerable interest from both chemical and biological points of view. Two representatives of this class have recently been synthesized, 1-methyl-β-D-ribofuranosylpyrazolo[4, 3-*d*]pyrimidine-7(6*H*)-selone[119] and 1-β-D-ribofuranosylpyrazolo[3, 4-*d*]pyrimidine-4(5*H*)-selone[120]. The synthetic approaches are illustrated in equation 54.

$$(54)$$
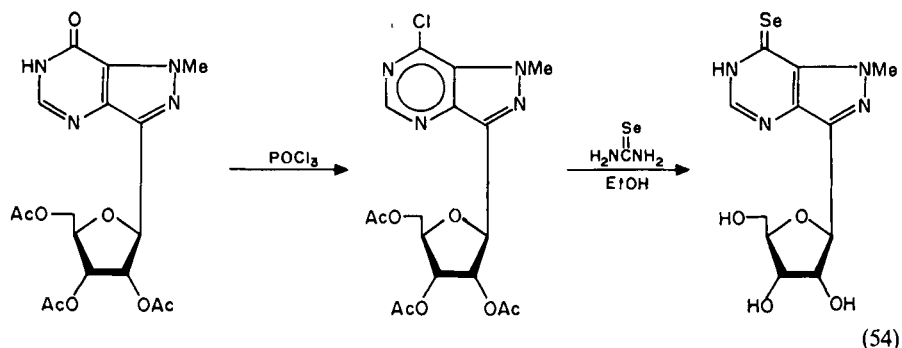
Schinazi and coworkers[121] reported the synthesis of several 5-phenylselenyl derivatives of pyrimidine nucleosides, by electrophilic addition of phenylselenyl chloride to the nucleoside under basic conditions (equation 55).
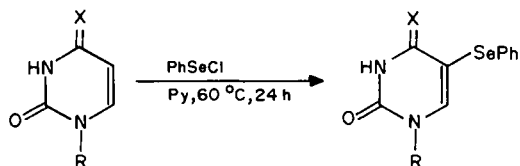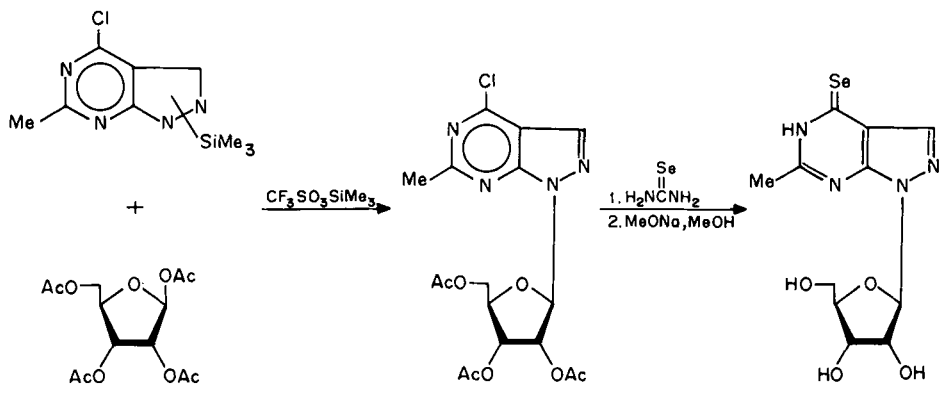
$$(55)$$

X = O, R = ribosyl
X = NH, R = ribosyl
X = O, R = 2-deoxyribosyl
X = O, R = arabinosyl
X = NH, R = arabinosyl

V. TELLUROCARBOHYDRATES AND ORGANOTELLURIUM
REAGENTS IN CARBOHYDRATE CHEMISTRY

Chemical transformations involving tellurium were, until recently, very rare. The explosive development of organoselenium chemistry has called the attention to the potential of tellurium reagents and a number of interesting transformations based on tellurium-containing species are now known.

