The Chemistry of Ketenes, Allenes and Related Compounds
Edited by Saul Patai

The chemistry of **ketenes, allenes and related compounds**

Part 1

Edited by

SAUL PATAI

The Hebrew University, Jerusalem

1980

JOHN WILEY & SONS

CHICHESTER – NEW YORK – BRISBANE – TORONTO

An Interscience ® Publication

British Library Cataloguing in Publication Data:

The chemistry of ketenes, allenes and related
compounds. – (Chemistry of functional groups).
Part 1

1. Allenes 2. Ketenes
I. Patai, Saul II. Series
547'.412 QD305.H8 79-42899

ISBN 0 471 99713 7
ISBN 0 471 27671 5 Set of 2 Vols

Typeset by Preface Ltd., Salisbury, Wiltshire.
Printed in Great Britain by Page Bros. (Norwich) Ltd., Norwich.

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Foreword

In the first volume of "The Chemistry of Functional Groups", which appeared in 1964 ("The Chemistry of Alkenes"), two chapters dealt with ketenes and cumulenes. In the fifteen years which passed since, the material published on these subjects grew so much that it fully justified the publication of a separate volume. The organization and presentation of this volume is in accordance with the general principles described in the "Preface to the Series", printed on the following pages.

Some of the chapters planned for this volume did not materialize. These were "The Photochemistry of Ketenes and Cumulenes", "Cycloadditions Involving Ketenes and Cumulenes" and "Rearrangements Involving Ketenes". It is hoped to include these chapters in one of the supplementary volumes planned for the Series.

Jerusalem, July 1979

SAUL PATAI

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 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
The Chemistry of Cyanates and their Thio Derivatives (*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*)
The Chemistry of the Carbon–Carbon Triple Bond (*two parts*)
Supplement A: The Chemistry of Double-bonded Functional Groups (*two parts*)
Supplement B: The Chemistry of Acid Derivatives (*two parts*)
The Chemistry of Ketenes, Allenes and Related Compounds (*two parts*)

Titles in press:

Supplement E: The Chemistry of Ethers, Crown Ethers, Hydroxyl Groups and their Sulphur Analogs
The Chemistry of the Sulphonium Group

Future volumes planned include:

The Chemistry of Organometallic Compounds
The Chemistry of Sulphur-containing Compounds
Supplement C: The Chemistry of Triple-bonded Functional Groups
Supplement D: The Chemistry of Halides and Pseudo-halides
Supplement F: The Chemistry of Amines, Nitroso and Nitro Groups and their Derivatives

Advice or 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, and who continues to help and advise me. 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.

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The Chemistry of Ketenes, Allenes and Related Compounds
Edited by Saul Patai

CHAPTER 1

Theoretical methods and their application to ketenes and allenes

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Abbreviations

a.u.	Atomic unit
CI	Configuration Interaction
CEPA	Coupled Electron Pair Approximation

D	Debye, unit of dipole moment
DZ	Double Zeta basis set
DZ + P	Double Zeta plus Polarization basis set
DZ + R	Double Zeta plus Rydberg basis set
FSGO	Floating Spherical Gaussian Orbitals
GVB	Generalized Valence Bond
IP	Ionization Potential
MBS	Minimum Basis Set
MINDO	Modified Intermediate Neglect of Differential Overlap
MR	Multiple Reference configurations
POL-CI	Polarization-type Configuration Interaction wave function
SCEP	Self-Consistent Electron Pairs
SCF	Self-Consistent-Field
S + D	Single and Double excitations
STO	Slater Type Orbital
TCSCF	Two Configuration Self-Consistent-Field
UHF	Unrestricted Hartree–Fock

I. INTRODUCTION

The present chapter is the logical successor to the 1963 paper, 'Wave mechanics and the alkene bond', by Coulson and Stewart[1]. Inasmuch as it may be assumed that the readers are familiar with the volume *The Chemistry of Alkenes,* in which the review by Coulson and Stewart appeared, we make no attempt to duplicate their work. It may be noted that nearly one half of the Coulson–Stewart chapter dealt with basic theory and its application to the hydrogen molecule. This was followed by a survey of existing *ab initio* results: e.g. a very nice discussion of acetylene was given, based on the minimum basis set (MBS) self-consistent-field (SCF) wave functions of McLean[2]. The MBS SCF results of Ransil[3] for first-row diatomics were also discussed in some detail. However, in 1962 the McLean and Ransil results represented a large fraction of the reliable *ab initio* wave functions for molecules with more than four electrons, so for larger molecules the Coulson–Stewart review inevitably turned to the simpler semiempirical methods. Later chapters dealt with the π-electron hypothesis, the Hückel approximation, and their application to various problems in molecular structure and spectroscopy.

Here we shall attempt to pick up where the Coulson–Stewart chapter left off, i.e. to present a review of developments in *ab initio* molecular electronic structure theory since 1962. It should perhaps be noted that we use the term *ab initio* to imply that no approximations have been made in the one- and two-electron integrals[4]

$$I(i|j) = \int \phi_i^*(1) \left\{ \frac{-\nabla_1^2}{2} - \sum_{A} \frac{Z_A}{r_{1A}} \right\} \phi_j(1)\, dv(1) \tag{1}$$

$$(ij|kl) = \int \phi_i^*(1)\, \phi_j^*(2)\, \frac{1}{r_{12}}\, \phi_k(1)\, \phi_l(2)\, dv(1)\, dv(2) \tag{2}$$

arising from the ordinary nonrelativistic Hamiltonian

$$H = \sum_i \left\{ \frac{-\nabla_i^2}{2} - \sum_A \frac{Z_A}{r_{iA}} \right\} + \sum_i \sum_{j>i} \frac{1}{r_{ij}} \tag{3}$$

In contrast semiempirical methods[5] resort to various approximate schemes, especially in evaluating the two-electron integrals $(ij|kl)$. Following a review of theoretical methods, we turn to a detailed survey of *ab initio* results for simple ketenes and allenes.

II. THE HARTREE–FOCK METHOD AND ITS RELIABILITY

A. Definitions

For closed-shell molecules the Hartree-Fock wave function is of the form

$$\psi_{\mathrm{HF}} = A(n)\, \phi_1(1)\, \phi_2(2) \ldots \phi_n(n) \tag{4}$$

in which $A(n)$, the antisymmetrizer for n electrons, has the effect of making a Slater determinant out of the orbital product on which it operates. The ϕs are spin orbitals, products of a spatial orbital χ and a one-electron spin function α or β. For any given molecular system, there are an infinite number of wave functions of form (4), but the Hartree–Fock wave function is the one for which the orbitals ϕ have been varied to yield the lowest possible energy:

$$E = \int \psi^*_{\mathrm{HF}} H \psi_{\mathrm{HF}}\, \mathrm{d}\tau \tag{5}$$

The resulting Hartree–Fock equations are relatively tractable due to the simple form of the energy E for single determinant wave functions:

$$E_{\mathrm{HF}} = \sum_i I(i|i) + \sum_i \sum_{j>i} [(ij|ij) - (ij|ji)] \tag{6}$$

To make this discussion more concrete we note that for singlet methylene (a species not unrelated to ketenes) the Hartree–Fock wave function is of the form

$$\psi_{\mathrm{HF}} = A(8)\; 1a_1\alpha(1)\; 1a_1\beta(2)\; 2a_1\alpha(3)\; 2a_1\beta(4)\; 1b_2\alpha(5)\; 1b_2\beta(6)\; 3a_1\alpha(7)\; 3a_1\beta(8) \tag{7}$$

The same energy expression (6) is also applicable to any open-shell system for which the open-shell electrons all have parallel spins. This follows from the fact that such Hartree–Fock wave functions can always be expressed as a single Slater determinant. A simple example is triplet methylene

$$\psi_{\mathrm{HF}} = A(8)\; 1a_1\alpha(1)\; 1a_1\beta(2)\; 2a_1\alpha(3)\; 2a_1\beta(4)\; 1b_2\alpha(5)\; 1b_2\beta(6)\; 3a_1\alpha(7)\; 1b_1\alpha(8) \tag{8}$$

for which the outer two $3a_1$ and $1b_1$ orbitals have parallel spins. For clarity it is often helpful to abbreviate (8):

$$\psi_{\mathrm{HF}} = 1a_1^2\; 2a_1^2\; 1b_2^2\; 3a_1\alpha\; 1b_1\alpha \tag{9}$$

Although solution of the Hartree–Fock equations for an open-shell system such as triplet methylene is more difficult than for the analogous closed shell system (7), the procedures are well established[6].

In fact methods are now available[7] for the solution of the Hartree–Fock equations for *any* system for which the energy expression involves only coulomb and exchange integrals:

$$J_{ij} = (ij|ij) \tag{10}$$

$$K_{ij} = (ij|ji) \tag{11}$$

Open-shell singlets are a class of systems that can be treated in this way, and one such example is the first excited singlet state (of $^1B_1$ symmetry) of methylene:

$$\psi_{HF} = \frac{1}{\sqrt{2}} 1a_1^2 2a_1^2 1b_2^2 3a_1\alpha \; 1b_1\beta$$
$$- \frac{1}{\sqrt{2}} 1a_1^2 2a_1^2 1b_2^2 3a_1\beta \; 1b_1\alpha \qquad (12)$$

In addition, these same generalized Hartree–Fock procedures[7] can be used for certain classes of multiconfiguration Hartree–Fock wave functions.

B. Basis Sets

To solve the Hartree–Fock equations exactly one must either expand the orbitals ϕ in a complete set of analytic basis functions or obtain strictly numerical (i.e. tabulated) orbitals. The former approach is impossible from a practical point of view for systems with more than two electrons, and the latter has been accomplished only for atoms and very recently[8] for a few diatomic molecules. Therefore the *exact* solution of the Hartree–Fock equations is abandoned for polyatomic molecules. Instead one adopts an incomplete (but reasonable) set of analytic basis functions and solves for the best variational [i.e. lowest energy (5)] wave function of form (4). Following the Chicago group we refer to such a wave function as being of self-consistent-field (SCF) quality. As one goes to very large basis sets, then, it is reasonable to refer to the resulting SCF wave function as near Hartree–Fock[9].

For large chemical systems, at present only *minimum basis sets* (MBS) can be used in *ab initio* theoretical studies. By the term 'large', we include molecular systems roughly the size of and larger than TCNQ–TTF, depicted in Figure 1. To our knowledge, the largest molecule treated to date by MBS SCF methods is the carbazole–trinitrofluorenone complex[11], $C_{25}N_4O_7H_{14}$, with 232 electrons. A minimum basis set includes one function for each orbital occupied in the ground state of each atom included in the molecule. For the first row atoms B, C, N, O and F, this means that a minimum basis includes 1s, 2s, $2p_x$, $2p_y$ and $2p_z$ functions.

Traditionally, minimum basis sets have been composed of Slater functions, such as those seen in Table 1 for the carbon atom. However, experience has shown that

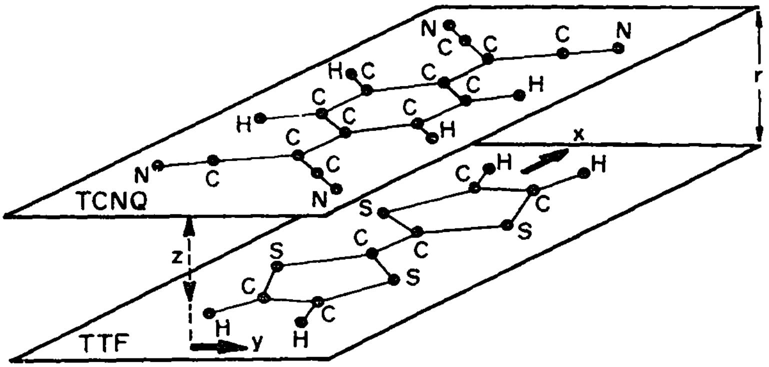

FIGURE 1. The tetracyanoquinodimethane–tetrathiafulvene complex[10] (TCNQ–TTF), a 'large' molecule by 1979 *ab initio* standards.

TABLE 1. Minimum basis set of Slater functions for the carbon atom. The orbital exponents zeta are optimum for the ^3P ground state of the carbon atom

Label	Analytic form	Exponent ζ
1s	$(\zeta^3/\pi)^{1/2} \exp(-\zeta r)$	5.673
2s	$(\zeta^5/3\pi)^{1/2} r \exp(-\zeta r)$	1.608
$2p_x$	$(\zeta^5/\pi)^{1/2} x \exp(-\zeta r)$	1.568
$2p_y$	$(\zeta^5/\pi)^{1/2} y \exp(-\zeta r)$	1.568
$2p_z$	$(\zeta^5/\pi)^{1/2} z \exp(-\zeta r)$	1.568

the evaluation of the molecular integrals (2) arising when Slater functions are employed is extremely time-consuming[12]. Therefore each Slater function in an MBS is typically replaced by a linear combination of three or four gaussian functions[13]. The resulting chemical predictions obtained with such STO-3G or STO-4G basis sets are usually indistinguishable from the corresponding Slater function results.

As we shall see shortly, minimum basis sets are inadequate for certain types of chemical predictions. Therefore a basis twice as large, and appropriately designated double zeta (DZ), is often used in theoretical studies. Here, however, it is not as fruitful to expand each Slater function as a linear combination of gaussians. Instead one uses gaussian functions $x^p y^q z^r e^{-\alpha r^2}$ directly in atomic SCF calculations and then *contracts*[14] them according to the atomic results. Perhaps the most widely used contracted gaussian DZ basis sets are those of Dunning[15], and his carbon atom basis is seen in Table 2. This basis has 9s and 5p original (or primitive) gaussian functions and is contracted to 4s and 2p. Thus the basis may be designated C(9s5p/4s2p).

Just as the double zeta basis logically follows the minimum set, the logical extension of the DZ set involves the addition of polarization functions[16]. Polarization functions are of higher orbital angular momentum than the functions occupied in atomic SCF wave function. That is, for carbon, d, f, g, . . . functions will be

TABLE 2. Double zeta contracted gaussian basis set (9s5p/4s2p) for the carbon atom ^3P ground state. Primitive gaussian s functions are of the form $(2\alpha/\pi)^{3/4} \exp(-\alpha r^2)$

Function type	Orbital exponents α	Coefficients
s	4232.61	0.002029
s	634.882	0.015535
s	146.097	0.075411
s	42.4974	0.257121
s	14.1892	0.596555
s	1.9666	0.242517
s	5.1477	1.000000
s	0.4962	1.000000
s	0.1533	1.000000
p	18.1557	0.018534
p	3.9864	0.115442
p	1.1429	0.386206
p	0.3594	0.640089
p	0.1146	1.000000

polarization functions. Fortunately d functions are far more important than f, f functions are far more important than g, and so on. For most chemical applications a double zeta plus polarization (DZ + P) basis including a single set of five d functions ($d_{x^2-y^2}$, d_{z^2}, d_{xy}, d_{xz}, d_{yz}) will be quite adequate for first-row atoms.

C. Structural Predictions

Ab initio theoretical methods have had the greatest impact on chemistry in the area of structural predictions[17-19]. A good illustration[20] of this is the methylene radical for which Foster and Boys[21] reported the first *ab initio* study in 1960. Foster and Boys predicted the structure of triplet methylene to be $r_e(C-H) = 1.12$ Å, $\theta_e(HCH) = 129°$. Unfortunately, however, the work of Foster and Boys was largely ignored due to the spectroscopic conclusion of Herzberg[22] that the lowest triplet state was linear. Herzberg's conclusion was greatly strengthened by a very influential semiempirical study of Longuet-Higgens and Jordan[23], who concurred that the ground state of CH_2 was linear.

And in fact it was not until 1970 that a definitive theoretical prediction[24] of the nonlinearity of $^3B_1$ CH_2 appeared. Fortunately, Bender and Schaefer's prediction was swiftly verified by the electron spin resonance experiments of Wasserman[25] and Bernheim[26]. For many chemists the structure of triplet methylene was the first genuine example of the usefulness of *ab initio* theoretical chemistry.

Turning from the specific to the more general, the most encouraging aspect of *ab initio* geometry predictions is their perhaps surprising reliability. Essentially all

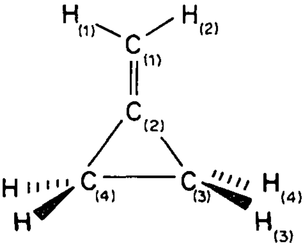

FIGURE 2. The methylenecyclopropane molecule, for which a complete *ab initio* structure determination is seen in Table 3.

TABLE 3. Minimum basis set (MBS) self-consistent-field (SCF) geometry prediction compared with experiment for methylenecyclopropane (see Figure 2)

Parameter	STO-3G	Experiment
$r(C_{(1)}=C_{(2)})$ (Å)	1.298	1.332
$r(C_{(2)}-C_{(3)})$ (Å)	1.474	1.457
$r(C_{(3)}-C_{(4)})$ (Å)	1.522	1.542
$r(C_{(1)}-H_{(1)})$(Å)	1.083	1.088
$r(C_{(3)}-H_{(3)})$ (Å)	1.083	1.09
$\theta(H_{(1)}C_{(1)}H_{(2)})$ (deg.)	116.0	114.3
$\theta(H_{(3)}C_{(3)}H_{(4)})$ (deg.)	113.6	113.5
$\theta(H_{(3)}C_{(3)}C_{(4)})$(deg.)	149.4	150.8

molecular structures appear to be reliably predicted at the Hartree–Fock level of theory. Even more encouraging, many structures are accurately reproduced using only MBS SCF methods. As shown by Pople and coworkers[17,19], this is especially true for hydrocarbons. A fairly typical example is methylenecyclopropane[27], seen in Figure 2, and its MBS SCF structure is compared with experiment in Table 3. Carbon–carbon bond distances differ typically by 0.02 Å from experiment and angles are rarely in error by more than a few degrees. In the same paper, Hehre and Pople[27] report full MBS SCF geometry optimizations for 13 other hydrocarbons containing four carbon atoms, and the results are equally impressive. Even for severely strained molecules such as bicyclo[1.1.0]butane, very reasonable agreement with the experimental structure is obtained. It is noteworthy that for only half of the C_4 hydrocarbons studied are experimental geometries available. Thus for many purposes theory may be considered complementary to experiment in the area of structure prediction.

For molecules including atoms in addition to C and H, MBS-SCF results are sometimes less reliable. This first became apparent from the work of Newton and coworkers[28] in 1970. For example, the F_2N_2 molecule has MBS SCF bond distances $r_e(N{-}F) = 1.384$ Å, $r_e(N{=}N) = 1.214$ Å, which are respectively 0.107 Å longer and 0.169 shorter than the experimental values[29]. We shall note several other examples later in comparison with more elaborate calculations.

In general double zeta (DZ) SCF structure predictions are considerably more reliable than those based on minimum basis sets. A noteworthy exception is the water molecule, for which MBS SCF[28] yields a bond angle of 100.0° and DZ SCF predicts[30] 112.6°, compared to the well-known experimental value of 104.5°. More typical are the HF and F_2 molecules, for which the MBS, DZ and experimental bond distances are 0.956 Å, 0.922 Å and 0.917 Å (HF), and 1.315 Å, 1.400 Å and 1.417 Å. In fact it can be argued[18], that if one is not going beyond the Hartree–Fock (single configuration) approximation, DZ SCF is often a reasonable stopping point.