Several review articles[122,123] and books[124-126] about many concepts of tellurium chemistry[127,128] have been published. However, no study devoted to the synthesis of tellurocarbohydrates has been published until a recent paper by Czyżewska-Chlebny and Michalska[129] appeared. This route involves condensation of a triethylammonium 2-tellurido-2-oxo-5,5-dimethyl-1,3,2-dioxaphosphorinane salt with 2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl bromide (equation 56). This is the first known synthesis of a tellurocarbohydrate, through a tellurophosphorus reagent.

(56)
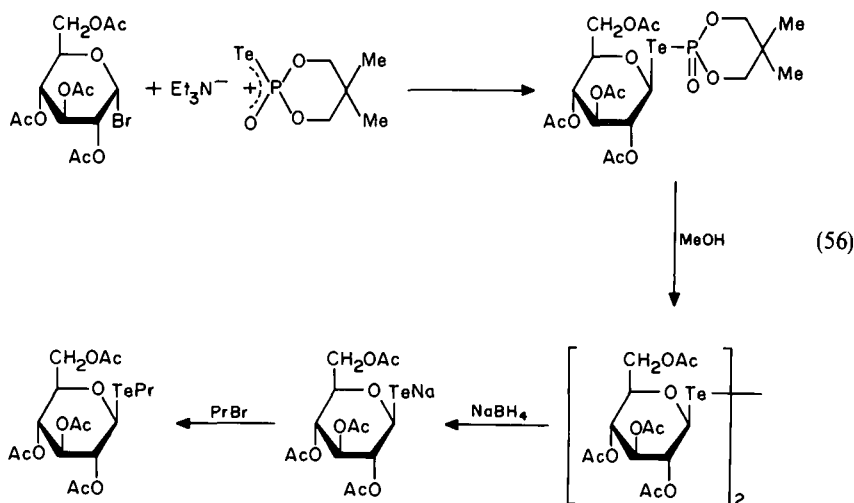
Other examples of synthetic applications of organotellurium reagents in carbohydrate chemistry have also been reported[130-132]. For example, bis(4-methoxyphenyl) telluroxide has been used as a convenient reagent for the conversion of thiocarbonyl derivatives of sugars into the corresponding oxo derivatives[130] in good yields (equations 57 and 58).

Carbohydrate alcohols can be converted into the corresponding benzyl ethers by reaction with the Vilsmeier salt, chloro(phenylmethylene)dimethylammonium chloride, giving the imidate salts, followed by reduction with sodium hydrogen telluride[131,132]. The

(57)

$$p\text{-}Ar_2TeO \tag{58}$$
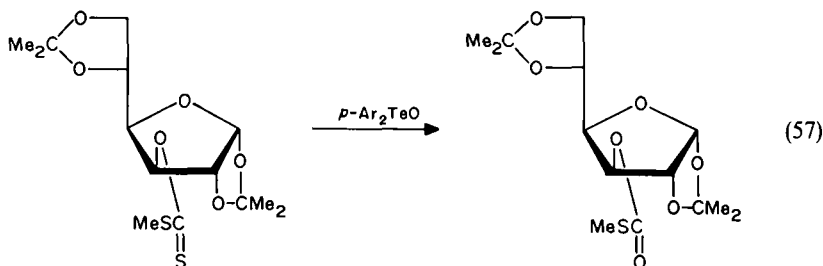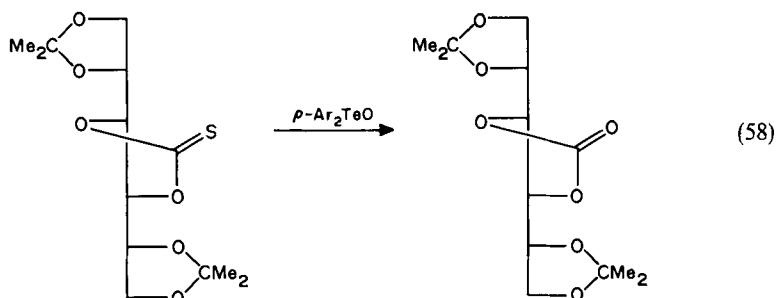
reaction proceeds under mild conditions, probably through the tellurobenzoate and hydrogen atom transfer (equation 59).

$$NaHTe \qquad -Te \quad H\ atom\ transfer \tag{59}$$
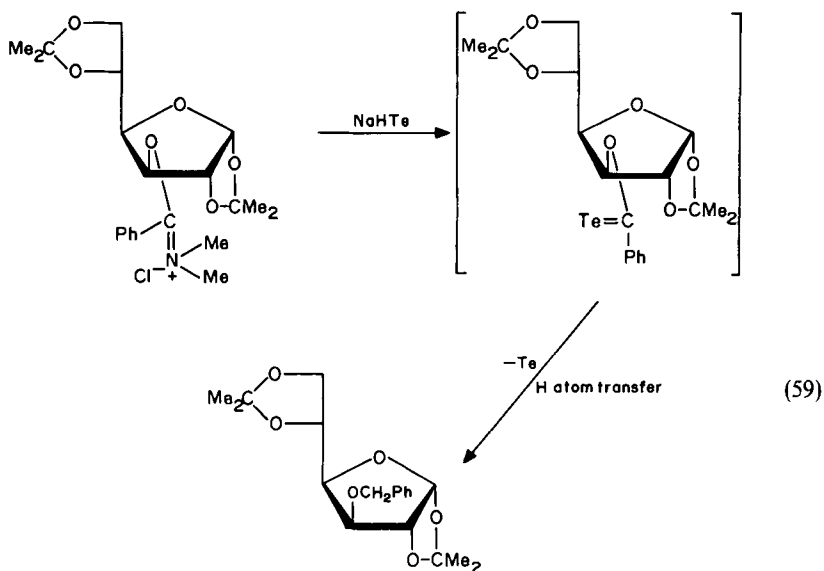
VI. BIOLOGICAL ACTIVITY OF SELENONUCLEOSIDE ANALOGS AND SELENO SUGARS

The biological activity of seleno-organic derivatives[90] in bioorganic chemistry has been known for a long time, especially the antitumor activity of selenonucleoside analogs[90,91]. For example, 6-selenoguanine and 6-thioguanine, which are good antitumor agents, prompted the synthesis of 6-selenoguanosine[92] as a potentially much more effective antitumor agent. Further, a comparative investigation showed that selenoguanine and selenoguanosine inhibit the growth of Sarcoma 180 ascites cells more effectively than the corresponding thionucleosides. Interestingly, β-2'-deoxy-6-selenoguanosine was found to have an activity approximately equal to that of the 6-thio congener, whereas the α-anomer was much less active than the corresponding α-2'-deoxy-6-thioguanosine. This important observation was confirmed by Milne and Townsend[96,97], who also observed that alkylation of both anomers at the exocyclic selenium atom appeared to cause a marked

decrease in antitumor activity. However, 6-selenoguanosine and 6-alkylselenoguanosine derivatives were found to be the most active compounds in these groups.

It is noteworthy[133] that 6-methylselenoguanosine is completely inactive as an inhibitor, whereas the 6-selenoguanosine–platinum(II) complex[134] complex exhibits antitumor activity against L1210 cells in mice and *in vitro* systems. Interestingly, the 8-substituted seleno cyclic GMP derivatives[102,103,105] showed some antitumor activity against murine leukemic cells (LS178Y) *in vitro* and *in vivo*.

Cyclic nucleotides[102] are more active than corresponding nucleosides. The previously mentioned analog of 8-isoselenouronium-cGMP hydrobromide is a very active inhibitor (98% inhibition)[5], and this illustrates its potential as an antitumor agent. Cytotoxicity of 6-selenopurine arabinoside and 6-alkylseleno derivatives has also been reported, but the cytotoxic effect of the above analogs was below 50% inhibition. Interestingly, the *in vitro* antitumor activity of 2-β-D-ribofuranosylselenazole 4-carboxamide[116,117] (selenazofurin) and its 5'-phosphate in comparison with the corresponding thiazole congeners were found to be more active towards P388 and L1210 cells in culture and also effective against Lewis lung carcinoma in mice.