Typically more sensitive to basis set than equilibrium geometries are transition states. This is true because potential energy surfaces are often rather flat in the vicinity of a saddle point (transition state). As an example, we cite the work of Poppinger, Radom and Pople[31] on the carboxime–cyanic acid rearrangement

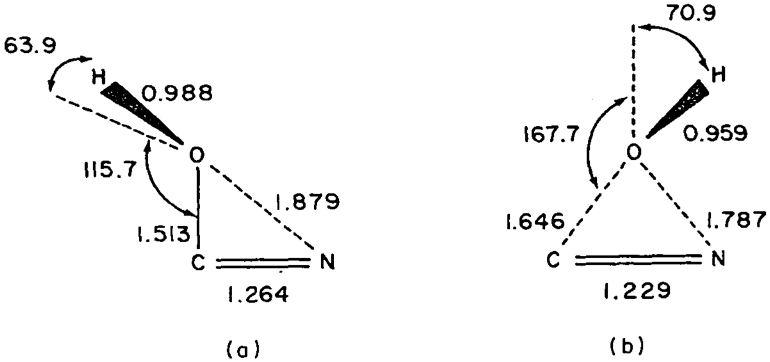

FIGURE 3. Comparison between transition states predicted for the carboxime–cyanic acid isomerization (equation 13): (a) minimum basis set (MBS) and (b) double zeta (DZ) self-consistent-field (SCF) results.

TABLE 4. Theoretical structures[a] of NH_2F and PH_2F compared with experiment[b]

	DZ	DZ + central d	Experiment
r_e (N–H) (Å)	1.011	1.008	1.026 ± 0.002
r_e (N–F) (Å)	1.428	1.389	1.400 ± 0.002
θ_e (HNH) (deg.)	102.8	103.0	102.1 ± 0.2
θ_e (HNF) (deg.)	101.4	100.6	99.8 ± 0.2
r_e (P–H) (Å)	1.420	1.416	1.412 ± 0.006
r_e (P–F) (Å)	1.634	1.600	1.582 ± 0.002
θ_e (HPH) (deg.)	98.6	96.7	99.0 ± 0.2
θ_e (HPF) (deg.)	96.8	98.0	96.3 ± 0.5

[a] Reference 32.

[b] NH_2F: D. R. Lide, *J. Chem. Phys.*, 38, 456 (1963).
PH_2F: R. L. Kuczkowski, *J. Amer. Chem. Soc.*, 90, 1705 (1968).

(equation 13). MBS SCF and DZ SCF transition-state geometries are compared in

$$\text{HONC} \rightarrow \text{HOCN} \tag{13}$$

Figure 3. There we see that the MBS and DZ saddle-point geometries are qualitatively different, the DZ prediction being presumably the more reliable. It should be noted that for several other transition states Poppinger finds better agreement between the two methods. More typical structural variations are ~ 0.05 Å in internuclear separations and 5° in angles.

As one goes to larger basis sets within the Hartree–Fock formalism, better agreement with experiment is frequently obtained. As implied above, the water molecule bond angle is much improved at the DZ + P level[30] to 106.1°. However, it is often the case that adding polarization functions has only a marginal effect on predicted geometries. A reasonable typical comparison is given in Table 4, which shows the predicted[32] and experimental structures of NH_2F and PH_2F. There the only polarization functions added were sets of d functions on the central N or P atom. The only pronounced improvement with respect to experiment is for the P–F separation in PH_2F, and this is improved by 0.034 Å when d functions are added to phosphorus. Pulay's good agreement with experiment for NH_2F and PH_2F suggests a high degree of reliability for their NHF_2 and PHF_2 predictions[32], where no experimental structures have been determined.

An interesting comparison of the three most frequently used basis sets is given in Table 5 for the linear HCNO molecule. The most sensitive geometrical parameter is the N–O bond distance, for which MBS is 0.095 Å too long, DZ is still 0.056 Å too

TABLE 5. Equilibrium geometry of HCNO, formonitrile oxide, from self-consistent-field (SCF) theory and experiment

	MBS[a]	DZ[a]	DZ + P[b]	Experiment[c]
r_e (H–C) (Å)	1.065	1.049	1.059	1.050
r_e (C–N) (Å)	1.155	1.133	1.129	1.169
r_e (N–O) (Å)	1.294	1.255	1.201	1.199

[a] Reference 31.

[b] Reference 33.

[c] P. R. Bunker, B. M. Landsberg, and B. P. Winnewisser, *J. Mol. Spectry.*, 74, 9 (1979).

long, but the DZ + P result is in nearly perfect agreement with experiment. For the CN distance the MBS treatment actually gives the best agreement with experiment. The experimental microwave spectrum is difficult to unravel for a quasilinear molecule such as HCNO, and in particular a reliable CH distance has only become available recently.

D. Energetic Predictions

Among the most chemically important energetic quantities are conformational energy changes, exothermicities or heats of reaction, dissociation energies, and activation energies or barrier heights. In general only the first of these, and sometimes the second, is reliably predicted at the Hartree–Fock level of theory. In other words, energetic quantities are often sensitive to the effects of electron correlation.

Conformational energy changes are almost without exception properly reproduced within the Hartree–Fock formalism. In fact certain types of barriers, typified by the ethane rotational barrier, are quite satisfactorily predicted[12] at the MBS SCF level of theory. More sensitive problems, such as the ammonia inversion barrier[34] and the rotational barrier of hydrogen peroxide[35], demand the inclusion of polarization basis functions.

Although Hartree–Fock exothermicities are often unreliable, there is at least one fairly large class of reactions for which consistently good agreement with experiment has been found. Generally speaking, heats of reaction for systems having closed-shell reactants and products are often predicted successfully[36]. More specifically, even better agreement with experiment is found for *isodesmic*[37] reactions, where the number of bonds of each type is conserved. In fact, reasonable predictions are often made at the MBS SCF level for isodesmic reactions. Further, such information can sometimes be used indirectly (or in conjunction with other thermochemical information) to predict quantities that might be very difficult to evaluate by more straightforward *ab initio* methods. A particularly interesting example is Radom's work[38] on the abstraction of a proton from phenol by various substituted benzenes.

The dissociation energies of covalent molecules are generally predicted poorly by single configuration SCF methods. Certainly the best known example is the F_2 molecule, for which the molecular Hartree–Fock energy lies about 1 eV *above* the Hartree–Fock energy of two fluorine atoms[39]. Unfortunately, this problem is often attributed to the 'perverse' nature of the fluorine atom. In fact, the near Hartree–Fock dissociation energy[40] of N_2 is 5.27 eV, only about half of experiment, 9.91 eV. In addition the near Hartree–Fock dissociation energy[41] of O_2 is 1.43 eV, only one-third of experiment, 5.21 eV. Thus we see that the Hartree–Fock dissociation energies of covalent molecules are consistently much less than experiment.

Another frequent failing of the Hartree–Fock method is in the prediction of the barrier heights or activation energies of chemical reactions. However, we will reserve until our discussion of electron correlation some of the more notorious failures. Here we must note that there are many classes of reactions for which Hartree–Fock theory does yield meaningful barrier heights. Two well-studied examples are the isomerizations shown in equations (14) and (15). For the HNC rearrangement comparison between SCF (40.2 kcal) and CI (34.9 kcal) barriers[42] reveals good qualitative agreement. However, the inclusion of d functions in the C and N basis sets

$$\mathrm{HNC} \rightarrow \mathrm{HCN} \tag{14}$$

$$\mathrm{CH_3NC} \rightarrow \mathrm{CH_3CN} \tag{15}$$

appears to be very important. For example, for the methyl isocyanide rearrangement the SCF barrier decreases[43] from 60 to 48 kcal when polarization functions are added to a DZ basis. The remaining discrepancy with the experimental activation energy of 38 kcal[44] is about equally due to correlation effects and the fact that the zero-point vibrational energy at the transition state is ~5 kcal less than for CH_3NC. Before leaving this class of molecules it is worth noting that hydrogen isocyanide is one of three intersteller molecules to date (the three are HNC, HCO^+ and HN_2^+) to be identified by *ab initio* theory prior to their laboratory detection.

Generally speaking, unimolecular reactions seem to be treated more reliably by Hartree–Fock methods than bimolecular systems. A second example is the geometrical isomerization of cyclopropane. This system has been studied in considerable detail by Salem and coworkers[45], who totally resolved the structure of the transition state within the full 21-dimensional hypersurface. Although their work involved only a minimum basis set, it went slightly beyond the SCF model in that 3 x 3 configuration interaction (CI) was included. The predicted barrier height was 53 kcal, in reasonable agreement with experiment, 64 kcal.

Finally, it must be noted that for many *attractive*[46] potential energy surfaces, i.e. those having no barrier or activation energy at all, Hartree–Fock methods are frequently reliable. The most carefully documented example[47,48] to date is the

$$H + Li_2 \rightarrow LiH + Li \tag{16}$$

reaction (16). One of the most important features of the $H + Li_2$ surface is the fact that the $C_{2v}HLi_2$ structure is a chemically bound entry. SCF theory suggests that the dissociation energy relative to LiH + Li is 20.2 kcal, in excellent agreement with the large-scale CI result of 22.4 kcal.

In conclusion, then, the Hartree–Fock formalism has very powerful predictive capabilities. However, large classes of chemical problems *cannot* be reasonably described, and a good deal of discretion is required on the part of the theoretician.

III. THE PROBLEM OF ELECTRON CORRELATION

A. The Concept

In the Hartree–Fock approximation one solves equations for the behavior of each electron in the averaged field of the remaining $(n - 1)$ electrons. Unfortunately, electrons respond to each other in an instantaneous manner via Coulomb's law. That is, the motions of the $[n(n - 1)]/2$ pairs of electrons are correlated, and it is precisely this *electron correlation* which is neglected in the Hartree–Fock model. The *correlation energy* is conveniently defined[4] as

$$E_c = E_{\text{exact}} - E_{\text{HF}} \tag{17}$$

i.e. the difference between the (nonrelativistic) exact energy and the Hartree–Fock limit energy. For this reason, quantum-mechanical calculations are sometimes judged by the percentage of the correlation energy obtained. For example, Meyer's pioneering theoretical study[49] of the water molecule yielded ~84% of the correlation energy.

B. Configuration Interaction (CI)

The most obvious way to go beyond the Hartree–Fock approximation is to include more than a single configuration in a variational manner[50]. For a molecule even as small as water, the number of possible configurations becomes very large with a reasonable (say DZ + P) basis set. Therefore one immediately looks for ways of eliminating unimportant configurations. A logical and widely accepted method of classifying configurations rests on the number of orbitals by which a configuration differs from the Hartree–Fock reference configuration. A *single excitation* ϕ_{Si} differs by one orbital from the reference configuration, a double excitation ϕ_{Dj} by two, and so on. Thus an arbitrary CI wave function is of the form

$$\psi_{CI} = \psi_{HF} + \sum_i C_{Si}\phi_{Si} + \sum_j C_{Dj}\phi_{Dj} + \sum_k C_{Tk}\phi_{Tk} + \sum_l C_{Ql}\phi_{Ql} + \dots \tag{18}$$

where C_{Tk} is the coefficient of the kth triple excitation.

The CI coefficients are determined to yield the lowest possible total energy by solving the secular equation or eigenvalue problem

$$\mathbf{HC} = \mathbf{EC} \tag{19}$$

The Hamiltonian matrix **H** in turn is composed of elements

$$H_{ij} = \int \phi_i H \phi_j \, d\tau \tag{20}$$

and these Hamiltonian matrix elements H_{ij} are linear combinations of one- and two-electron integrals (1) and (2).

The most obvious reason for a classification of configurations according to (18) is that Hamiltonian matrix elements

$$\int \psi_{HF} H \phi_{Tk} \, d\tau = \int \psi_{HF} H \phi_{Ql} \, d\tau = 0 \tag{21}$$

between the SCF reference configuration and all triple, quadruple, quintuple, ... excitations are identically zero. Thus if we take the SCF wave function as a zero-order wave function in perturbation theory, then all triple and higher excitations make no contribution to the wave function to first order. For this reason, CI including all single and double excitations is the goal of a number of the most powerful theoretical methods[51–55] for the treatment of electron correlation. For the water molecule with a DZ + P basis and the $1a_1$ (or oxygen 1s) orbital constrained to be always doubly occupied, there are 1026 single and double excitations. Calculations of this type are now relatively routine, requiring only ~10 min on the newer minicomputers[56–58].

For small molecules single and double (S + D) excitations give rise to almost all of the correlation energy. For the water molecule, for example, S + D CI accounts for ~95–96% of the correlation energy[50,59]. However, as molecular size increases, it is now widely accepted[51,60] that higher excitations become more important. For example, Sasaki[61] has recently estimated that for the pyrrole molecule C_4H_5N S + D CI will account for only 80% of the correlation energy. It should be noted that many of the important higher excitations involve the core (carbon and nitrogen 1s in the case of pyrrole) orbitals, and should be relatively unimportant for chemical predictions. Thus it is likely that S + D CI will account for perhaps 90% of the critical *valence* correlation energy of molecules the size of pyrrole.

Perhaps the most successful variational method for treating triple and quadruple excitations includes single and double excitations relative to several reference configurations[62,63]. The motivation for this approach is the observation[64] that an important quadruple excitation invariably differs by two orbitals from an important double excitation. For small molecules this multiple reference procedure (MR S + D CI) is capable of extremely reliable predictions[65].

Among nonvariational procedures for treating higher excitations, the coupled electron pair approximation (CEPA)[60] has proven to be quite useful[51,53]. A simpler, but still useful estimate of the 'unlinked cluster' effects is Davidson's approximation[66]:

$$\Delta E_Q \approx (1 - C_0^2)\,\Delta E_D \tag{22}$$

which gives the correlation energy due to quadruple excitations in terms of C_0, the coefficient of the SCF configuration in the S + D CI, and ΔE_D, the correlation energy due to double excitations. The form of Davidson's correction is rather satisfying, since it shows in a transparent manner that quadruple excitations become more important as (a) the SCF configuration becomes a smaller fraction of the S + D CI wave function and (b) the correlation energy due to double excitations increases.

Before leaving this section, a simpler but very widely used type of CI wave function should be mentioned. Based in part on the perturbation theory ideas of Silverstone and Sinanoglu[67], the *first-order wave function* was introduced by Schaefer and Harris[68] in 1968. Such a CI wave function was designed to include 'all orbital occupancies in which at most one electron is assigned to an orbital beyond the valence shell'. Since in a typical molecule there are several valence orbitals not occupied in the Hartree–Fock approximation, the first-order wave function does allow for higher than double excitations, although the total number of configurations is often much less than the S + D CI. A modified form (designated POL-CI) of the first-order wave function has been used very successfully by Goddard and coworkers[69] in conjunction with their generalized valence bond (GVB) orbitals[70]. The essentials of this method for the selection of configurations have also been partially utilized by Wahl and coworkers in their important MCSCF[71] and CI[72] studies. For a recent assessment of the first-order method, the reader is referred to Liu's recent research[73] on the CO molecule.

C. Structural Predictions

Since Hartree–Fock equilibrium geometries are in general quite reliable, it is relatively unusual to see CI studies of structural parameters alone. However CI molecular structures often appear as a by-product of energetic studies and give us an idea of the reliability to be expected from various levels of theory.

There are situations in which very high structural accuracy is needed, for example in the prediction of the microwave frequencies of intersteller molecules[74]. One such molecule, for which a comparison between many methods is possible, is HOCN, cyanic acid. In Table 6 are presented complete structural predictions from

TABLE 6. Theoretical molecular structures for HOCN, cyanic acid. The first two columns are from Reference 31 and the last four columns from Reference 33

	MBS SCF	DZ[a] SCF	DZ[b] SCF	DZ CI	DZ + P SCF	DZ + P CI
r_e(H–O) (Å)	0.993	0.956	0.958	0.975	0.948	0.962
r_e(O–C) (Å)	1.355	1.300	1.307	1.336	1.283	1.305
r_e(C–N) (Å)	1.159	1.142	1.149	1.181	1.135	1.159
θ_e(HOC) (deg.)	105.2	116.7	116.3	115.8	109.7	109.3
θ_e(OCN) (deg.)	175.9	177.6	177.1	176.0	178.6	177.7

[a] Pople-type 4-31G basis set.
[b] Dunning–Huzinaga double zeta set.

TABLE 7. Geometries of HCN predicted at various levels of theory

	r_e(H–C) (Å)	r_e(C–N) (Å)
MBS SCF[a]	1.070	1.153
DZ SCF[b]	1.051	1.140
DZ + P SCF[c]	1.063	1.137
Near Hartree–Fock[d]	1.058	1.127
TZ + P S + D CI[c]	1.068	1.153
Very large basis S + D CI[d]	1.064	1.148
Experiment[e]	1.066	1.153

[a] Reference 28.
[b] R. Ditchfield, W. J. Hehre and J. A. Pople, *J. Chem. Phys.*, 54, 724 (1971).
[c] Reference 74.
[d] Reference 75.
[e] V. W. Laurie and D. R. Herschbach, *J. Chem. Phys.*, 37, 1687 (1962).

six different theoretical levels. One conclusion drawn from Table 6 which appears to be of general validity[4] is that the effect of electron correlation is to lengthen bond distances. Although the experimental structure of cyanic acid is not yet known, one can probably assume that the DZ + P CI geometry is quite close to the exact result. Thus we see that polarization functions are quite important in determining the H–O–C bond angle. The predicted bond distances from the simpler methods are generally in good agreement with the DZ + P CI results, with the notable exception that the MBS SCF distances are off by 0.03–0.05 Å.

Similar comparisons can be made for the HCN molecule and are seen in Table 7. HCN is unusual in that the very simplest theoretical calculation, the MBS SCF, yields a geometry closer to experiment than does the most exhaustive CI[75], carried out with a basis set four times as large. The origin of this seeming paradox is twofold. First, the MBS SCF result is very fortuitous, especially as regards the CN bond distance. Further study of Table 7 shows that extension of the basis set lowers the MBS SCF bond distance from 1.153 Å to 1.127 Å. However, electron correlation then increases the bond distance from 1.127 Å back to 1.153 Å. This precise cancellation between basis set and correlation errors occurs from time to time but not as a general rule.

The second lesson learned from Table 7 is that CI including all single and double excitations, even when carried out with a near Hartree–Fock basis, does *not* yield the exact molecular structure. Although the errors are small, 0.002 Å for the C–H distance and 0.005 Å for r_e(C–N), they are genuine discrepancies, reflecting the importance of higher excitations in the CI expansion.

As noted above, one of the most frequently used[51,53] approximate treatments of higher CI excitations is the coupled electron pair approximation (CEPA)[60]. A very significant and thorough application of this method to diatomic hydrides is the work of Meyer and Rosmus[76]. Their bond distance predictions are given in Table 8, and are seen to be in very good agreement with experiment. This is particularly impressive, since the Hartree–Fock approximation is already quite reliable for these simple systems[77]. Among the first-row hydrides LiH through HF, the improvement of CEPA over the S + D CI results is most apparent for OH and HF, systems for which core–valence correlation effects should be small.

In conclusion, we can say that good qualitative agreement, say 0.01 Å in bond distances, is readily obtained from *ab initio* methods, often at the SCF level. Further, CI methods with large basis sets can usually guarantee 0.005 Å bond

TABLE 8. Theoretical and experimental values for the equilibrium bond distances r_e (Å) of the first- and second-row diatomic hydrides

	Near Hartree–Fock	S + D CI	CEPA	Experiment
LiH	1.606	1.598	1.599	1.595
BeH	1.338	1.341	1.344	1.343
BH	1.221	1.235	1.238	1.232
CH	1.104	1.119	1.122	1.120
NH	1.018	1.034	1.039	1.037
OH	0.950	0.966	0.971	0.971
HF	0.898	0.912	0.917	0.917
NaH	1.916	1.891	1.891	1.887
MgH	1.725	1.724	1.728	1.730
AlH	1.647	1.644	1.645	1.646
SiH	1.516	1.523	1.526	1.520
PH	1.414	1.421	1.426	–
SH	1.331	1.339	1.344	1.341
HCl	1.266	1.273	1.278	1.275

distance reliability. However, at the present time, a reliability of 0.001 Å appears attainable only for very simple systems, as exemplified by the beautiful work of Lie, Hinze and Liu[65] on diatomic CH.

D. Energetic Predictions

The earliest examples of the deficiency of the Hartree–Fock approximation involved the dissociation energies of diatomic molecules, e.g. F_2[9,39] and O_2[41]. A more recent example is the work of Kirby-Docken and Liu[73] on the $X^1\Sigma^+$ ground state of CO. Using a large basis set of Slater functions, they carried out an 11-configuration SCF calculation to define the valence orbitals, which include the 2π and 6σ orbitals as well as those occupied in the Hartree–Fock configuration:

$$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 1\pi^4 \tag{23}$$

This was followed by a full valence CI (which includes up to sextuple excitations) of 176 configurations. This allows the CI potential energy curve to have the proper shape (i.e. the C and O atoms separate properly[4]) and the resulting dissociation energy, 11.32 eV, agrees very well with experiment[78], 11.23 eV. By comparison, the Hartree–Fock dissociation energy[16], 7.93 eV, contains an error of 3.3 eV or 76 kcal/mol. The same paper contains a detailed theoretical examination of the vibrational spectroscopy of CO and shows that both the valence CI and first-order wave functions provide good agreement with the experimental dipole moment function.

Possibly the most spectacular energetic failure to date of the Hartree–Fock approximation occurs for the $F + H_2$ reaction[79]. The DZ + P SCF barrier height is 29.3 kcal, compared to the experimental activation energy of only 1.7 kcal. Thus Hartree–Fock theory predicts that the $F + H_2$ reaction will not occur at all under normal conditions, while in fact this system is extremely reactive. Fortunately, even a modest CI, using first-order wave functions and a DZ + P basis yields a low predicted barrier[79], in agreement with experiment. More recent studies[80] have shown that the $F + H_2$ system is one for which higher than double excitations are critically important. That is, S + D CI, even carried out with a near Hartree–Fock basis set, yields a barrier of ~ 6 kcal. However, including all single and double excitations relative to *seven* reference configurations (the full valence CI) lowers the predicted barrier by ~ 3 kcal. The remaining discrepancy with the experimental activation energy appears to be primarily due to the fact that the reactants F + H_2 have more zero-point vibrational energy than does the transition-state structure[80].

Some of the energetic failings of the Hartree–Fock approximation can be corrected using rather simple models. An important example is the singlet–triplet separation $\Delta E(^3B_1 - {}^1A_1)$ in methylene. Definitive CI studies[81] suggest a value of 11 ± 2 kcal, but the Hartree–Fock limit is much larger, 24.8 kcal[82]. However, comparison of the SCF orbital occupancies, equations (7) and (8), for $^1A_1$ and $^3B_1$ CH_2 suggests an inconsistency. That is, although the $3a_1$ and $1b_1$ orbitals are equally utilized in the $^3B_1$ SCF wave function, the $1b_1$ orbital is not occupied at all in (7), the $^1A_1$ SCF description. This suggests[81,83] that a comparable treatment of the $^1A_1$ state is the two-configuration (TC) SCF wave function:

$$\begin{aligned}\psi &= C_1\, 1a_1^2 2a_1^2 1b_2^2 3a_1^2 \\ &\quad + C_2\, 1a_1^2 2a_1^2 1b_2^2 1b_1^2 \end{aligned} \tag{24}$$

Detailed calculations[82] do indeed show that the TCSCF energy of singlet CH_2 is 10.9 kcal above the SCF energy of triplet CH_2 as one approaches the Hartree–Fock limit. Thus we see that a relatively simple theoretical model provides good agreement with large-scale CI calculations. Based on this agreement a $\Delta E(^3B_1 - {}^1A_1)$ value of – 18.6 kcal (singlet state lies lower here) can be predicted with some confidence for SiH_2, a molecule for which such extensive CI studies would be more difficult. Additional predictions[84] based on this *ab initio* model are given for halocarbenes in Table 9.

As another example of the importance of electron correlation in energetic predictions, we turn to a larger molecule, glyoxal $(HCO)_2$. The ground and three lowest triplet states of glyoxal have electron configurations

$$^1A_g \ldots 5b_u^2 6a_g^2 1a_u^2 6b_u^2 1b_g^2 7a_g^2 \tag{25}$$

$$^3A_u \ldots 5b_u^2 6a_g^2 1a_u^2 6b_u^2 1b_g^2 7a_g 2a_u \tag{26}$$

$$^3B_u \ldots 5b_u^2 6a_g^2 1a_u^2 6b_u^2 7a_g^2 1b_g 2a_u \tag{27}$$

$$^3B_g \ldots 5b_u^2 6a_g^2 1a_u^2 1b_g^2 7a_g^2 6b_u 2a_u \tag{28}$$

The first *ab initio* study[85] of the three triplet states (26)–(28) was carried out at the DZ SCF level. The most surprising results concerned the ^3B_u or $\pi \rightarrow \pi^*$ triplet state, which was predicted to have a structure quite different from the ground state. The ^3B_u C–C distance was 1.353 Å, much less than the 1.508 Åfor the ground state, and the C=O separation was predicted to be 1.356 Å, as opposed to the much shorter 1.215 ground-state value. Thus the lowest $\pi \rightarrow \pi^*$ triplet state has a diradical character quite unlike the ^1A_g ground state. Although this result was unexpected, the reliability (discussed above) of DZ SCF geometry predictions is quite high and these bond distances are probably within 0.02 Å of the exact (unknown) values.

Much more suspect was the very low excitation energy T_e, 14,900 cm^{-1}, predicted for the ^3B_u state. This result was well below the experimental 19,200 cm^{-1} T_e value[86] for the $n \rightarrow \pi^*$ triplet state (^3A_u), thought to be the lowest triplet of glyoxal. For this reason, the theoretical study was extended[87] to the DZ + P SCF and DZ CI levels, and these results are illustrated in Figure 4. There we see indeed that both d functions on C and O and CI raise the relative energy of the ^3B_u state. An additional correction for higher excitations was made using Davidson's formula[66]

TABLE 9. Structural and energetic predictions for simple carbenes. Theoretical results are from Reference 84 and experimental values are in parentheses

	Triplet structure			Singlet structure			
Molecule	r(C–H) (Å)	r(C–X) (Å)	θ (deg.)	r(C–H) (Å)	r(C–X) (Å)	θ (deg.)	ΔE (singlet – triplet)
CH_2	1.075	–	128.8	1.106 (1.11[a])	–	102.5 (102.4[a])	12.3
CHF	1.077	1.321	120.4	1.111 (1.121[b])	1.325 (1.314[c])	102.2 (101.6[c])	– 9.2
CHCl	1.075	1.735	123.3	1.101 (1.12[d])	1.762 (1.689[d])	102.0 (103.4[d])	– 1.6
CHBr	1.075	1.891	125.6	1.103	1.972	102.6	1.1
CF_2	–	1.311	117.8	–	1.306 (1.300[e])	104.3 (104.9[e])	– 45.3
CCl_2	–	1.730	125.5	–	1.756	109.4	– 13.5

[a] G. Herzberg, *Electronic Spectra of Polyatomic Molecules,* D. Van Nostrand Company, Princeton, New Jersey, 1967.

[b] Assumed.

[c] A. J. Merer and D. N. Travis, *Can. J. Phys.,* 44, 1541 (1966).

[d] A. J. Merer and D. N. Travis, *Can. J. Phys.,* 44, 525 (1966).

[e] C. W. Matthews, *Can. J. Phys.,* 45, 2355 (1967).

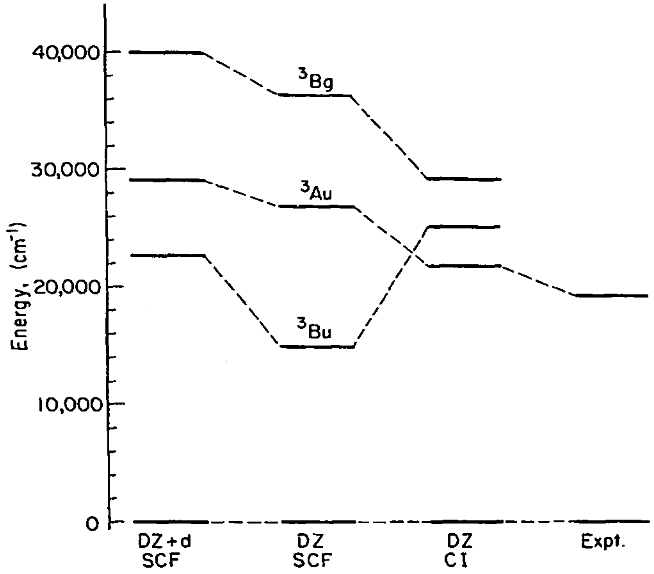

FIGURE 4. Adiabatic excitation energies T_e for the three lowest triplet states of glyoxal. The three different levels of theory plotted on the x axis are described in the text.

and this suggests that the actual position of the ^3B_u state is at $T_e \sim 28{,}000$ cm^{-1}, lying very close to the second $n \rightarrow \pi^*$ triplet, the ^3B_g state. Thus it is clear that Hartree–Fock energy differences should not be considered particularly reliable unless there are strong reasons for believing that the correlation energies of the states involved are nearly equal.

It should be finally noted that there are a significant number of chemical reactions which Hartree–Fock theory is inherently incapable of describing. A particularly well-studied[88] example is the carbyne least-motion insertion reaction:

$$CH(^2\Pi) + H_2 \rightarrow CH_3 \qquad (29)$$

The orientation of the four atoms during the least-motion approach is illustrated at the bottom of Figure 5. The problem arises because the electron configuration for the reactants is

$$^2\Pi \ CH + H_2 \ 1a_1^2 2a_1^2 3a_1^2 4a_1^2 1b_1 \qquad (30)$$

while that for the product CH_3 radical is (retaining the common C_{2v} elements of symmetry)

$$^2A_2'' \ CH_3 \ 1a_1^2 2a_1^2 3a_1^2 1b_2^2 1b_1 \qquad (31)$$

Thus the least-motion insertion is Woodward–Hoffman-forbidden[89] and should have a large barrier.

From a theoretical viewpoint (30) and (31) represent distinctly different solutions to the Hartree–Fock equations. That is, single-configuration Hartree–Fock theory does not allow a continuous description of the potential energy surface of this reaction. The simplest qualitatively meaningful treatment of the least-motion insertion would be a two-configuration SCF involving both (30) and (31) in a variational manner. Such a treatment has been reported recently, with the TCSCF

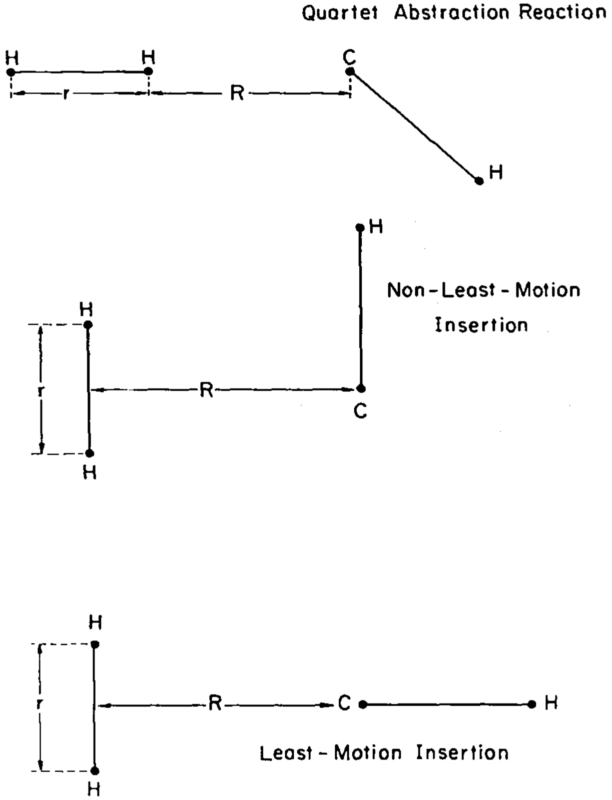

FIGURE 5. Geometrical approaches investigated for the CH + H_2 reaction.

being followed by S + D CI in terms of a DZ + P basis set[88]. The results are summarized in Figure 6, where it is seen that the barrier is indeed large, ~ 76 kcal.

For completeness it must be noted that there are *non*-least-motion pathways for (29) which involve no barrier at all. One such pathway is depicted in the middle of Figure 5, and the corresponding potential energy surface is given in Figure 7. Thus carbynes (of which CH is the simplest) are quite analogous to carbenes[90] in the mechanism of their insertion reactions with saturated hydrocarbons.

The above examples are obviously by no means exhaustive, and the reader is referred elsewhere[4, 91] for discussions in greater depth. Hopefully, however, the selected examples will allow at least a zero-order evaluation of *ab initio* theoretical studies appearing in the literature.

IV. THE ELECTRONIC STRUCTURE OF KETENE

A. Ground State of Ketene

Ketene and allene are both important examples of the quality of prediction attainable from *ab initio* ground-state calculations. As shown in Table 10, the optimized structure of ground-state ketene as determined by the authors[92] is

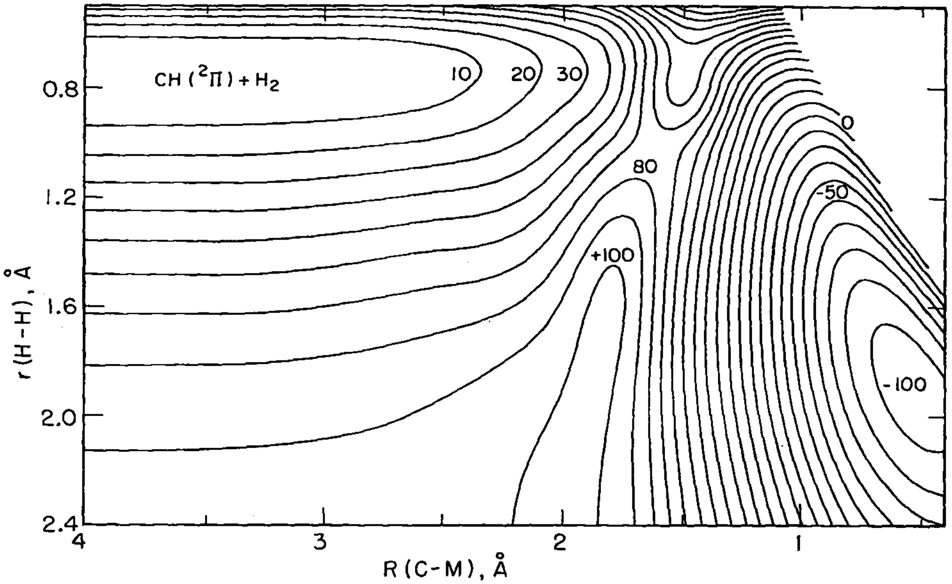

FIGURE 6. Configuration interaction potential energy surface for the least-motion insertion reaction CH($^2\Pi$) + H_2 → CH_3. See bottom of Figure 5 for the coordinate system adopted.

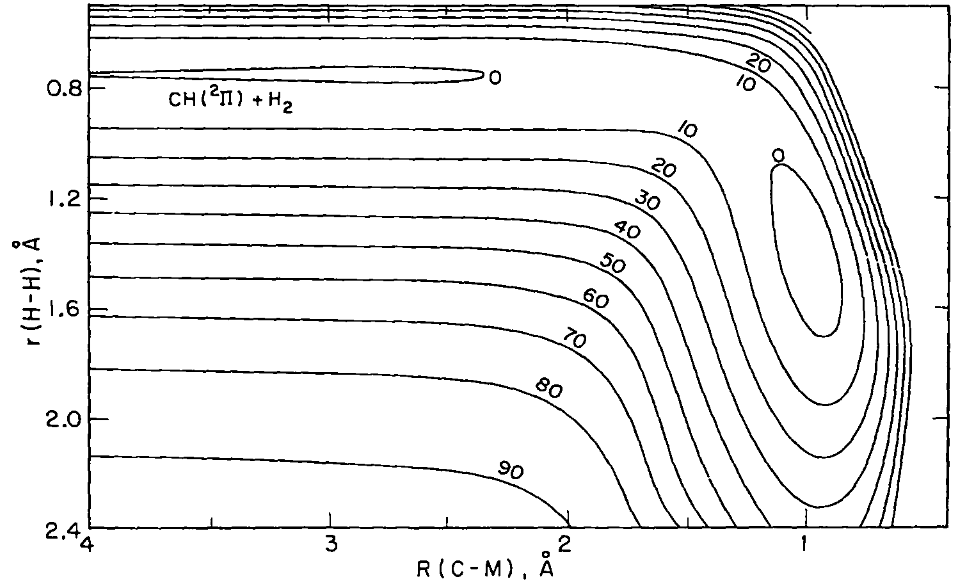

FIGURE 7. Configuration interaction potential energy surface for the non-least-motion insertion reaction CH($^2\Pi$) + H_2 → CH_3. See middle of Figure 5 for the coordinate system used.

TABLE 10. Ground-state structure of ketene

	Experiment[a]	DZ SCF[b]	MBS SCF[c]
R(C=O) (Å)	1.161 ± 0.010	1.171	1.18
R(C=C) (Å)	1.314 ± 0.010	1.311	1.30
R(C–H) (Å)	1.071 ± 0.002	1.070	–
θ(HCH) (deg.)	122.3 ± 0.2	120.1	–

[a] R(C=O) and R(C=C) from Reference 93; R(C—H) and θ(HCH) from Reference 95.
[b] Reference 92.
[c] Reference 94.

within the error limits of experimental measurement of the C=O and C=C bond lengths[93]. These calculations were performed at the SCF level of theory and used a Huzinga–Dunning[15] double zeta (DZ) basis set. An earlier minimum basis set SCF study by Del Bene[94] produced a slightly longer C=O bond length prediction, though still within 0.02 Å of experiment. Recent SCF calculations[96] where the double zeta basis set was supplemented by polarization functions (DZ + P) yielded a bond angle prediction of 122.0°, again in good agreement with experiment.