Among seleno derivatives of sugars, dimethylarsinous acid esters[12] of glucose[31] and galactose[30-34] were found to display carcinostatic activity[12,30,31,34,135] *in vivo* against mice leukemias (P388 and L1210 test systems).

VII. CONCLUSIONS

The synthesis of selenium intermediates and seleno sugars and the study of their transformations afford an heuristic approach for a new synthetic methodology not only in carbohydrate chemistry but also in general synthetic organic chemistry. The recent use of organoselenium and organotellurium reagents has become a key factor in these fascinating fields. Selenium derivatives of carbohydrates (selenoglycosides, selenophenyl intermediates) may now be considered important functional groups and very good precursors for the synthesis of various groups of sugars. The variety of methods for the functionalization of selenium intermediates of sugar molecules provides a number of attractive synthetic routes to various classes of compounds of particular interest.

In the near future, further developments concerning new procedures and reagents and also discoveries of new aspects of the reactivity of selenium and tellurium intermediates of carbohydrates and nucleosides may be expected. For these reasons, we believe that these fields will remain a rich area of investigation for many years to come.

VIII. REFERENCES

1. K. J. Irgolic and M. V. Kudchadker, 'Organic Chemistry of Selenium', in *Selenium* (Eds. R. A. Zingaro and W. C. Cooper), Van Nostrand Reinhold, New York, 1974, Chap. 8, p. 408.
2. D. L. Klayman and W. H. S. Gunther (Eds.), *Organic Selenium Compounds: Their Chemistry and Biology*, Wiley, New York, 1973.
3. H. J. Reich, *Organoselenium Oxidations*, in *Oxidation in Organic Chemistry*: Part C (Ed. W. S. Trachanowsky), Academic Press, New York, 1978, Chap. 1, p. 1.
4. D. L. J. Clive, *Aldrichim. Acta*, **11**, 43 (1978).
5. D. L. J. Clive, *Tetrahedron*, **34**, 1049 (1978).
6. H. J. Reich, *Acc. Chem. Res.*, **12**, 22 (1978).
7. S. V. Ley, *Chem. Ind. (London)*, 101 (1985).
8. D. Liotta and R. Monaham, III, *Science*, **231**, 356 (1968).
9. K. C. Nicolaou and N. A. Petasis, *Selenium in Natural Product Synthesis*, CIS, Philadelphia, 1984.
10. Z. J. Witczak and R. L. Whistler, *Heterocycles*, **19**, 1719 (1982).
11. Z. J. Witczak, *Tetrahedron*, **41**, 4781 (1985).