The equilibrium structure of ground-state ketene has C_{2v} symmetry with reflection planes coincident with the plane of the molecule and perpendicular to the

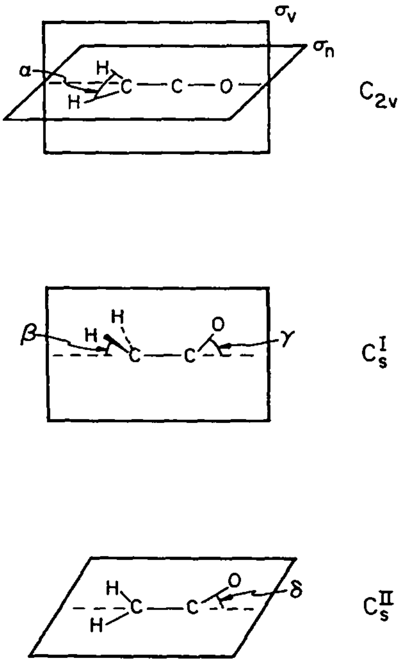

FIGURE 8. Ketene geometries. The ground state of ketene has C_{2v} symmetry. There are two distinct C_s symmetry types which are appropriate for low-lying excited states. In what is designated C_s^I, the reflection plane perpendicular to the molecular plane of the C_{2v} structure is preserved. The hydrogens can be positioned out of the original molecular plane at an angle β, and the oxygen at an angle γ. In C_s^{II}, the molecule is planar but the oxygen is bent away from the C–C axis at an angle δ.

plane of the molecule, as shown in Figure 8. Thus, from a valence set of atomic orbitals, molecular orbitals of symmetry type a_1, b_1 and b_2 can be constructed. By analogy with methylene, the most common convention for designating b_2 orbitals is that they are antisymmetric with respect to reflection through the plane perpendicular to the plane of the molecule, such as an antisymmetric combination of the 1s atomic orbitals on the hydrogens. a_2-Type orbitals can be constructed only from 2p atomic functions on the hydrogens or 3d functions on the carbons or oxygen and should not be important for valence states. The early approximate molecular orbital calculations of Dixon and Kirby[97] give the ground-state orbital occupancy, which was later confirmed by *ab initio* studies.

$$1a_1^2 2a_1^2 3a_1^2 4a_1^2 5a_1^2 6a_1^2 7a_1^2 1b_2^2 1b_1^2 2b_2^2 2b_1^2 \qquad (32)$$

2p atomic orbitals of oxygen and the carbons can combine to produce the π orbitals typically identified with double bonds. The designation of π orbitals, of course, is strictly appropriate for linear molecules only. However, for formaldehyde only the in-plane 2p orbitals can mix with the hydrogen 1s orbitals, so it is customary to refer to the out-of-plane combinations of 2p C and O atomic orbitals as π molecular orbitals. The oxygen n orbital is then perpendicular to the orientation of the π orbitals. For ketene, it is probably less appropriate to make n and π designations; however, if we chose to extend the formaldehyde description we would expect an out-of-plane b_1 orbital for the C=C π bond. The C=O π bond would be perpendicular to this making it a b_2-type MO, and the oxygen n orbital would then have to be a b_1 orbital.

In Table 11 are given orbital energies at the DZ predicted equilibrium geometry. Both DZ and DZ + P results are displayed, along with the Mulliken populations based on the DZ + P basis set. The orbital energies are quite similar for the two basis sets and may be compared with the experimental photoelectron spectrum via Koopmans theorem[98]. Baker and Turner[99] identify three adiabatic ionization potentials at 9.64, 14.62 and 16.08 eV and a fourth (for which the true adiabatic peak may be obscured by the second band) at 13.84 eV. The observed first ionization potential is clearly associated (in the molecular orbital picture) with the removal of an electron from the $2b_1$ orbital ($\epsilon = 0.3674$ hartree $= 10.00$ eV). However, the next three orbital energies [$\epsilon(2b_2) = 15.26$ eV, $\epsilon(1b_1) = 17.46$ eV and $\epsilon(1b_2) = 17.89$ eV] are significantly higher than the observed adiabatic IPs. This is probably due to neglect of electronic reorganization in the positive ion states and their somewhat different geometries. It is also worth noting that correlation effects can alter the ordering of ionic states predicted on the basis of either Koopmans theorem or direct hole-state calculations[4].

The Mulliken populations in Table 11 indicate the qualitative character of the molecular orbitals. The methylene carbon with a total atomic population of 6.58 has the largest partial negative charge. The oxygen is less negatively charged (0.28 'electrons') while the central carbon has a total atomic population less than that of a neutral carbon atom. The $2b_1$ orbital has its greatest electron density on the methylene carbon. The largest oxygen 2p population is in the $1b_1$ orbital, indicating it most closely corresponds to an n orbital, though again the n and π designations are not entirely appropriate. The -0.65 a.u. orbital energy of the $1b_1$ orbital is consistent with oxygen n orbital energies of other carbonyls, such as glyoxal[100]. The experimental value of the dipole moment[101] is 1.4 D. The double zeta SCF calculations predict a value of 2.2 D, but if polarization functions are included, 1.8 D is predicted. The remaining difference of 0.4 D or about 25% is about the error expected for evaluating dipole moments with uncorrelated wave functions[102].

TABLE 11. Ground-state orbital energies and Mulliken populations for ketene[a]

			Methylene carbon			Hydrogen		Carbon			Oxygen		
Orbital	ϵ (DZ)	ϵ (DZ + P)	s	p	d	s	p	s	p	d	s	p	d
$1a_1$	−20.6421	−20.6333	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	2.000	0.000	0.000
$2a_1$	−11.4165	−11.4035	0.000	0.000	0.000	0.000	0.000	2.000	0.000	0.000	0.000	0.000	0.000
$3a_1$	−11.2590	−11.2488	2.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
$4a_1$	−1.5011	−1.4713	0.010	0.003	0.001	−0.001	−0.001	0.363	0.223	0.029	1.235	0.098	0.040
$5a_1$	−1.0708	−1.0582	0.953	0.082	0.017	0.088	0.004	0.327	0.346	0.014	0.042	0.033	0.002
$6a_1$	−0.7557	−0.7597	0.164	0.160	0.002	0.107	0.002	0.257	0.031	0.000	0.332	0.833	0.003
$7a_1$	−0.6855	−0.6830	0.073	0.650	0.018	0.186	0.003	0.032	0.374	0.001	0.102	0.376	−0.001
$1b_2$	−0.6687	−0.6573	0.000	0.670	0.000	0.228	0.004	0.000	0.401	0.000	0.000	0.457	0.007
$1b_1$	−0.6539	−0.6415	0.000	0.096	0.003	0.000	0.000	0.000	0.560	0.010	0.000	1.317	0.012
$2b_2$	−0.5610	−0.5609	0.000	0.434	0.007	0.179	0.002	0.000	0.172	0.033	0.000	0.985	0.008
$2b_1$	−0.3684	−0.3674	0.000	1.231	0.006	0.000	0.005	0.000	0.304	0.045	0.000	0.404	−0.001
	Function totals		3.199	3.326	0.054	0.787	0.019	2.979	2.412	0.133	3.711	4.503	0.070
	Atom totals			6.579		0.807			5.524			8.284	

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[a] From Reference 92.

The lowest unoccupied orbitals of ketene are the $3b_2$, roughly a C=O π^* orbital, and the $3b_1$, which may be thought of as a C=C π^* orbital. Two configuration test calculations[92] on the ground state show little correlation effect except for the $2b_1^2 \rightarrow 3b_1^2$ substituted configuration which results in an energy lowering of 0.0242 a.u. However, this is sufficiently small that one can be sure that the configuration corresponding to the SCF wave function strongly dominates the exact solution of the Schrödinger equation. The closeness of the SCF-predicted equilibrium geometry with the experimental results is possible, in part, because of this.

B. Excited States and Reactions

Since ketenes are convenient sources of carbene radicals[103], the photochemistry of ketene has received considerable experimental and theoretical attention. One of the most characteristic features of ketene photochemistry is a dependence on the wavelength of the absorbed radiation[104]. Both triplet and singlet methylene appear to be formed[105] at wavelengths less than 3700 Å, but the triplet fraction reported varies[106,107] from 26% at 2139 Å to 75% at 3660 Å. Since the first excited state of the CO molecule is high-lying, spin conservation requires that triplet and singlet methylene originate, respectively, with excited triplet and singlet states of ketene.

Experimental studies of the ketene electronic spectrum have not yielded any explanations of the photochemistry. At very short wavelengths, the absorption bands appear sharp. Price, Teegan and Walsh[108] were able to recognize six band systems between 54,680 and 75,180 cm^{-1} as being the $n = 3, 4, 5, 6, 7$ and 8 members of a $\pi \rightarrow ns$ Rydberg series. At longer wavelengths, Price and coworkers suggested that the strong system of diffuse bands around 2100 Å (47,600 cm^{-1}) may arise from a carbonyl $\pi \rightarrow \pi^*$ excitation and that the 3200 Å (31,300 cm^{-1}) system probably arises from the excitation of a nonbonding electron on the oxygen atom. Still lower in energy in the region between about 3700 Å and 4700 Å, Dixon and Kirby[97] analysed the ketene absorption spectrum and predicted a $^3A_2$ state and a $^1A_2$ state to occur at 22,400 and 27,700 cm^{-1}, respectively. These states correspond to the orbital occupancy

$$\ldots 7a_1^2\,1b_2^2\,1b_1^2\,2b_2^2\,2b_1\,3b_2 \tag{33}$$

They also predicted a $^3A_1$ state at 30,300 cm^{-1} arising from the occupancy

$$\ldots 7a_1^2\,1b_2^2\,1b_1^2\,2b_2^2\,2b_1\,3b_1 \tag{34}$$

The corresponding $^1A_1$ state was predicted to lie around 57,000 cm^{-1}. After analysing the spectrum progressions, Dixon and Kirby were able to conclude that the equilibrium structures of the $^3A_2$ and $^1A_2$ states have in-plane bent CCO skeletons.

Rabelais, McDonald, Scherr and McGlynn[109] examined the spectrum between 1940 Å and 3800 Å and came to nearly the same conclusions. However, they suggest that the $^3A_1$ is partially responsible for the absorption bands assigned to the $^3A_2$ and $^1A_2$ states by Dixon and Kirby. They also predict a lower energy of 47,000 cm^{-1} for the excited $^1A_1$ state.

The more recent experimental work of Laufer and Keller[110] indicates substantially lower values of 21,300 and 19,200 cm^{-1} for the first excited singlet and triplet states, respectively, than the previous determinations. Furthermore, they conclude that a single singlet–singlet transition is responsible for the absorption spectrum in the region between 2600 Å and 4700 Å and that there are no spin-forbidden transitions. This contradiction with other experimental results leaves the nature of the low-lying states quite unclear.

TABLE 12. Ketene excited states[a]

C_{2v} symmetry		Final symmetry		Minimum basis SCF results[b]				
				Structural parameters				Excitation energy (cm^{-1})
State	Excitation	State	Excitation	R (C=O)	R (C=C)	γ	δ	
$^1A_1$	g.s.	–	–	1.18	1.30	–	–	0.0
$^3A_2$	$2b_1 \rightarrow 3b_2$	$C_s^{II}\,{}^3A''$	$2a'' \rightarrow 10a'$	1.26	1.36	–	53	19,800
$^1A_2$	–	$C_s^{II}\,{}^1A''$	–	1.24	1.37	–	50	26,900
$^3A_1$	$2b_1 \rightarrow 3b_1$	$C_s^{I}\,{}^3A'$	$9a' \rightarrow 10a'$	1.20	1.54	57	–	13,800
2^1A_1	–	$C_s^{I}\,{}^1A'$	–	–	–	–	–	–
2^3A_1	$2b_2 \rightarrow 3b_2$	$C_s^{II}\,{}^3A'$	$2a'' \rightarrow 3a''$	–	–	–	–	–
3^1A_1	–	$C_s^{II}\,{}^1A'$	–	–	–	–	–	–

[a] Structural parameters defined in Figure 8. Bond lengths are in Angstroms and angles are in degrees.
[b] Reference 94.
[c] Reference 92.

A number of important theoretical studies have been undertaken with the intent of explaining the electronic absorption spectrum by determining the excited state energies, or unravelling the photochemistry by looking at dissociation pathways. A notable semiempirical study by Yoshida and Kobayashi[111] supported the conclusions of Dixon and Kirby by predicting the $^3A_2$, $^1A_2$, $^3A_1$ and $^1A_1$ excited states to lie in the regions 19,000–30,000, 22,000–31,000, 27,000–40,000 and 49,000–66,000, respectively. Interestingly, Yoshida and Kobayashi also assigned the weak band around 46,500 cm^{-1} observed by Knox, Norrish and Porter[112] to be a $^1B_1$ state arising from an $n \rightarrow \sigma^*$ excitation with electronic configuration

$$\ldots 7a_1^2\,1b_2^2\,1b_1^2\,2b_2^2\,2b_1\,8a_1 \qquad (35)$$

A number of *ab initio* studies of ketene have been reported in the literature[92,94,96,113-119]. Those of Del Bene[94], Basch[118], Dykstra and Schaefer[92] and Harding and Goddard[117] have the most bearing on ketene excited states. The work of Del Bene is of particular importance because it confirmed the conclusion of Dixon and Kirby[97] that the $^3A_2$ and $^1A_2$ states were in-plane bent. Del Bene treated excited states by performing a CI calculation which included 36 singly substituted configurations, relative to the ground state and using ground-state orbitals. Such a procedure will give energies roughly equivalent with those obtained by an open-shell SCF procedure, since open-shell SCF can be reformulated as a CI problem involving single substitutions of the open-shell SCF configuration[7]. Performing independent ground- and excited-state calculations may produce small nonorthogonality between states of the same spin and symmetry, whereas in Del Bene's approach all states are necessarily orthogonal. For three excited states, the C–C–O in-plane or out-of-plane angle was optimized along with the C=O and C=C bond lengths.

As represented in Figure 8, bending of the C–C–O axis reduces the molecular symmetry to C_s. For in-plane bending, all a_1 and b_2 orbitals become a', and all b_1 orbitals become a''. For out-of-plane bending, a_1 and b_1 orbitals become a', and b_2 orbitals become a''. Del Bene's geometry optimization results which are included in Table 12, show several interesting features. The $2b_1 \rightarrow 3b_2$ promotion produces in-plane C–C–O bending. The $2b_1 \rightarrow 3b_1$ promotion produces out-of-plane bending and surprisingly lengthens the C=C bond to a distance typical of a single bond.

Double zeta SCF results^c

Structural parameters							Excitation energy (cm^{-1})
R (C=O)	R (C=C)	R (C–H)	α	β	γ	δ	
1.171	1.311	1.070	120.1	–	–	–	0.0
1.200	1.459	1.076	117.8	–	–	48.3	11,710
1.201	1.455	1.076	118.3	–	–	49.1	13,940
1.190	1.519	1.069	124.1	23.9	53.3	–	15,220
1.195	1.514	1.069	124.3	24.7	52.2	–	18,070
1.422	1.315	1.077	116.6	–	–	51.7	23,020
1.423	1.315	1.077	116.6	–	–	51.8	24,360

These results are largely supported by the DZ SCF calculations[92] of the authors, also presented in Table 12. In these more recent calculations[92] all structural parameters for six excited states were fully optimized. As seen in Figure 9, the energy lowering from geometry optimization is large. Unlike Del Bene, we find no reversal of the ordering of the $^3A_2$ and $^3A_1$ states upon optimization, though there is a reduction in the separation energy. It is quite clear that both $2b_1 \rightarrow 3b_2$ and $2b_1 \rightarrow 3b_1$ produce low-lying excited states, but since correlation effects could be several thousand wave numbers, a definite prediction as to which is the lowest is not yet possible.

Basch[118] performed SCF and multiconfiguration SCF calculations on four ketene excited states with a double zeta basis that was augmented by a diffuse S function. [The established convention (also employed here) for designating b_1 and b_2 orbital symmetry is opposite that used in Basch's paper.] One of the most interesting to come out of Basch's research is that the $^3B_1$ and $^1B_1$ states of ketene have significant Rydberg character. The calculated (vertical) $^1A_1 \rightarrow {}^1B_1$ excitation energy is 51,600 cm^{-1}, in reasonable agreement with the experimental $n = 3$ member (54,680 cm^{-1}) of the Price[108] Rydberg series.

Basch did not optimize geometries and did not consider the $^3A_1$ state studied by Del Bene[94]. To provide a more comprehensive understanding of the excited states of ketene, Dykstra and Schaefer[92] performed SCF calculations on 18 excited states at the predicted ground-state equilibrium geometry (vertical geometry) with a DZ basis, a double zeta plus polarization set (DZ + P), and a third basis in which diffuse or Rydberg functions were added to the DZ set (DZ + R). Using the even-tempered criterion of Raffenetti and Ruedenberg[120], two additional primitive Gaussian functions of s and p type were added to each C and O atom in the DZ + R basis. For carbon the added s functions have exponents $\alpha = 0.0474$ and 0.0146, while the p functions have exponents $\alpha = 0.0365$ and 0.0117. For oxygen the analogous four exponents are $\alpha = 0.0862, 0.0261, 0.0637$ and 0.0190.

The calculated excitation energies are given in Table 13 along with predicted dipole moments. The DZ and DZ + P predictions are quite comparable for all states considered. In general the excitation energies are slightly raised by the addition of polarization functions. The average difference between the two results is 2200 cm^{-1}; Similarly the DZ and DZ + P dipole moments are in rather close agreement, the average absolute value for the difference being 0.33 D.

The Rydberg functions dramatically lower the excitation energies of the $^3B_1$ and $^1B_1$ states to 44,300 and 45,900 cm^{-1}, respectively, from the DZ + P results of 77,100 and 84,700 cm^{-1}. With the inclusion of Rydberg functions, the $^3B_1$ state is

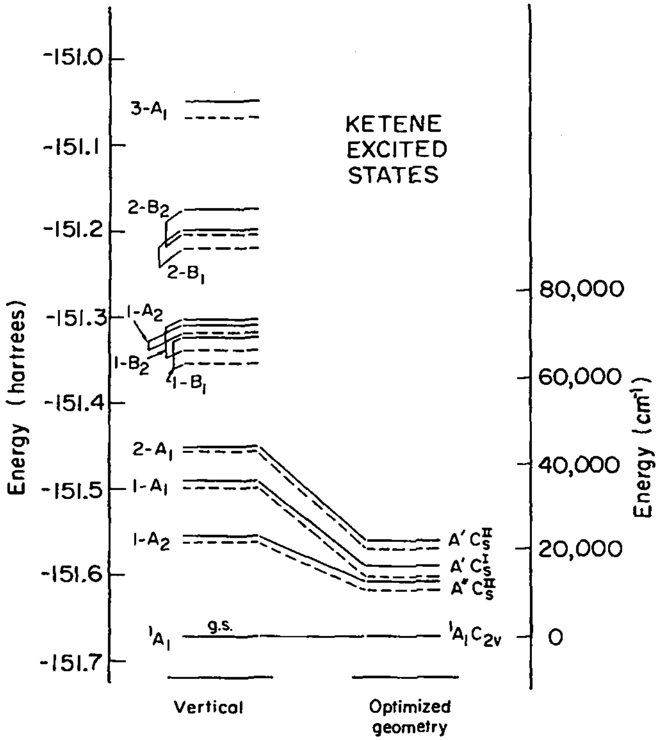


FIGURE 9. Ketene excited singlet states (solid lines) and triplet states (dotted lines). The vertical excitation energies are all for the geometry of the $^1A_1$ ground state. The optimized results refer to geometries separately determined for each state, and the reduced symmetry and corresponding state designations are shown.

predicted to be the third lowest-lying triplet. The other states for which excitation energies are substantially reduced by the DZ + R basis also involve excitation of an electron to the $8a_1$ orbital. Thus one can conclude that the Rydberg character of this orbital is relatively insensitive to the electronic state in which it appears. The very large excitation energies of the highest states (e.g. $3\,^3A_1$ and $4\,^1A_1$ states) are surely unrealistic because correlation effects may be extremely large for states so high in energy. However, calculation of the energy of these states indicates that while the electron configurations are plausible, the states are not low-lying.