12. R. A. Zingaro, *Chem. Scr.*, **8A**, 51 (1975).
13. W. A. Bonner and A. Robinson, *J. Am. Chem. Soc.*, **72**, 354 (1950).
14. G. Wagner and G. Lehmann, *Pharm. Zentralhalle*, **100**, 160 (1961).
15. G. Wagner and P. Nün, *Pharmazle*, **22**, 548 (1967).
16. J. Kocourek, J. Klenha and V. Jiracek, *Chem. Ind. (London)*, 1937 (1963).
17. Z. J. Witczak, *Nucleosides Nucleotides*, **2**, 295 (1983).
18. R. Walter, in *Peptides: Chem. Biochem., Proc. Am. Peptide Symp., 1st*, Marcel Dekker, New York, 1968, p. 467; *Chem. Abstr.*, **73**, 56379e (1970).
19. L. Laitem, P. Thibaut and L. Christiaens, *J. Heterocycl. Chem.*, **13**, 469 (1976).
20. J. Jaurequi-Adeu, *Adv. Protein Chem.*, **21**, 387 (1966).
21. O. H. Muth (Ed.), *Selenium in Biomedicine*, Avi Publishing, Westport, 1966.
22. I. Rosenfold and O. Beath, *Selenium Biobotany, Biochemistry, Toxicity and Nutrition*, Academic Press, New York, 1964.
23. R. J. Shamberger, *Biochemistry of Selenium*, Plenum Press, New York, 1983.
24. W. Schneider and F. Wrede, *Chem. Ber.*, **50**, 793 (1917).
25. G. Wagner and P. Nühn, *Arch. Pharm.*, **297**, 461 (1964).
26. H. Frenzel, P. Nühn and G. Wagner, *Arch. Pharm.*, **302**, 63 (1969).
27. W. Kudelska and M. Michalska, *Tetrahedron*, **37**, 2994 (1981).
28. M. Michalska, J. Michalski and I. Orlich-Krezel, *Tetrahedron*, **34**, 2821 (1978).
29. M. Michalska, J. Michalski and I. Orlich-Krezel, *Pol. J. Chem.*, **53**, 253 (1979).
30. J. R. Daniel and R. A. Zingaro, *Phosphorus Sulfur*, **4**, 179 (1978).
31. R. A. Zingaro and J. K. Thompson, *Carbohydr. Res.*, **29**, 147 (1973).
32. C. D. Mickey, P. H. Javora and R. A. Zingaro, *J. Carbohydr. Nucleos. Nucleot.*, **1**, 291, (1974).
33. C. L. Baimbridge, C. D. Mickey and R. A. Zingaro, *J. Chem. Soc. Perkin Trans. I*, 1395 (1975).
34. J. R. Daniel and R. A. Zingaro, *Carbohydr. Res.*, **64**, 69 (1978).
35. G. C. Chen, C. H. Banks, K. J. Irgolic and R. A. Zingaro, *J. Chem. Soc. Perkin Trans. I*, 2288 (1980).
36. R. Lipka and M. Michalska, *Carbohydr. Res.*, **113**, 317 (1983).
37. G. Jaurand, J. M. Beau and P. Sinaÿ, *J. Chem. Soc., Chem. Commun.*, 572, 701 (1981).
38. K. Mori, *Tetrahedron Lett.*, 1609 (1976).
39. S. Current and K. B. Sharpless, *Tetrahedron Lett.*, 5078 (1978).
40. K. C. Nicolaou and Z. Lysenko, *Tetrahedron Lett.*, 1259 (1977).
41. K. C. Nicolaou and Z. Lysenko, *J. Am. Chem. Soc.*, **99**, 3186 (1977).
42. D. L. J. Clive, G. Chittattu, N. J. Curtis, W. A. Kiel and C. K. Wong, *J. Chem. Soc., Chem. Commun.*, 725 (1978).
43. D. L. J. Clive, G. Chittattu and C. K. Wong, *Can. J. Chem.*, **55**, 3894 (1977).
44. D. L. J. Clive, C. K. Wong, W. A. Kiel and S. M. Menchen, *J. Chem. Soc., Chem. Commun.*, 379 (1978).
45. D. L. J. Clive, G. Chittattu and C. K. Wong, *J. Chem. Soc, Chem. Commun.*, 441 (1978).
46. S. David, A. Lubineau and J. M. Vatele, *J. Chem. Soc., Chem. Commun.*, 701 (1975).
47. S. David, A. Lubineau and J. M. Vatele, *J. Chem. Soc., Perkin Trans. 1*, 1831 (1976).
48. K. Torssel and M. P. Tyagi, *Acta Chem. Scand., Ser. B*, **31**, 297 (1977).
49. S. David and A. Lubineau, *Nouv. J. Chim.*, **1**, 375 (1977).
50. Y. Nishimura, H. Umezawa and S. Umezawa, *Tetrahedron Lett.*, **22**, 77 (1981).
51. T. Van Es, *Carbohydr. Res.*, **5**, 282 (1967).
52. J. Mieczkowski, A. Konowal and A. Zamojski, *Pol. J. Chem.*, **57**, 75 (1983),
53. A. P. Kozikowski, K. L. Sorgi and R. J. Schmiesing, *J. Chem. Soc., Chem. Commun.*, 477 (1980); A. P. Kozikowski, R. J. Schmiesing and K. L. Sorgi, *J. Am. Chem. Soc.*, **102**, 6580 (1980).
54. K. B. Sharpless and R. F. Lauer, *J. Am. Chem.*, **94**, 7154 (1972).
55. K. B. Sharpless and R. F. Lauer, *J. Org. Chem.*, **37**, 3973 (1972).
56. K. B. Sharpless, M. W. Young and F. R. Lauer, *J. Am. Chem. Soc.*, **94**, 154 (1972); **95**, 2697 (1973).
57. K. B. Sharpless, M. W. Young and F. R. Lauer, *Tetrahedron Lett.*, 1979 (1973).
58. H. Paulsen, F. R. Heiker, J. Feldmann and K. Heyns, *Synthesis*, 636 (1980).
59. B. P. Mundy and W. G. Bornmann, *J. Org. Chem.*, **49**, 5264 (1984).
60. J. M. Lancelin, J. R. Pougny and P. Sinaÿ, *Carbohydr. Res.*, **136**, 369 (1985).
61. F. Freeman and K. D. Robarge, *Carbohydr. Res.*, **137**, 89 (1985).
62. R. M. Adlington, J. E. Baldwin, A. Basak and R. P. Kozyrod, *J. Chem. Soc., Chem. Commun.*, 944 (1983).

63. B. Geise and J. Dupuis, *Angew. Chem., Int. Ed. Engl.*, **22**, 622 (1983).
64. B. Geise and J. Dupuis, *Tetrahedron Lett.*, **25**, 1369 (1984).
65. G. Geise, J. Dupuis, T. Hasskerl and J. Meixner, *Tetrahedron Lett.*, **24**, 703 (1983).
66. J. Dupuis, B. Geise, D. Rüegge, H. Fischer, H. G. Korth and R. Sustmann, *Angew. Chem., Int. Ed. Engl.*, **23**, 896 (1984).
67. P. Rollin, V. Verez Bencomo and P. Sinaÿ, *Synthesis*, 134 (1984).
68. K. C. Nicolaou, S. P. Seitz, W. J. Sipio and J. F. Blount, *J. Am. Chem. Soc.*, **101**, 3884 (1979); **102**, 3784 (1980).
69. D. Goldsmith, D. Liotta, C. Lee and G. Zima, *Tetrahedron Lett.*, 4801 (1979).
70. J. L. Fourney, G. Henry and P. Jouin, *Tetrahedron Lett.*, **21**, 455 (1980).
71. K. Furuichi, S. Yogai and T. Miwa, *J. Chem. Soc., Chem. Commun.*, 66 (1980).
72. T. Sakakibara, I. Takei, E. Ohara and R. Sudoh, *J. Chem. Soc., Chem. Commun.*, 261 (1981).
73. P. A. Grieco, Y. Yokoyama and E. Williams, *J. Org. Chem.*, **43**, 1283 (1978).
74. P. A. Grieco, E. Williams, H. Tanaka and S. Gilman, *J. Org. Chem.*, **45**, 3537 (1980).
75. Z. J. Witczak, *J. Carbohydr. Chem.*, **3**, 359 (1984).
76. H. Paulsen and K. Todt, *Adv. Carbohydr. Chem.*, **23**, 115 (1968).
77. H. Paulsen, *Angew. Chem., Int. Ed. Engl.*, **5**, 495 (1966).
78. D. Horton and D. H. Hutson, *Adv. Carbohydr. Chem.*, **18**, 123 (1963).
79. S. Inokawa, *Kagaku (Kyoto)*, **24**, 901 (1969); *Chem. Abstr.*, **72**, 90757r (1970).
80. Z. J. Witczak and R. L. Whistler, *J. Carbohydr. Chem.*, **2**, 351 (1983).
81. H. Yamamoto and S. Inokawa, *Adv. Carbohydr. Chem. Biochem.*, **42**, 135 (1984).
82. K. Blumberg, A. Fuccello and T. Van Es, *Carbohydr. Res.*, **59**, 351 (1977).
83. T. Van Es and R. L. Whistler, *Tetrahedron*, **23**, 2849 (1967).
84. T. Van Es and J. J. Rabelo, *Carbohydr. Res.*, **29**, 252 (1973).
85. J. J. Rabelo and T. Van Es, *Carbohydr. Res.*, **30**, 202 (1973); **30**, 318 (1973); **32**, 175 (1974).
86. T. Van Es and J. J. Rabelo, *Carbohydr. Res.*, **36**, 408 (1974).
87. R. J. Suhadolnik, *Nucleoside Antibiotics*, Wiley–Interscience, New York, 1970; R. J. Suhadolnik, *Nucleosides as Biological Probes*, Wiley–Interscience, New York, 1979.