Some idea of the size of correlation effects on vertical excitation energies of the $^1A_2$, $^3A_2$ and the first two $^3A_1$ states of ketene can be seen from the calculations of Harding and Goddard[117]. They used a DZ basis and determined generalized valence bond[7] (GVB) wave functions for the four excited states and ground state at the experimental ground-state geometry. The outermost eight electrons were correlated in the GVB treatment and the predicted excitation energies are given in Table 14. In addition, GVB CI calculations, also in Table 14, were performed. The GVB CI wave functions include configurations which are important with respect to the GVB wave function and thus should give the dominant electron correlation effect.

TABLE 13. SCF vertical excitation energies for ketene[a]

		Energy (cm^{-1})			Dipole moment (D)		
Electron configuration	State	DZ	DZ + R	DZ + P	DZ	DZ + R	DZ + P
$\ldots 7a_1^2 1b_2^2 1b_1^2 2b_2^2 2b_1^2$	$^1A_1$	0	0	0	−2.16	−2.22	−1.81
$\ldots 7a_1^2 1b_2^2 1b_1^2 2b_2^2 2b_1 3b_2$	$^3A_2$	24,120	23,670	25,570	−3.68	−3.72	−3.44
	$^1A_2$	25,700	25,270	27,520	−3.54	−3.58	−3.30
$\ldots 7a_1^2 1b_2^2 1b_1^2 2b_2^2 2b_1 3b_1$	$^3A_1$	38,030	37,410	40,790	−3.25	−3.21	−3.04
	$2\,^1A_1$	39,700	39,180	42,920	−3.39	−3.39	−3.12
$\ldots 7a_1^2 1b_2^2 1b_1^2 2b_2 2b_1^2 3b_2$	$2\,^3A_1$	47,030	46,490	49,440	0.07	0.04	0.56
	$3\,^1A_1$	48,440	47,890	51,470	0.07	0.03	0.55
$\ldots 7a_1^2 1b_2^2 1b_1^2 2b_2^2 2b_1 8a_1$	$^3B_1$	69,810	44,330	69,820	−1.97	−0.85	−2.44
	$^1B_1$	76,500	45,930	75,670	−4.10	−0.90	−4.24
$\ldots 7a_1 1b_2^2 1b_1^2 2b_2^2 2b_1^2 3b_2$	$^3B_2$	72,990	72,610	77,120	1.09	1.03	1.39
	$^1B_2$	80,970	80,500	84,680	0.66	0.61	1.12
$\ldots 7a_1^2 1b_2^2 1b_1^2 2b_2 2b_1^2 3b_1$	$2\,^3A_2$	77,460	76,280	80,020	0.96	1.27	1.44
	$2\,^1A_2$	79,430	78,120	82,030	0.68	1.02	1.20
$\ldots 7a_1 1b_2^2 1b_1^2 2b_2^2 2b_1^2 3b_1$	$2\,^3B_1$	98,930	98,020	103,110	2.29	2.58	2.55
	$2\,^1B_1$	103,510	102,450	108,110	1.61	2.03	1.95
$\ldots 7a_1^2 1b_2^2 1b_1^2 2b_2 2b_1^2 8a_1$	$2\,^3B_2$	102,550	78,040	101.820	−2.19	−2.00	−1.94
	$2\,^1B_2$	108,880	79,070	108,060	−1.63	−1.13	−1.79
$\ldots 7a_1 1b_2^2 1b_1^2 2b_2^2 2b_1^2 8a_1$	$3\,^3A_1$	132,370	111,390	132,100	−0.10	2.34	0.25
	$4\,^1A_1$	136,770	112,970	136,410	0.16	2.61	0.59

[a] All calculations were carried out at the predicted (DZ) ground-state equilibrium geometry. A negative dipole moment implies polarity C^+O^-.

TABLE 14 GVB vertical excitation energies for ketene[a]

	Excitation energies			
	GVB		GVB CI	
State	(eV)	(cm^{-1})	(eV)	(cm^{-1})
$^3A_2$	3.97	32,000	3.62	29,200
$^1A_2$	4.13	33,300	3.69	29,800
$^3A_1$	5.39	43,500	5.39	43,500
2^3A_1	6.82	55,000	7.37	59,400

[a] Table is adapted from Reference 117. The GVB results are taken as the GVB(4/PP) values in Reference 117.

The excitation energies of Harding and Goddard are larger than those obtained at the one-configuration SCF level. This is not a surprising result, since electron correlation is generally expected to be more important in closed-shell states, where all orbitals are doubly occupied, than open-shell states. The inclusion of additional configurations (GVB CI) refines the excitation energy predictions and reduces the $^3A_2-^1A_2$ state separation. The ordering of states at this level of treatment is unchanged from SCF results.

As already shown in Table 12 and Figure 9, geometry effects for the first six excited states are quite important. In the Dykstra and Schaefer[92] calculations, the positions of the hydrogens were relaxed when the excited-state structures were optimized. This resulted in an out-of-plane bending of the methylene group for the C_s^I states (see Figure 8). A comparison of these results with the minimum basis results of Del Bene[94] is of interest. We find that the DZ results yield much lower excitation energies. Also, Del Bene finds a separation of 7100 cm^{-1} between the $^3A''$ and $^1A''$ states, whereas a much smaller separation of 2200 cm^{-1} is predicted with the DZ basis. Thus it would appear that the minimum basis set yields energetic results quite different from those found near the Hartree–Fock limit, which is approached by our DZ + P results. For the $^3A''$ state, we predict C=O and C=C bond distances of 1.200 and 1.459 Å, where Del Bene predicts 1.26 and 1.36 Å. Similarly, for the $^1A''$ states, the DZ SCF predicted values are 1.201 and 1.455 Å, compared to Del Bene's 1.24 and 1.37 Å. The in-plane bond angle is predicted to be ~ 50° by both Del Bene and Dykstra and Schaefer for both the $^3A''$ and $^1A''$ states.

The vertical and adiabatic excitation energies of the $^3A_1$ ($^3A'$) and 2^1A_1 ($2^1A'$) states differ by over 20,000 cm^{-1}. For the $^3A'$ state, this enormous relative energy lowering was predicted by Del Bene, whose calculations suggested that the T_e value for the $^3A'$ is actually lower than those for the $^3A''$ and $^1A''$ states. In any case, the $^3A'$ and $^1A'$ states are quite low-lying, and will have to be dealt with in any comprehensive discussion of ketene photodissociation.

A complicating feature in understanding the electronic states of ketene may be realized from Figure 10, which is a correlation diagram for the lowest electronic states. The particular point we wish to note here concerns the connection between the lowest $^3A'$ and $^3A''$ states. For geometries with no elements of symmetry, of course, these two states are of the same irreducible representation, namely ^3A. To study the changeover between the two states, a geometry roughly half-way between the two was chosen:

$$R(\text{C=O}) = 1.20\ \text{Å},\ R(\text{C=C}) = 1.47\ \text{Å},\ R(\text{C=H}) = 1.07\ \text{Å};$$

$$\alpha = 121°, \beta = 12°, \gamma = 27°, \delta = 24°.$$

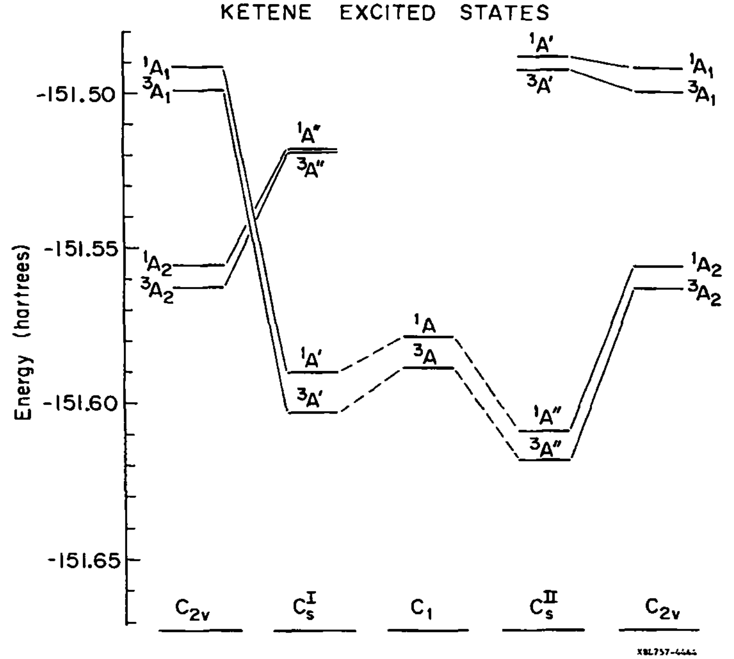


FIGURE 10. Correlation of lowest-lying states. The C_{2v} vertical excitation energies of the lowest two singlets and triplets are connected by a solid line with their optimized energy level in C_s^I or C_s^{II} symmetry. Above the lowest states of each C_s symmetry are the energies of the other two states at the geometry of the lower singlet or triplet. Allowing the oxygen to internally rotate from C_s^{II} to C_s^I type structure reduces the molecular symmetry to C_1 or no symmetry. Thus, the lowest singlet and triplet must correlate, as shown by dotted lines. An intermediate geometry was chosen for the C_1 energy levels.

As seen in Figure 10, there appears to be a barrier between the $^3A'$ and $^3A''$ states. A reliable prediction of the nature and position of this barrier would of course require examination of many other geometries. Also depicted in Figure 10 is the fact that when the $^3A''$ state (equilibrium geometry C_s^{II}) is studied with geometry appropriate to the $^3A'$ C_s^I equilibrium, it becomes quite high in energy. A true barrier in this internal rotation problem is a consequence of an avoided crossing in C_1 symmetry. Hence, it may be possible that the curve for the upper triplet state will have a minimum in a C_1 or totally unsymmetric structure. The relevant singlet states should be analogous.

The difficult problem of the dissociation of ketene has been approached by Basch[118] and Pendergast and Fink[119]. Basch calculated several points on a least-motion path (C_{2v} symmetry) for the ground state, $^3A_2$, $^1A_2$, $^3B_1$ and $^1B_1$ states. The $^3B_1$ and $^1B_1$ states were found to dissociate to $CH_2 + CO$ without a barrier, a result confirmed by the authors[92]. The A_2 states cross with B_1 states; however, in the C_s^{II} symmetry (in-plane bent) of the minimum energy structure of the A_2 states, the B_1 states will have the same irreducible representation, A'', and the B_1 and A_2 states

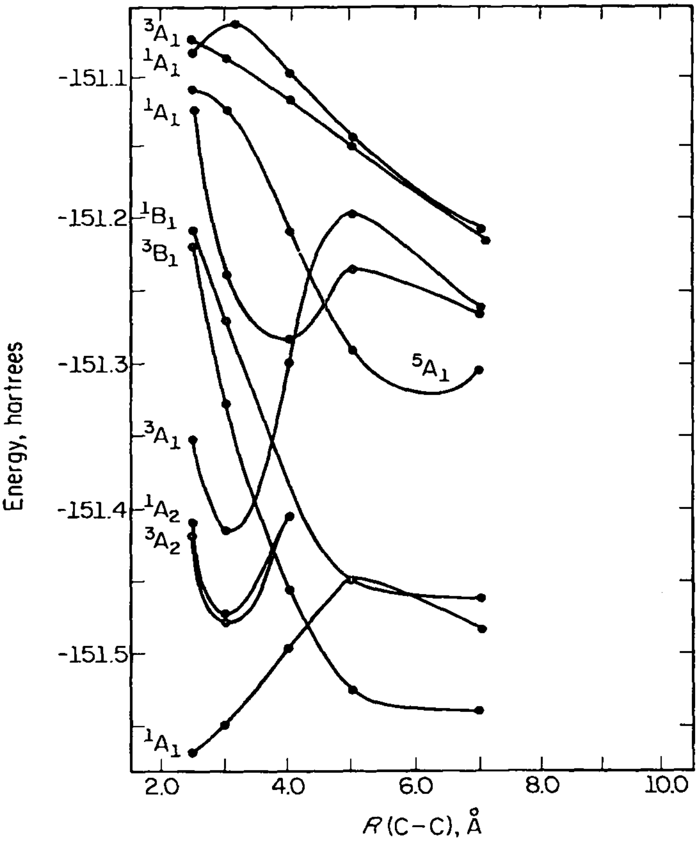


FIGURE 11. Ketene CI energies for the linear dissociation. Reproduced with permission from P. Pendergast and W. H. Fink, *J. Amer. Chem. Soc.*, 98, 648 (1976).

will have an avoided crossing. Excitation to the A_2 states could then lead to dissociation. The ground state has a very large activation barrier to dissociation.

Pendergast and Fink[119] accounted for some correlation effects by performing a CI calculation with a small set of selected configurations. They examined a C_{2v} least-motion dissociation of ketene for eight excited states and their results are represented in Figure 11. In addition, they also considered least-motion dissociation from an in-plane bent structure, with the results shown in Figure 12. Their C_{2v} curves are qualitatively similar to those obtained by Basch. The in-plane bent dissociation curves are quite important because they show that vertical excitation to the $^1A_2$ state would provide enough energy to directly dissociate on the bent pathway. The $^3A_2$ ($^3A''$) state has an even lower barrier to dissociation.

The theoretical studies of ketene excited states and its dissociation have resolved a few questions and provided interesting predictions of the nature of the states. However, it is clear that very important questions remain which will require large-scale calculations to fully account for basis set and correlation effects. It does seem likely, though, that further theoretical progress over the next several years will help unravel the details of ketene photochemistry.

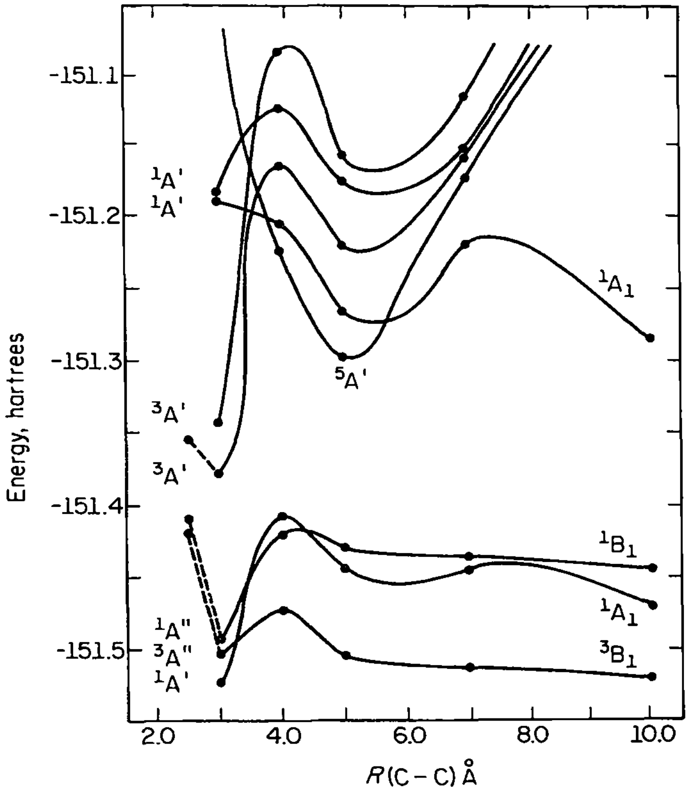
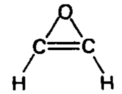


FIGURE 12. Ketene CI energies for the bent dissociation. The leftmost points connected with dashed lines to the solid curves correspond to the energies of the C_{2v} symmetry states. Reproduced with permission from P. Pendergast and W. H. Fink, *J. Amer. Chem. Soc.*, 98, 648 (1976).

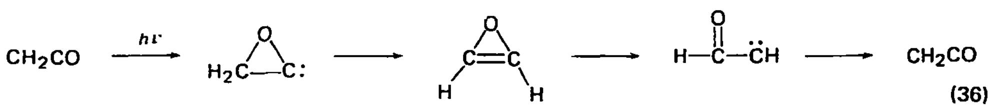
C. C_2H_2O Isomers

Photolysis studies of isotopically labelled ketene by Russell and Rowland[121] suggested that production of an appreciable yield of ^{14}CO from ^{14}CO from $^{14}CH_2CO$ requires the active participation of an oxirene intermediate (1). After observing



(1)

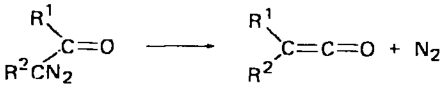
scrambling of ^{14}C in ketene following irradiation, they suggested one possible reaction pathway (equation 36). Production of the cyclic carbene was postulated to



(36)

occur from rearrangement of an electronically excited singlet state. This idea is not consistent with the theoretical studies already discussed which show that the lowest two singlet states (and triplet states) are C—C—O bent. Scrambling of ^{14}C and production of ^{14}CO from initial $^{14}CH_2CO$ is possible because of the symmetric positions of the carbons in the oxirene structure.

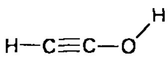
In later experiments, Montague and Rowland[122] reacted isotopically labelled methylene with CO and determined that only singlet methylene leads to formation of oxirene. These two studies[121,122] suggest the importance of oxirene and formyl carbene as intermediates in reactions of excited ketene, and also perhaps in the Wolff decomposition and rearrangement of diazo ketones (equation 37). Since the


(37)

mechanism of this reaction is unknown, theoretical methods have been applied to help unravel some of the details of the possible intermediates. MINDO and NDDO semiempirical results of Dewar and Ramsden[123], for instance, indicate that formyl carbene is higher in energy than oxirene and furthermore rearranges without any barrier into ketene. The *ab initio* SCF calculations of Strausz and coworkers[124], however, show oxirene to be less stable than formyl carbene by 11.8 kcal, with a ring-opening activation energy of 7.3 kcal. SCF calculations[125] with a smaller basis set and without optimization of geometrical parameters have predicted essentially identical energies for oxirene and formyl carbene, with both around 70 kcal less stable than ketene.

Oxirene and formyl carbene appear to be sufficiently high in energy — perhaps above the ketene dissociation limit — that their importance in equation (36) may be as transition states rather than as stable intermediates. Lower energy structures, however, are plausible and should not be ignored in considering ketene-related reactions. Baird and Taylor[126], for example, have shown from SCF calculations that the triplet state of formyl carbene is substantially more stable than the singlet state, with the predicted singlet—triplet separation being around 25 kcal.

A recent study by Dykstra[96] has compared the structures and energies of ketene and oxirene and a little-studied isomer, ethynol (2). While ethynol is not experi-


(2)

mentally known, SCF calculations of Radom, Hehre and Pople[127] suggested that it may lie only 35 kcal above ketene. In addition, extensive SCF calculations of Bouma and coworkers[128] have recently demonstrated the stability of vinyl alcohol, an analogous molecule. Used in the calculations of Dykstra[96] were both a double zeta (DZ) basis set and a double zeta plus polarization function set (DZ + P). Calculations were done both at the one-configuration self-consistent-field (SCF) level and with well correlated wave functions using the self-consistent electron pairs method (SCEP)[54,129]. SCEP is an efficient iterative procedure that variationally includes into a wave function dominated by a closed-shell reference configuration the doubly and then singly substituted configurations. Recently, SCEP has been extended[130] so that following the singles and doubles treatment, diagonally substituted (e.g. $i^2j^2 \rightarrow a^2b^2$) closed-shell quadruple configurations are variationally

TABLE 15. Optimized structures of oxirene and ethynol[96]

	DZ SCF	DZ + P SCF
Oxirene		
R(C=C) (Å)	1.261	–
R(C–O) (Å)	1.548	1.467
R(C–H) (Å)	1.057	–
θ(CCH) (deg.)	162.49	162.65
Ethynol		
R(C–H) (Å)	1.051	–
R(C≡C) (Å)	1.193	–
R(C–O) (Å)	1.322	–
R(O–H) (Å)	0.953	–
θ(COH) (deg.)	115.56	109.50

added to the total wave function. The virtual or external orbitals used for the quadruples are natural orbitals from the singles and doubles wave function and thus the set of quadruple configurations include those which are important for size-consistency[55] corrections. The DZ + P calculation on ethynol spanned a huge space of over 63,000 symmetry-adapted configurations.

Geometrical parameters of oxirene and ethynol were fully optimized at the DZ SCF level and bond angles were reoptimized with the DZ + P basis. The predicted structural parameters are given in Table 15. The oxirene results show a much longer C—O bond length than predicted by MINDO/3 calculations[123] but are in agreement with earlier *ab initio* results[124]. The C—O bond length was reoptimized with the DZ + P basis because it affects the C—O—C and C—C—O angles. However, contraction of bond lengths when polarization functions are added at the SCF level is expected[4] and thus, the true bond length is probably between 1.47 and 1.55 Å. The energy lowering for reoptimization of the C—O bond length was 3.3 kcal and can probably be taken as an upper limit to relative energy errors arising from geometrical structure errors.

Predicted relative energies of the C_2H_2O isomers with the two basis sets and SCF and SCEP (correlated) wave functions are given in Table 16. Correlation effects stabilize ketene relative to ethynol by about 1 kcal. This is the same for DZ and DZ + P results indicating roughly additive polarization and correlation effects on the relative energies. Polarization functions stabilize ketene more than ethynol and oxirene. The relative energy of ethynol is raised by 6 kcal and after the correlated treatment the energy of ethynol is predicted to be 35.4 kcal above ketene. The calculations on oxirene indicate clearly that it is at least 80 kcal above ketene and perhaps closer to 85 kcal. The net polarization function effect should be more

TABLE 16. Summary of energies of ethynol and oxirene relative to ketene (kcal)[96]

	Ethynol	Oxirene
DZ SCF	28.3	86.0
DZ SCEP	29.1	78.9
DZ + P SCF	34.3	86.6
DZ + P SCEP	35.4	–

TABLE 17. Energies of CH_2CS isomers[133]

Isomer	E_{SCF} (a.u.)	ΔE (kcal)
Thioketene, $H_2C{=}C{=}S$	−474.29314	0.0
Ethynyl mercaptan, $H{-}C{\equiv}C{-}SH$	−474.26515	17.6
Thiirene, 	−474.08301	131.9

than a 0.6 kcal relative destabilization, since the reoptimization of the C—O length in oxirene represents somewhat of an inequivalent treatment at the DZ + P SCF level. Finally, SCF calculations at 28 points on the potential surface around the ethynol equilibrium structure point to a non-negligible barrier for the rearrangement into ketene[96].

Analogous to ketene, oxirene and ethynol are the CH_2CS isomers, thioketene, thiirene and ethynyl mercaptan. Ethynyl mercaptan and thiirene have been detected in a matrix[131], though apparently not in the gas phase[132]. Recently, Rosmus and coworkers[133] have studied the electronic states of the thioketene radical cation and have included in their work SCF calculations on neutral CH_2CS isomers. A basis set somewhat larger than double zeta was used in these calculations, but geometries were deduced from similar molecules rather than being optimized. The results, given in Table 17 show the ring structure to be very high in energy while the substituted acetylene is much more stable.

V. THE ELECTRONIC STRUCTURE OF ALLENE

Allene has been the subject of a number of *ab initio* studies[114,134–143]. The ground-state structure of allene has the two CH_2 groups perpendicularly oriented giving rise to overall D_{2d} molecular symmetry. Theoretical predictions of the ground-state bond lengths and bond angle are in good agreement with the high-resolution infrared spectra results of Maki and Toth[144] (Table 18). FSGO calculations of Talaty and coworkers[140] yielded a C=C bond length of 1.34 Å and a rather large H—C—H angle of 126°. Earlier SCF calculations of Preuss and Janoschek[136] gave a C=C bond length of 1.310 Å, quite close to the experimental value. Full geometry optimizations have been carried out at the SCF level with an STO-3G minimum basis by Radom and collaborators[138] and with a double zeta basis by Dykstra[141]. The results are given in Table 18.

The *ab initio* wave functions for allene show that the ground-state occupancy is

$$1a_1^2\, 1b_2^2\, 2a_1^2\, 3a_1^2\, 2b_2^2\, 4a_1^2\, 3b_2^2\, 1e^4\, 2e^4 \tag{38}$$

TABLE 18. Ground-state structure of allene

	Experiment[a]	MBS SCF[b]	DZ SCF[c]
R(C=C) (Å)	1.308	1.288	1.310
R(C–H) (Å)	1.087	1.083	1.074
θ(HCH) (deg.)	118.2	116.2	117.6

[a] Reference 144.
[b] STO-3G minimum basis; Reference 138.
[c] Reference 141.

and that the lowest unoccupied or virtual orbital is the 3e orbital. While the ground state is well characterized, there is little understanding of excited states. A study of the electronic spectrum of allene by Sutcliffe and Walsh[145] gave several Rydberg series at wavelengths shorter than about 2000 Å, but no definitive results on the energies of the lowest valence states.

Schaad and coworkers[135] considered allene excited states theoretically. They used a small basis set and performed an SCF calculation on the ground state at the experimental geometry. Using the occupied and virtual g.s. orbitals, they evaluated the energies of substituted configurations corresponding to valence excited states. This procedure, of course, could give sizeable errors since the excited-state wave functions are not variationally determined, but at least these results may give some idea of the ordering of excited states. The lowest excited states found by Schaad all arise from the promotion of an electron from the highest occupied orbital (2e) to the lowest virtual (3e) for a net occupancy of

$$\ldots 4a_1{}^2 3b_2{}^2 1e^4 2e^3 3e^1 \tag{39}$$

However, because of the degeneracy of the e orbitals, this occupancy corresponds to singlet and triplet states of total symmetry A_1, A_2, B_1 and B_2, for a total of eight possible states. The energies of these states at vertical excitation are given in Table 19.

The major interest in most of the theoretical studies of allene has been the problem of internal rotation. When allene twists away from the D_{2d} symmetry of the ground state, only D_2 symmetry is preserved. When it becomes planar, the symmetry is D_{2h}. The lowest closed-shell state has the D_2 occupancy

$$1a_1{}^2 2b_1{}^2 2a_1{}^2 3a_1{}^2 2b_1{}^2 4a_1{}^2 3b_1{}^2 1b_3{}^2 1b_2{}^2 2b_2{}^2 2b_3{}^2 \tag{40}$$

and the D_{2h} occupancy

$$1a_g{}^2 1b_{1u}{}^2 2a_g{}^2 3a_g{}^2 2b_{1u}{}^2 4a_g{}^2 3b_{1u}{}^2 1b_{3u}{}^2 1b_{2g}{}^2 1b_{2u}{}^2 1b_{3g}{}^2 \tag{41}$$

The correlation of the highest occupied and lowest virtual orbitals upon internal rotation is shown in Table 20.

The planar $2b_{3u}$ virtual orbital energy is quite low and, in fact, Buenker[134] showed that the orbital is so low-lying that the closed shell ^1A_g state is not the lowest state of planar allene. Buenker determined that the ^1A_u open-shell state

TABLE 19. Allene excitation energies[a]

State	Energy (eV)	Energy (cm^{-1})
$^3A_1$	4.887	39,400
$^3B_2$	5.078	41,000
$^3B_1$	6.522	52,600
$^3A_2$	6.713	54,100
$^1A_2$	6.865	55,400
$^1B_1$	7.263	58,600
$^1A_1$	9.633	77,700
$^1B_2$	10.792	87,000

[a] From Reference 135. All states correspond to the 2e → 3e excitation.

TABLE 20. Allene SCF orbital energies (a.u.) at optimum geometries[141]

	D_{2d} symmetry		D_2 symmetry			D_{2h} symmetry	
		90°		75°	15°		0°, planar
Improved virtual orbitals (IVO)[a]	$5a_1$	0.2946	$5a_1$	0.2945	0.2919	$5a_g$	0.2854
	$4b_2$	0.2619	$4b_1$	0.2618	0.2627	$4b_{1u}$	0.2665
	3e	0.1596	$3b_2$	0.1758	0.2036	$2b_{2u}$	0.1842
	–	–	$3b_3$	0.1413	0.0569	$2b_{3u}$	0.0327
Occupied orbitals	2e	−0.3776	$2b_3$	−0.3588	−0.2797	$1b_{3g}$	−0.2567
	–	–	$2b_2$	−0.3955	−0.4603	$1b_{2u}$	−0.4979
	1e	−0.6141	$1b_2$	−0.6085	−0.5841	$1b_{2g}$	−0.5795
	–	–	$1b_3$	−0.6189	−0.6274	$1b_{3u}$	−0.6301
	$3b_2$	−0.6317	$3b_1$	−0.6319	−0.6352	$3b_{1u}$	−0.6353
	$4a_1$	−0.7193	$4a_1$	−0.7195	−0.7218	$4a_g$	−0.7161
	$2b_2$	−0.9667	$2b_1$	−0.9697	−0.9667	$2b_{1u}$	−0.9804
	$3a_1$	−1.0821	$3a_1$	−1.0872	−1.0821	$3a_g$	−1.1058

[a] See Reference 7.

arising from the $1b_{2g} \rightarrow 2b_{2u}$ excitation was about 6 kcal lower than the closed-shell singlet and estimated that the real difference could be five times that. The separation between the ^3A_u and ^1A_u states was estimated to be less than 0.1 eV (2.3 kcal). Furthermore, it was suggested that the singlet might have a relative minimum in the planar form. The SCF calculations of Schaad and coworkers yielded a smaller value for the energy difference of the closed-shell states, 3.15 eV (73 kcal), a ^3A_u–^1A_u separation of 0.09 eV and a very small separation for the ^1A_u and ^1A_g states of 0.03 eV(90.7 kcal).

The work of Schaad and collaborators showed that the second lowest planar singlet state was an A_g state arising from the $1b_{2g}{}^2 \rightarrow 2b_{2u}{}^2$ double substitution. The lowest two D_{2d} singlets were found to be the $^1A_2$ and $^1B_1$ states. As the molecule twists, the $^1B_1$ state correlates with a D_2 symmetry $^1A_1$ state having the occupancy

$$\ldots 1b_3{}^2 1b_2{}^2 2b_2{}^2 2b_3 3b_3 \tag{42}$$

while the $^1A_2$ state becomes a $^1B_1$ state with occupancy

$$\ldots 1b_3{}^2 1b_2{}^2 2b_2 2b_3{}^2 3b_3 \tag{43}$$

As shown qualitatively in Figure 13, the ground $^1A_1$ state will have an avoided crossing with the $^1A_1$ state that correlates with the D_{2d} $^1B_1$ state. Thus, the transition state for allene internal rotation is an open-shell electronic state.

Most recently, the problem of internal rotation has been attacked by Dykstra[141], Staemmler[142] and Seeger, Krishnan, Pople and Schleyer[143]. Dykstra and Seeger and coworkers determined optimum structures of the planar allene states at the SCF level. These predictions are given in Table 21. Energies of the states have been calculated at several levels of theory. In all three studies[141–143] double zeta quality or nearly double zeta quality basis sets and extended basis sets (e.g. DZ + P) were used at the SCF level. Seeger and coworkers used a spin-unrestricted[146] (UHF) approach for their open-shell SCF calculations. Correlation effects were included for some of the states with the DZ bases. A summary of the results is presented in Table 22.

Seeger and coworkers alone considered the closed-shell 2^1A_g state. Their results indicate that this state is over 100 kcal above the ground state and therefore, in D_2

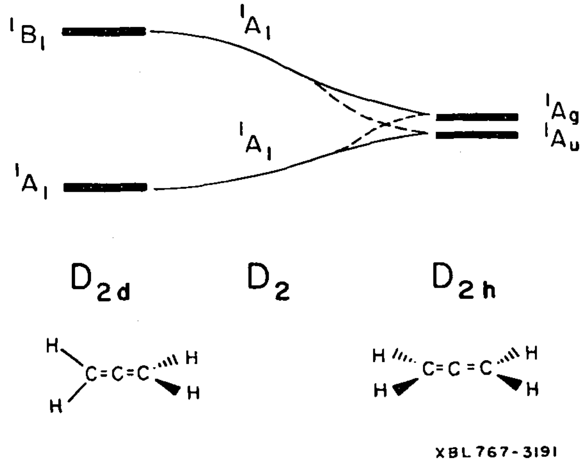


FIGURE 13. Qualitative potential energy curves for the lowest D_2 symmetry $^1A_1$ states of allene which could correlate with the two lowest planar singlet states and the D_{2d} $^1A_1$ ground state. The avoided crossing is indicated by the dashed lines.

symmetry, should not produce any avoided crossing with the lower totally symmetric $^1A_1$ states.

The geometry optimization by Dykstra showed that the ^1A_u and ^3A_u states have nearly identical structures and the correlated treatments of Staemmler and Seeger and coworkers show that these states are, in fact, very close in energy, perhaps less than 1 kcal and probably not greater than 2 kcal. The closeness of these energies is an indication that there is little correlation of the $1b_{3g}$ $2b_{3u}$ pair of electrons. The effect on relative energies of these states when including polarization functions is small. However, correlation effects raise the state energies relative to the $^1A_1$ ground state by around 5 kcal. Calculations at the SCF level on the ^1A_g state predict an energy of about 70 kcal above the $^1A_1$ state. Correlation effects raise this by about 6 kcal more, placing this closed shell state about 20 kcal above the ^1A_u state.

A very significant result of Seeger's work is the predicted distortion of planar allene away from D_{2h} symmetry. As represented in Figure 14, C–C–C bending

TABLE 21. Predicted structures of planar allene states

	MBS SCF[a]			DZ SCF[b]		
Allene State	R(C=C) (Å)	R(C–H) (Å)	θ(HCH) (deg.)	R(C=C) (Å)	R(C–H) (Å)	θ(HCH) (deg.)
^1A_g	1.322	1.072	111.5	1.330	1.074	119.6
^3A_u	1.359	1.086	122.1	1.360	1.078	116.6
^1A_u	–	–	–	1.361	1.077	116.6
2^1Ag	1.313	1.120	126.4	–	–	–

[a] Reference 143.
[b] Reference 141.

TABLE 22. Energies of planar allene states

Author	Calculation	State energies (a.u.)/ΔE (kcal) relative to the ground state				
		$^1A_1$ planar	^1A_g	^3A_u	^1A_u	2^1A_g
Dykstra[141]	DZ SCF	−115.8303	−115.7195 69.5	−115.7566 46.2	−115.7545 47.6	–
	DZ + P SCF	−115.8834	−115.7750 68.0	−115.8057 48.8	−115.8026 50.7	–
	DZ SCEP[a]	−115.9739	−115.8524	–	–	–
Staemmler[142]	DZ SCF	−115.8078	– 76.2	–	−115.7315 47.9	–
	DZ + P SCF	−115.8451	–	–	−115.7658 49.8	–
	DZ CI[a]	−115.8700	–	–	−115.7827 54.8	–
Seeger and coworkers[143]	DZ SCF(UHF)[b]	−115.6984	−115.5837 72.0	−115.6394 37.0		−115.4882 131.9
	Ext. SCF(UHF)[c]	−115.8607	−115.7479 70.8	−115.8028 36.4	–	−115.6585 126.9
	DZ CI[a]	−115.9635	–	−115.8787 55.0	–	–

[a] Correlated wave functions.
[b] 4-31G basis.
[c] 6-31G* basis.

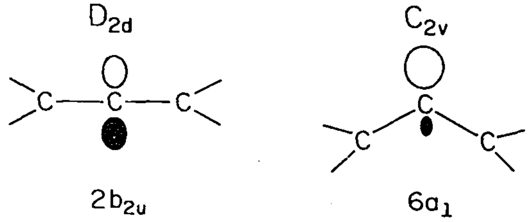


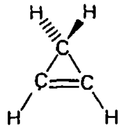
FIGURE 14. Acquisition of s-character in planar allene by the in-plane $2b_{2u}$ molecular orbital under C–C–C bending. Reproduced with permission from R. Seeger, R. Krishnan, J. A. Pople and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 99, 7103 (1977).

allows the $2b_{2u}$ orbital ($6a_1$ in the C_{2v}symmetry of C–C–C bent allene) to acquire s-character. Seeger and coworkers pointed out that if the $2b_{2u}$ is occupied, the orbital may be stabilized by this mixing and lead to a lower energy bent structure. They tested this idea and predicted that the minimum-energy geometry of the ^3A_u state (or $^3A_2$ state in C_{2v} symmetry) is with a C–C–C angle of 135° and a C=C bond length of 1.381 Å. UHF (SCF) and CI energies indicated that this structure is 6 kcal lower than the D_{2h} constrained structure. Therefore, the barrier for internal rotation should be about 6 kcal below the ^1A_u state (D_{2h} constrained) relative energy, or about 50 kcal. This value is the same as estimated by Seeger and coworkers from experimental values for the barrier in substituted allenes[147] and ethylenes.

The energies of the stable isomers of allene have been determined in several studies[138,139,148]. Analogous to ketene isomers, the three carbons and four hydrogens can be arranged as a substituted acetylene, propyne (3), or in a ring, as cyclopropene (4). Peyerimhoff and Buenker[148] performed SCF calculations and their

$H—C\equiv C—CH_3$

(3)



(4)

results with a DZ basis are given in Table 23. Radom and coworkers[138] used a similar basis set but achieved a more reasonable ordering of the isomer stabilities by optimizing the molecular structures using a minimal STO-3G basis. Later, Hariharan and Pople[139] recalculated the isomer energies with a larger basis set that included polarization functions (6-31G*). Allene is still found to be very close in energy to propyne. However, unlike the C_2H_2O isomers, polarization functions lower the energy of the ring configuration and cyclopropene is predicted to be only about 25 kcal less stable than propyne.

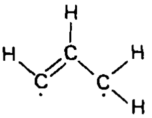
Recently, Davis, Goddard and Bergman[149] have investigated the ring opening of cyclopropene. They used a DZ basis supplemented by d polarization functions on the carbons. Calculations were performed at the SCF level and with the inclusion of some correlation effects at the GVB and GVB CI[7] level. The conclusion of their

TABLE 23. Energies of C_3H_4 isomers

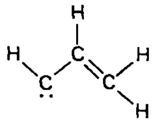
	Total energies (a.u.)/energies relative to propyne (kcal)		
Isomer	DZ SCF[a]	6-31G SCF[b]	6-31G* SCF[c]
Propyne	−115.8177	−115.82156	−115.86337
Allene	−115.8204	−115.82089	−115.86070
	−1.7	0.4	1.7
Cyclopropene	−115.7635	−115.76540	−115.82294
	34.0	35.2	25.4

[a] Reference 148.
[b] Reference 138.
[c] Reference 139.

work is that the lowest energy path for ring-opening involves simultaneous breaking of a C–C single bond and rotation of the methylene group to an overall planar 1,3-diradical structure (5). The activation energy is predicted to be between 38 and 42 kcal. This diradical state may then convert to a vinyl carbene state (6). Davis and



(5)



(6)

collaborators find that singlet vinyl carbene is up to about 6 kcal lower than the diradical transition state. The corresponding triplet state is 12 kcal lower than the singlet. They also find that the singlet and triplet states of (6) have a large barrier between the *syn* and *anti* forms while the singlet diradical (5) has a low barrier. They conclude that cyclopropene ring-opening proceeds directly to the planar diradical intermediate.