88. S. Hanessian and A. G. Pernet, *Adv. Carbohydr. Chem. Biochem.*, **33**, 111 (1976).
89. G. D. Daves and C. C. Cheng, *Prog. Med. Chem.*, **13**, 303 (1976).
90. J. J. Jaffe and H. G. Mautner, *Cancer Res.*, **20**, 381 (1960).
91. J. J. Jaffe and H. G. Mautner, *Cancer Res.*, **18**, 938 (1958).
92. L. B. Townsend and G. H. Milne, *J. Heterocycl. Chem.*, **7**, 753 (1970).
93. G. H. Milne and L. B. Townsend, *J. Heterocycl. Chem.*, **8**, 379 (1971).
94. S. M. Chu, *J. Med. Chem.*, **14**, 254 (1971).
95. C. Y. Shine and S. H. Chu, in *Nucleic Acid Chemistry: Improved and New Synthetic Procedures, Methods and Techniques* (Eds. L. B. Townsend and R. S. Tipson), Wiley–Interscience, New York, 1978, Vol. 2, p. 673.
96. G. H. Milne and L. B. Townsend, *Biochim. Biophys. Acta*, **269**, 344 (1972).
97. G. H. Milne and L. B. Townsend, *J. Med. Chem.*, **17**, 263 (1974).
98. S. H. Chu and D. D. Davidson, *J. Med. Chem.*, **15**, 1088 (1972).
99. G. H. Milne and L. B. Townsend, *J. Chem. Soc., Perkin Trans. 1*, 2677 (1972).
100. D. S. Wise and L. B. Townsend, *J. Heterocycl. Chem.*, **9**, 1461 (1972).
101. D. S. Wise and L. B. Townsend, in *Nucleic Acid Chemistry: Improved and New Synthetic Procedures, Methods and Techniques* (Eds. L. B. Townsend and R. S. Tipson), Wiley–Interscience, New York, 1978, Vol. 1, p. 413.
102. S. M. Chu, C. Y. Shine and M. Y. Chu, *J. Med. Chem.*, **17**, 406 (1974).
103. C. Y. Shine and S. H. Chu, *J. Heterocycl. Chem.*, **12**, 493 (1975).
104. C. Y. Shine and S. H. Chu, *J. Chem. Soc., Chem. Commun.*, 319 (1975).
105. S. H. Chu, C. Y. Shine and M. Y. Chu, *J. Med. Chem.*, **18**, 559 (1975).
106. S. H. Chu, C. Y. Shine and M. Y. Chu, *J. Pharm. Sci.*, **64**, 1343 (1975).
107. G. H. Milne and L. B. Townsend, *J. Heterocycl. Chem.*, **13**, 745 (1976).
108. G. H. Milne and L. B. Townsend, *J. Carbohydr. Nucleosides Nucleotides*, **3**, 177 (1976).
109. D. S. Wise and L. B. Townsend, *Tetrahedron Lett.*, 755 (1977).
110. D. S. Wise and L. B. Townsend, *J. Chem. Soc., Chem. Commun.*, 271 (1979).
111. D. S. Wise, G.H. Milne and L. B. Townsend, *Heterocycles*, **15**, 345 (1981).
112. M. Sekine and T. Hata, *Chem. Lett.*, 801 (1979).
113. H. Takaku, T. Namoto and K. Kimura, *Chem. Lett.*, 1221 (1981).