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The Chemistry of Ketenes, Allenes and Related Compounds
Edited by Saul Patai

CHAPTER 2

Structural chemistry*

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I. INTRODUCTION

A. General Considerations

It is the purpose of the present chapter to give a review of structural features of cumulated systems and their relation to other observable, especially spectroscopic, effects. Structural chemistry, therefore, is understood as a discussion of bond lengths, bond angles, dihedral angles and conformations of molecules under definite conditions of measurement, and the relation of these properties to local molecular environments and electronic characteristics.

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*This chapter is dedicated to the memory of R. Kuhn (1900–1967), Nobel prize laureate and pioneer in the field.

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There are several objectives in the discussion of complete molecular structures. The first is the determination of the geometrical arrangements of atoms in space, i.e. the characterization for the lowest electronic state of the deepest minimum in the potential energy surface that specifies the energy of the groups of atoms which comprise the molecular unit as a function of their internuclear distances. The second is the discussion of the directional curvatures at this minimum. In addition, it is interesting to explore this multidimensional surface in the vicinity of the deepest minimum for the location of adjacent minima, and to become aware of the heights of the barriers which separate them.

The solution of these problems by theoretical, quantum-chemical procedures at a level useful to practising chemists, i.e. for medium-sized and large molecules, is still limited. A discussion of theoretical results concerning structural problems is therefore mainly restricted to parent molecules and to some simple hydrocarbon systems.

The experimental techniques for determining structural features may be classified as quantitative and qualitative procedures. Quantitative methods cover X-ray diffraction (X) for the solid state, and for the gas phase electron diffraction (ED) and rotational and/or vibration–rotation spectra derived from microwave (MW) absorptions, Raman (R) and/or infrared (i.r.) spectral records. Qualitative procedures include measurements of dipole moments in solution, nuclear magnetic resonance (n.m.r.) experiments and measurements of infrared band shifts.

After some qualitative arguments concerning the molecular structures of cumulated systems we shall survey the variety of cumulenes whose structures have been determined quantitatively. Emphasis is given to the internuclear distances in the cumulenic moiety. The particular geometrical situations of special systems containing cumulenic functionalities are also discussed.

The structural situations of atoms and bonds in cumulenes are related to characteristic features observed in infrared, n.m.r. and X-ray photoelectron (ESCA) spectra of these molecules. These latter spectral data are also used as a basis for further qualitative discussions of the molecular structures of cumulenes. Generally, the situations of $R^1R^2C=$, $=NR^3$ and $=C=O$ structural subunits are compared with those in related systems, such as ethylenes $R^1R^2C=CH_2$, imines $R^1R^2C=NR^3$, ketones $R^1R^2C=O$, etc.

The geometries of the cumulenic molecular skeletons give rise to different types of isomerism, which will be discussed in detail. Effects associated with the chirality of certain cumulenes and their relation to observable optical properties are treated in a subsequent chapter of this volume 'Chirality and chiroptical properties'.

The next topic of structural chemistry concerns intramolecular motions involving the cumulenic skeletons (stereoisomerizations) and internal rotations about single bonds of cumulenic molecules, i.e. this topic includes barriers to isomerization and related problems, such as magnetic nonequivalence of ^1H and ^{13}C nuclei in cumulenes.

The three main types of problem associated with conformations of cumulenes are the relative populations of conformers, e.g. *trans* (*syn*), *gauche* and/or *cis* (*anti*), as a function of the experimental conditions, the potential barrier height hindering rotation around single bonds and the relation of such barriers to electronic features of the molecules.

B. Structural Implications from Valence Bond Theory

Valence bond (VB) theory using hybridization arguments for the heavy atoms predicts that, apart from the planar ketenes and thioketenes as well as their higher

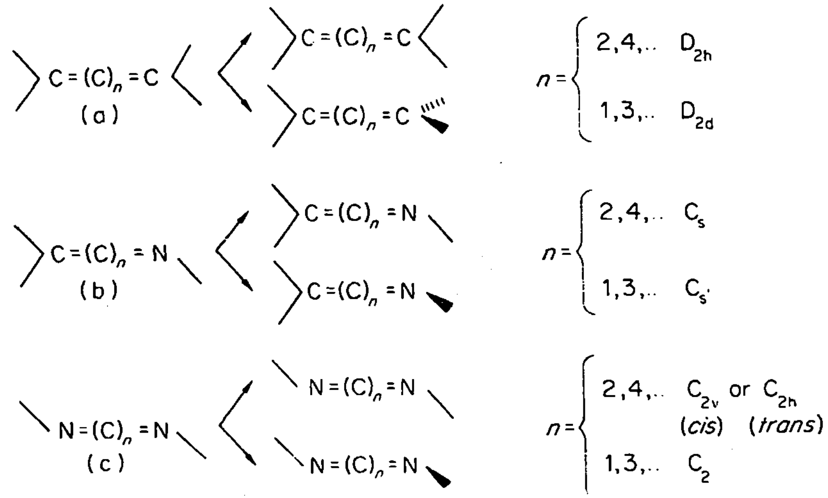
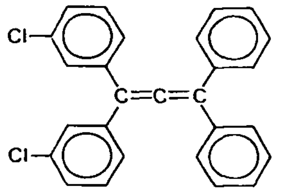


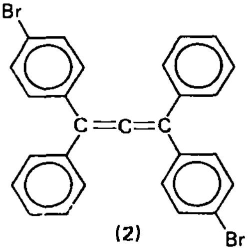
FIGURE 1. Geometries of cumulenes and azacumulenes according to their number of inner carbon atoms.

homologues, carbon cumulenes (a) and the azacumulenes (b) and (c) (Figure 1) should have a linear heavy atom grouping and should be nonplanar for odd *n* and planar for even *n*[1]. For nonplanar cumulenes substituents attached to different terminal atoms are expected to lie in perpendicular planes. In Figure 1 the cumulated moieties containing only carbon and nitrogen as heavy atoms and the ideal symmetries of the corresponding molecular skeletons are summarized. These symmetries correspond to those of the parent molecules with only hydrogen atoms as ligands.



(1)

$\mu = 1{\cdot}57$ D

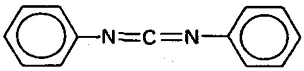


(2)

$\mu = 1{\cdot}92$ D

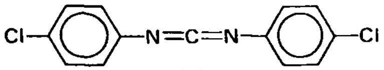
Measurements of dipole moments of phenyl-substituted cumulenes and comparisons with calculated dipole moments from group moment increments have played a central role for the semiquantitative support of the above geometrical predictions of VB theory. In case of the allenes ($n = 1$, Figure 1) the experimental dipole moments μ of the tetraphenylallenes 1 and 2 were used to propose the antiplanar configuration for these cumulated systems[2]. Correspondingly, the dipole moments of the diphenylcarbodiimides 3–5 and diisopropylcarbodiimide (6) supported their antiplanar molecular arrangements[3].

The structural implications from VB theory for cumulated systems have been



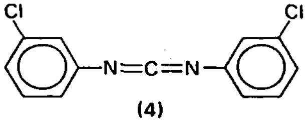
(3)

$\mu = 1{\cdot}70$ D[3c]



(5)

$\mu = 0{\cdot}70$ D[3c]



(4)

$\mu = 2{\cdot}13$ D[3c]

i-Pr—N=C=N—Pr-*i*

(6)

$\mu = 2{\cdot}08$ D[3c]

confirmed quantitatively by experimental and theoretical procedures for a large variety of different molecules.

II. BOND LENGTHS AND BOND ANGLES IN CUMULENES

A. Concerning some Differences in Experimentally Determined Molecular Structures

Apart from being structural characteristics, bond lengths and bond angles are molecular properties which can be used to provide insight into the nature of chemical bonds. In connection with valence bond theory numerical values for these structural data are interpreted in terms of the gross effect of molecular environment upon the structural units under consideration. Such discussions rely preferentially upon bond lengths. Furthermore, it has been found empirically that bond lengths may be linearly related to other molecular properties, such as nuclear spin–spin coupling constants or infrared frequencies.

An ideal measurement of a bond length would provide a value for r_e, i.e. the distance between two nuclei in the hypothetical vibrationless state of a free molecule. Any real measurement, naturally, will yield a distance which is averaged over vibrational motions of the nuclei, different in the two principal methods of measurement in the gas phase, spectroscopy and electron diffraction[4]. Detailed knowledge of the vibrational motions, i.e. the determination of an appropriate force field, is then a prerequisite to correct averaged distances determined by each method to equilibrium values. To make this correction for large molecules represents a formidable task and is often abandoned.

From the molecular spectra (MW, R, i.r.) one obtains the rotational constants for a given vibrational state of the molecule, i.e. rotational constants a_0, b_0, c_0 for the ground and vibrational electronic states. Usually, these constants define ground-state moments of inertia via reciprocal relations, i.e. $I_a^0 = \hbar^2/2a_0$, etc.

The moments of inertia $I_\alpha^0(\alpha = a, b, c)$ differ in a complicated way from I_α^e, the moments calculated from the equilibrium structure r_e. In general, it is not possible to express I_α^0 as an explicit average over the vibrational coordinates, as the rotational constants include a contribution from Coriolis interactions with excited states. Only in a few cases is there enough information available to obtain accurate values for $I_\alpha^e(\alpha = a, b, c)$.

Therefore, most structures determined by spectroscopy are of the so-called r_0 type, which is operationally explained. An r_0 structure is defined as a set of geometric parameters which reproduce the observed values of I_α^0 for a given molecule. The r_0 structure is uniquely defined only for diatomic molecules and a few special polyatomic compounds, such as the linear XY_2 molecules (e.g. O=C=O and S=C=S). In more complicated molecules the r_0 structure is not unique, since one can calculate further structures from the moments of inertia which will not be identical because of the finite inertial defect[4]. When the number of independent structural parameters exceeds three, one must use ground-state moments of more than one isotopic species or else assume reasonable values for the parameters or some portion of the molecule in order to obtain the r_0 structure. Since the change of mass affects the vibrational motions as well, the resulting structure will depend upon the choice of isotopic species. To reduce this problem, often more isotopic species than necessary are studied and then, using a least-squares procedure, a 'best' structure is obtained. However, the result is still dependent on the choice of input data. Consequently, an r_0 structure is not unambiguously defined. On the other hand, an r_0 structure is not useless, since the distances between heavy atoms are often relatively insensitive to the choice of data for the calculation. However, owing to the lack of an unambiguous operational definition an r_0 structure is unsuitable for the detection of small differences in bond distances or for an interpretation of these for different molecules in terms of electronic effects.

In order to avoid these problems r_s or 'substitution' structures are used. The r_s coordinates of a given atom in a molecule are determined by the isotopic shifts in the moments of inertia when that atom (and no other) is substituted. At present, isotopic substitution at each atom is not always feasible. However, it is possible to determine r_s structures by microwave spectroscopy, since its high sensitivity and high resolution permits the study of many isotopic molecules in their natural abundancies. In infrared and Raman spectroscopy isotopic substitution is almost solely restricted to replacement of hydrogen by deuterium. A complete r_s structure requires single isotopic substitution on every atom. The r_s parameters will not reproduce the ground-state moments I_α^0, but will generally give calculated moments which are smaller. Usually, the r_s parameters provide a closer approximation to the r_es. The important advantage of the r_s structure lies in its unambiguous operational definition and therefore, when comparing bond lengths in a series of molecules, one can have more confidence when the bond lengths are determined by the substitution method.

Interatomic distances from experimental intensity and radial distribution (RD) curves of electron diffraction studies are also obtained from operationally defined procedures, which include background corrections, transformations with modification functions, with trial models and structural refinements. Such r_a structures from electron diffraction data may be refined to r_α structures using a reasonable force field for the vibrational motions of the molecules.

Assuming the electron diffraction r_α values to provide a consistent set of bond lengths there remains the problem of their relation to the spectroscopic r_s distances (or r_0 structures). Generally, both the methods (r_0 and r_α) are assumed to be comparable in an r_z structure which may be calculated if the harmonic potentials necessary to provide the necessary correction terms are known. Up to now there have been not many examples where an accurate comparison has been made between these different types of structural data.

Consequently several distinct types of gas-phase structural data are reported in this chapter without explicit notation as to type, and these structures may differ from each other by considerably more than the strictly experimental uncertainties. If available, data from different experimental procedures are summarized, to illustrate differences in apparent structures determined by these methods.

Structural data from X-ray diffraction studies on solids have also to be considered. Here packing forces in the crystal and other factors may influence the experimentally determined structure.

With this in mind, one should be careful in trying to interpret small structural variations in differently substituted cumulenes in terms of 'substituent effects' or contributions of resonance structures for the description of electronic ground states.

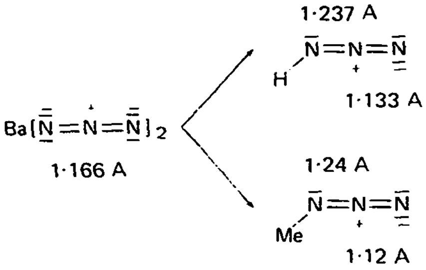
B. Experimental Structural Data

1. Allenes, ketenes, ketene imines, carbodiimides and thioketenes

In Table 1 bond lengths and bond angles of allenes are summarized. For the parent molecule allene (**7**) only some of the available structure determinations have been given.

The set of acyclic allenes includes molecules with σ-inductive donors (**10, 12, 23**) and acceptors (**19**), mesomeric donors (**13–15, 17, 18**) and acceptors (**16, 20**), as well as mesomerically rather indifferent substituents, such as the phenyl group (**21**). The most important observation, especially in connection with the model concept of the 'D_{2d} molecule' for the calculation of various molecular properties of allenes[27–31], is the fact that the two allenic C=C double bonds retain their linear arrangements and their bond lengths upon substitution, i.e. the two C=C bond lengths remain identical to within 0.01 Å upon asymmetric substitution. Exceptions are only observed for the compounds **18** and **23**, in which, remarkably, the C=C double bonds where substitution takes place are largely unaffected whereas the C=C bonds with no substituents are considerably shortened.

The above observations of the constancy of the C=C bond units in allenes upon asymmetric substitution are by no means self-evident. Substitution of the symmetrical azide anion by a hydrogen atom or a methyl group is associated with considerable bond length variations in the cumulenic moiety[32].



The relative insensitivity of the two allenic double bonds towards substitution indicates that interactions between substituents R and the cumulenic moiety C=C=C should be treated as interactions of R with the triatomic heavy-atom grouping as an integer chemical group with characteristic, intrinsic properties and that a model with a rigid molecular allenic skeleton is appropriate for quantitative treatments of molecular properties of allenes[27–31].

The allenic bond length (standard bond length 1.31 Å) is somewhat shorter than the bond lengths in ethylenes (standard bond length 1.34 Å)[33].

Though there exists no general correlation between carbon–carbon bond lengths and carbon–carbon spin–spin coupling constants $^1J(^{13}C-^{13}C)$[34] the correlation in Figure 2 shows qualitatively the intermediate character of the allenic bond between

TABLE 1. Bond lengths and bond angles in allenes

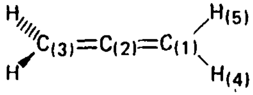
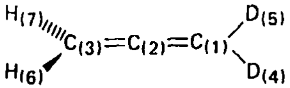
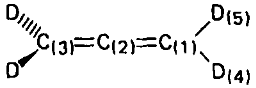
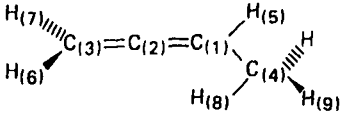
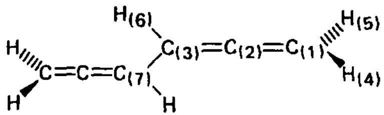
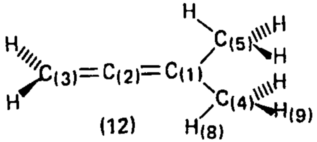
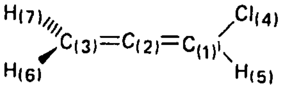
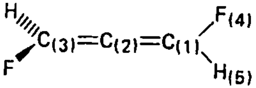
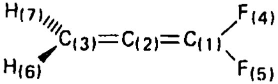
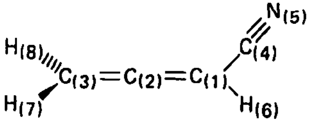
	Bond lengths, r		Bond angles, α			
Molecule	Bond	r (Å)	Angle	α (deg.)	Method[a]	Reference
 (7)	$C_{(1)}{=}C_{(2)}$	1.308	$H_{(4)}C_{(1)}H_{(5)}$	118.2	I.r., R	5
		1.309		116.9	I.r., R	6
		1.311		118.4	ED	7
		1.3091		118.28	I.r., R	8
	$C_{(1)}{-}H_{(4)}$	1.087				5
		1.069				6
		1.081				7
		1.0862				8
 (8)	$C_{(1)}{=}C_{(2)}$	1.308	$H_{(6)}C_{(3)}H_{(7)}$	119	I.r., R	9
		1.308		118.2	MW	10
	$C_{(2)}{=}C_{(3)}$	1.308				9
		1.308				10
	$C_{(3)}{-}H_{(6)}$	1.080				9
		1.087				10
 (9)	$C_{(1)}{=}C_{(2)}$	1.308	$D_{(4)}C_{(1)}D_{(5)}$	118.1	I.r., R	5
		1.3090		118.25	I.r., R	8
	$C_{(1)}{-}D_{(4)}$	1.086				5
		1.0849				8
 (10)	$C_{(1)}{=}C_{(2)}$	1.33	$H_{(6)}C_{(3)}H_{(7)}$	120	MW	11
		$(1.31)^b$				
	$C_{(2)}{=}C_{(3)}$	1.33	$H_{(5)}C_{(1)}C_{(4)}$	120		
		$(1.31)^b$				
	$C_{(1)}{-}H_{(5)}$	1.07	$H_{(8)}C_{(4)}H_{(9)}$	107		
	$C_{(3)}{-}H_{(6)}$	1.07	$C_{(2)}C_{(1)}C_{(4)}$	123		
	$C_{(1)}{-}C_{(4)}$	1.48				
		$(1.52)^b$				
	$C_{(4)}{-}H_{(8)}$	1.09				
 (11)	$C_{(1)}{=}C_{(2)}$	1.3123	$C_{(2)}C_{(3)}C_{(7)}$	123.5	ED	12
	$C_{(2)}{=}C_{(3)}$	1.3123	$C_{(2)}C_{(1)}H_{(4)}$	120		
	$C_{(3)}{-}C_{(7)}$	1.4656	$C_{(2)}C_{(3)}H_{(6)}$	118		
	C–H	1.1043				