114. N. Zylber, J. Zylber and A. Gaudemer, *J. Chem. Soc., Chem. Commun.*, 1084 (1978).
115. C. Boullais, N. Zylber, J. Zylber, J. Guilhem and A. Gaudemer, *Tetrahedron*, **39**, 759 (1983).
116. P. C. Srivastava and R. K. Robins, *J. Med. Chem.*, **26**, 445 (1981).
117. W. J. Hennen, B. C. Hinshaw, T. A. Riley, S. G. Wood and R. K. Robins, *J. Org. Chem.*, 1741 (1985).
118. P. D. Cook and D. J. McNamara, *J. Heterocycl. Chem.*, **23**, 155 (1986).
119. B. G. Ugarkar, R. K. Robins and G. R. Revankar, *Nucleosides, Nucleotides*, **3**, 233 (1984).
120. B. G. Ugarkar, H. B. Cottam, P. A. McKernan, R. K. Robins and G. R. Revankar, *J. Med. Chem.*, **27**, 1026 (1984).
121. R. F. Schinazi, J. Arbiser, J. J. S. Lee, T. I. Kalman and N. H. Prusoff, *J. Med. Chem.*, **29**, 1293 (1986).
122. N. Petragnani and M. Moura Campos, *Organomet. Chem. Rev.*, **2**, 61 (1967).
123. K. J. Irgolic and R. Zingaro, in *Organometallic Reactions* (Eds. E. Becker and M. Tsutsui), Wiley, New York, London, 1971.
124. W. C. Cooper (Ed.), *Tellurium*, Van Nostrand Reinhold, New York, 1971.
125. K. J. Irgolic, in *Houben-Weyl, Methoden der Organischen Chemie*, 4th ed., Vol. E12, Georg Thieme, Stuttgart, New York, in press.
126. K. J. Irgolic, *The Organic Chemistry of Tellurium*, Gordon and Breach, New York, 1974.
127. K. J. Irgolic, *J. Organomet. Chem.*, **103**, 91 (1975); **130**, 411 (1978); **158**, 235 (1978); **189**, 65 (1980); **203**, 368 (1980).
128. N. Petragnani and J. V. Comasseto, *Synthesis*, 1 (1986).
129. J. Czyżewska-Chlebny and M. Michalska, *J. Chem. Soc., Chem. Commun.*, 693 (1985).
130. S. V. Ley, C. A. Meerholz and D. H. R. Barton, *Tetrahedron, Suppl. 1*, **37**, 213 (1981).
131. D. H. R. Barton and S. W. McCombie, *J. Chem. Soc., Perkin Trans. 1*, 1574 (1975).
132. A. G. M. Barrett, R. W. Read and D. H. R. Barton, *J. Chem. Soc., Perkin Trans. 1*, 2184 (1980).
133. A. I. Ross, K. G. Agrawal, S. H. Chu and R. E. Parks, Jr., *Biochem. Pharmacol.*, **22**, 141 (1973).
134. M. Maeda, N. Abiko and T. Sasaki, *J. Med. Chem.*, **24**, 167 (1981).
135. C. H. Banks, J. R. Daniel and R. A. Zingaro, *J. Med. Chem.*, **22**, 572 (1979).

Author Index

This author index is designed to enable the reader to locate an author's name and work with the aid of the reference numbers appearing in the text. The page numbers are printed in normal type in ascending numerical order, followed by the reference numbers in parentheses. The numbers in *italics* refer to the pages on which the references are actually listed.

Subject Index