TABLE 1 – *continued*

Molecule	Bond lengths, r		Bond angles, α		Method[a]	Reference
	Bond	r (Å)	Angle	α (deg.)		
 (12)	$C_{(1)}=C_{(2)}$	1.308	$H_{(6)}C_{(3)}H_{(7)}$	118.2	MW	13
	$C_{(2)}=C_{(3)}$	1.308	$C_{(4)}C_{(1)}C_{(5)}$	116.4		
	$C_{(3)}-H_{(6)}$	1.067	$C_{(1)}C_{(4)}H_{(8)}$	110.8		
	$C_{(4)}-H_{(8)}$	1.091	$C_{(1)}C_{(4)}H_{(9)}$	111.1		
	$C_{(4)}-H_{(9)}$	1.088				
	$C_{(1)}-C_{(4)}$	1.514				
 (13)	$C_{(1)}=C_{(2)}$	1.309	$C_{(2)}C_{(1)}Cl_{(4)}$	122.2	MW	14
	$C_{(2)}=C_{(3)}$	1.309				
	$C_{(1)}-Cl_{(4)}$	1.736				
 (14)	$C_{(1)}=C_{(2)}$	1.304	$C_{(2)}C_{(1)}H_{(5)}$	121.1	MW	15
	$C_{(1)}-F_{(4)}$	1.335	$C_{(2)}C_{(1)}F_{(4)}$	124.2		
 (15)	$C_{(1)}=C_{(2)}$	1.302	$H_{(6)}C_{(3)}H_{(7)}$	117.8	MW	16
	$C_{(2)}=C_{(3)}$	1.306	$C_{(2)}C_{(3)}H_{(6)}$	121.1		
	$C_{(3)}-H_{(6)}$	1.086	$F_{(4)}C_{(1)}F_{(5)}$	110.2		
	$C_{(1)}-F_{(4)}$	1.323	$C_{(2)}C_{(1)}F_{(4)}$	124.9		
 (16)	$C_{(1)}=C_{(2)}$	1.308	$H_{(7)}C_{(3)}H_{(8)}$	118.2	MW	17
	$C_{(2)}=C_{(3)}$	1.308	$C_{(2)}C_{(1)}C_{(4)}$	122.5		
	$C_{(1)}-H_{(6)}$	1.067				
	$C_{(3)}-H_{(7)}$	1.067				
	$C_{(1)}-C_{(4)}$	1.409				
	$C_{(4)}\equiv N_{(5)}$	1.164				

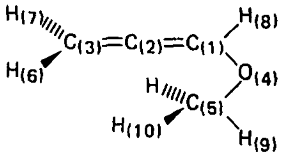
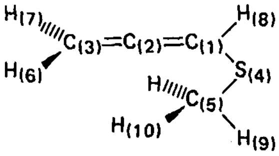
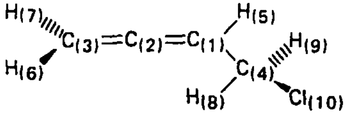
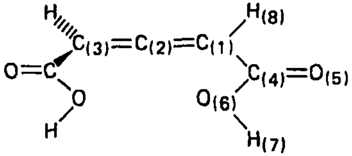
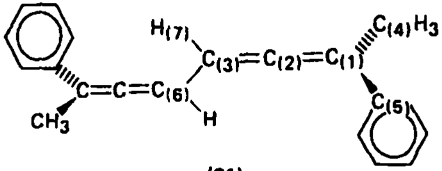
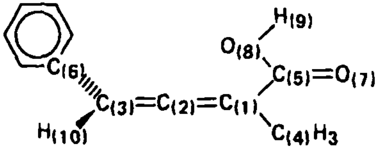
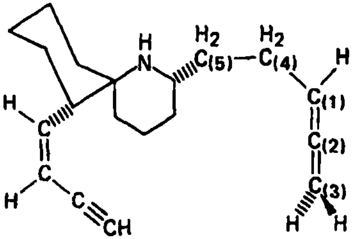
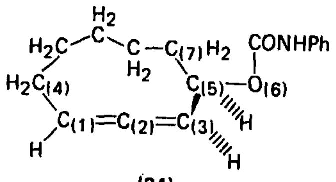
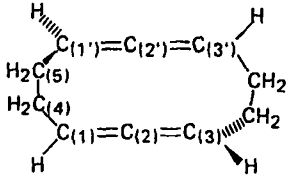
 (17)	$C_{(1)}=C_{(2)}$	1.318	$C_{(2)}C_{(1)}O_{(4)}$	125.3	ED	18
	$C_{(2)}=C_{(3)}$	1.318	$C_{(1)}O_{(4)}C_{(5)}$	115.0		
	$C_{(1)}-O_{(4)}$	1.375	$C_{(2)}C_{(3)}H_{(6)}$	120.0		
	$O_{(4)}-C_{(5)}$	1.427	$O_{(4)}C_{(5)}H_{(9)}$	109.5		
	$C_{(5)}-H_{(9)}$	1.10				
	$C_{(3)}-H_{(6)}$	1.08				
	$C_{(1)}-H_{(8)}$	1.08				
 (18)	$C_{(1)}=C_{(2)}$	1.327	$C_{(2)}C_{(1)}S_{(4)}$	125.4	ED	19
	$C_{(2)}=C_{(3)}$	1.282	$C_{(1)}S_{(4)}C_{(5)}$	98.1		
	$C_{(1)}-S_{(4)}$	1.745	$C_{(2)}C_{(3)}H_{(6)}$	120		
	$S_{(4)}-C_{(5)}$	1.800				
	$C_{(5)}-H_{(9)}$	1.107				
	$C_{(3)}-H_{(6)}$	1.087				
	$C_{(1)}-H_{(8)}$	1.087				
 (19)	$C_{(1)}=C_{(2)}$	1.312	$C_{(2)}C_{(1)}C_{(4)}$	121.6	MW	20
	$C_{(2)}=C_{(3)}$	1.312	$C_{(2)}C_{(3)}H_{(6)}$	120.8		
	$C_{(1)}-H_{(5)}$	1.080	$C_{(2)}C_{(1)}H_{(5)}$	120.0		
	$C_{(3)}-H_{(6)}$	1.082	$C_{(1)}C_{(4)}H_{(8)}$	107.0		
	$C_{(4)}-H_{(8)}$	1.095	$H_{(8)}C_{(4)}H_{(9)}$	111.0		
	$C_{(4)}-Cl_{(10)}$	1.809	$C_{(1)}C_{(4)}Cl_{(10)}$	109.6		
 (20)	$C_{(1)}=C_{(2)}$	1.295				
	$C_{(2)}=C_{(3)}$	1.300				
	$C_{(1)}-C_{(4)}$	1.475 (1.472)^{c}	$C_{(1)}C_{(2)}C_{(3)}$	177.7	X	21
	$C_{(4)}=O_{(5)}$	1.218 (1.227)	$C_{(2)}C_{(1)}C_{(4)}$	122.2		
	$C_{(4)}-O_{(6)}$	1.293 (1.294)	$C_{(2)}C_{(1)}H_{(8)}$	118		
	$C_{(1)}-H_{(8)}$	0.85 (0.95)	$C_{(1)}C_{(4)}O_{(5)}$	121.7		
	$O_{(6)}-H_{(7)}$	0.91 (0.93)	$C_{(1)}C_{(4)}O_{(6)}$	114.1		

TABLE 1 – *continued*

Molecule	Bond lengths, *r*		Bond angles, α		Method[a]	Reference
	Bond	*r* (Å)	Angle	α (deg.)		
 (21)	$C_{(1)}=C_{(2)}$ $C_{(2)}=C_{(3)}$ $C_{(1)}-C_{(5)}$ $C_{(1)}-C_{(4)}$ $C_{(3)}-C_{(6)}$	1.310 1.306 1.491 1.505 1.470	$C_{(1)}C_{(2)}C_{(3)}$ $C_{(2)}C_{(1)}C_{(5)}$ $C_{(2)}C_{(3)}C_{(6)}$ $C_{(2)}C_{(1)}C_{(4)}$	179.0 121.2 124.3 120.3	X	22
 (22)	$C_{(1)}=C_{(2)}$ $C_{(2)}=C_{(3)}$ $C_{(1)}-C_{(4)}$ $C_{(1)}-C_{(5)}$ $C_{(3)}-C_{(6)}$ $C_{(5)}=O_{(7)}$ $C_{(5)}-O_{(8)}$	1.312 1.302 1.503 1.478 1.470 1.225 1.304	$C_{(1)}C_{(2)}C_{(3)}$ $C_{(2)}C_{(1)}C_{(4)}$ $C_{(2)}C_{(1)}C_{(5)}$ $C_{(1)}C_{(5)}O_{(8)}$ $C_{(2)}C_{(3)}C_{(6)}$	177.5 123.3 119.6 115.8 121.9	X	23
 (23)	$C_{(1)}=C_{(2)}$ $C_{(2)}=C_{(3)}$ $C_{(1)}-C_{(4)}$ $C_{(4)}-C_{(5)}$	1.308 1.280 1.491 1.548	$C_{(1)}C_{(2)}C_{(3)}$ $C_{(2)}C_{(1)}C_{(4)}$ $C_{(1)}C_{(4)}C_{(5)}$	177.6 123.2 108.7	X	24

 (24)	$C_{(1)}=C_{(2)}$ $C_{(2)}=C_{(3)}$ $C_{(3)}-C_{(5)}$ $C_{(5)}-O_{(6)}$ $C_{(5)}-C_{(7)}$ $C_{(1)}-C_{(4)}$	1.31 1.32 1.49 1.46 1.53 1.50	$C_{(1)}C_{(2)}C_{(3)}$ $C_{(2)}C_{(1)}C_{(4)}$ $C_{(2)}C_{(3)}C_{(5)}$ $C_{(3)}C_{(5)}C_{(7)}$	168.0 121.9 121.2 112.0	X	25
 (25)	$C_{(1)}=C_{(2)}$ $C_{(2)}=C_{(3)}$ $C_{(1)}-C_{(4)}$ $C_{(4)}-C_{(5)}$ $C_{(2)}\cdots C_{(2')}$ $C_{(2)}\cdots C_{(1')}$ $C_{(3)}\cdots C_{(3')}$	1.299 1.295 1.494 1.520 3.208 3.094 3.090	$C_{(1)}C_{(2)}C_{(3)}$ $C_{(2)}C_{(1)}C_{(4)}$ $C_{(1)}C_{(4)}C_{(5)}$	174.0 124.7 113.2	X	26

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[a] I.r., R = infrared and/or Raman spectroscopy, MW = microwave spectroscopy, ED = electron diffraction, X = X-ray diffraction.

[b] Cf. Reference 49.

[c] Values for the symmetry-related structural units.

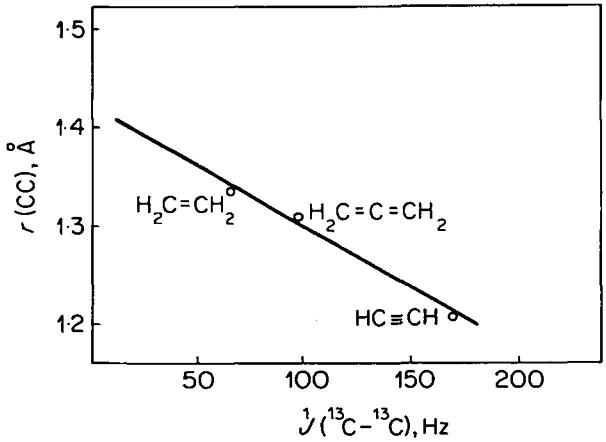
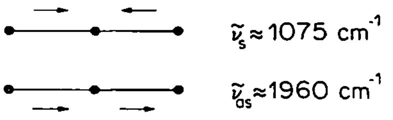


FIGURE 2. Correlation of bond lengths and one-bond carbon–carbon coupling constants in unsaturated systems.

the ethylenic C=C double bond and the acetylenic C≡C triple bond (standard bond length 1.20 Å).

Qualitatively, the carbon atoms of the allenic C=C=C systems are characterized by ^{13}C-n.m.r. chemical shifts of $\delta_C = 73.5$ p.p.m. (relative to TMS) for the terminal carbon atom and $\delta_C = 212.6$ p.p.m. for the central carbon atom[29b], whereas the ethylenic carbon atoms exhibit a resonance at $\delta_C = 122.8$ p.p.m. and the acetylenic carbon atoms at $\delta_C = 73.8$ p.p.m. (values for the parent hydrocarbons)[35].

Further characterizations of the allenic C=C=C system are the vibrational frequencies of $\tilde{\nu} \approx 1960$ cm^{-1} and $\tilde{\nu} \approx 1075$ cm^{-1}[5,6,8]. These vibrational frequencies may be associated with coupled stretching modes in the C=C subunits of the linear triatomic allenic vibrator. The frequency of $\tilde{\nu}_s \approx 1075$ cm^{-1} corresponds to the symmetrical stretching vibration, whereas $\tilde{\nu}_{as} \approx 1960$ cm^{-1} is associated with the antisymmetrical stretching mode.

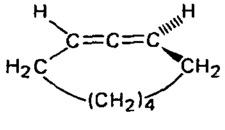


The symmetric stretching mode involves no change in dipole moment in symmetrically substituted allenes, so it will not be infrared active, though it should appear in the Raman spectrum. In asymmetric substituted allenes this mode is also active in the infrared, i.e. in allenes with no centre of symmetry.

The asymmetric stretching mode is generally observed as a strong infrared band. Band shifts upon substitution are discussed in Reference 36. All structure determinations that have been performed in the gas phase are consistent with molecules where the substituents at the terminal allenic carbon atoms are arranged in perpendicular planes and there is a linear arrangement of the allenic $C_{(1)}C_{(2)}C_{(3)}$ grouping.

For the acyclic allenes, whose structures have been determined in the crystal state by X-ray diffraction procedures (20–23), the $C_{(1)}C_{(2)}C_{(3)}$ angles show small deviations of 2–3° from the ideal value of 180°. This small departure from linearity can probably be accounted for in terms of crystal forces.

On the other hand, in cyclic allenes, such as 24 and 25, ring strain results in considerable deviations of the $C_{(1)}C_{(2)}C_{(3)}$ grouping from linearity. This deviation amounts to 6.0° in the ten-membered cyclic allene 25 and is as much as 12.0° in the nine-membered cyclic allene 24. Infrared and n.m.r. studies have also indicated ring strain in the allenic moiety in the nine-membered 1,2-cyclononadiene (26)[37],

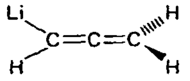


(26)

which has been recently corroborated by force field calculations[38]. In its chemical properties, however, 26 behaves essentially like a normal allene[37a].

Infrared and ^{13}C-n.m.r. data of the allenic moiety can be used to discuss qualitatively the structures of lithiated allenes in solution. As these systems may be obtained from reactions of allenes, $R_2C{=}C{=}CHR$, or propargylic compounds, $R_2HCC{\equiv}CR$, an acetylenic structure represents an alternative for the description of such systems.

The ^{13}C-n.m.r. data of allenyl lithium (27) in tetrahydrofuran[39], especially the ^{13}C chemical shifts, indicate that the allenic structure is appropriate to describe 27.

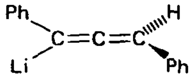


δ_c = 87·2, 196·4, 43·3 p.p.m.

(27)

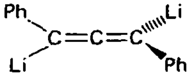
$^1J(^{13}C{-}H)$ = 123, 162 Hz

From the infrared absorption bands, i.e. the positions of the asymmetric stretching frequencies, it has been concluded[40] for lithiated systems, such as 28–30, that in nonpolar solvents (hexane or ether) the lithium atoms form largely covalent bonds, and thus stabilize allenic structures.



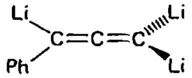
(28)

$\tilde{\nu}_{as}$ = 1870 cm^{-1}



(29)

$\tilde{\nu}_{as}$ = 1790 cm^{-1}



(30)

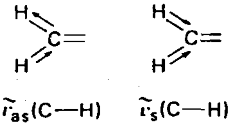
$\tilde{\nu}_{as}$ = 1800 cm^{-1} (hexane)

Change to strongly coordinating media (e.g. hexamethylphosphoric triamide), where the covalency of the lithium with the carbon is less, results in a shift of the infrared frequencies to about 2050 cm^{-1}, which is indicative of an acetylenic structure. The exact structures of such systems are, of course, not known. However, quantum-chemical calculations may give some ideas about the geometries of polylithiated 'allenes' (cf. Section II.C).

The bond lengths between ligand atoms and the allenic skeleton exhibit values comparable with those in corresponding ethylenes $RCH{=}CH_2$. Also bond angles (RCH or R^1CR^2) are quite similar in both kinds of molecules.

However, the allenic C–H bond length (r(C–H) ≈ 1.069–1.087 Å) seems to be somewhat shorter than that of ethylenes (r(C–H) ≈ 1.084–1.103 Å)[33]. The difference manifests in different one-bond carbon–proton coupling constants of $^1J(^{13}C-H) = 168.2$ Hz for allene (7) and $^1J(^{13}C-H) = 156.2$ Hz for ethylene[35] which may be related qualitatively to C–H bond distances[35]. Again, the allenic system takes a position between ethylene and acetylene [$^1J(^{13}C-H) = 249.0$ Hz for $HC{\equiv}CH$)[35].

Other correlations between C–H bond lengths and spectroscopic properties exist, e.g. the linear correlation of r(C–H) and the averaged C–H stretching vibrations $\tilde{\nu}$(C–H) of the antisymmetric $\tilde{\nu}_{as}$(C–H) and symmetric $\tilde{\nu}_s$(C–H) combination of the CH_2 group vibrations as defined below[41]. This correlation is displayed in Figure 3 for several different cumulenes. However, it is also valid for other CH_2 systems.



$$\tilde{\nu}(C-H) = 1/2[\tilde{\nu}_s(C-H) + \tilde{\nu}_{as}(C-H)]$$

$$\Delta\tilde{\nu}(C-H) = \tilde{\nu}_{as}(C-H) - \tilde{\nu}_s(C-H)$$

A property paralleling the C–H bond lengths or one-bond carbon–proton coupling constants in ethylene, allene and acetylene is the C–H bond polarity of these molecules. This can be seen from the difference in carbon and hydrogen atomic charges of these molecules (Figure 4), which have been obtained from electron population analyses using *ab initio* STO-3G MO calculations[30,42].

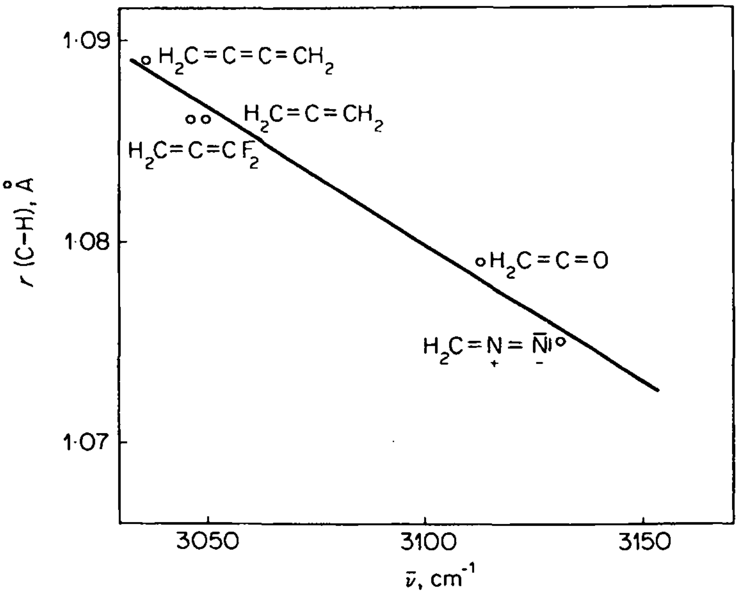


FIGURE 3. Correlation of C–H bond lengths and the averaged antisymmetric and symmetric combinations of the methylene group C–H stretching vibrations.

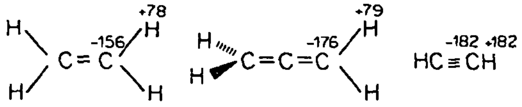
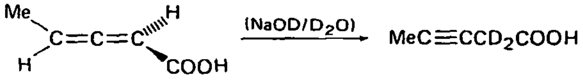
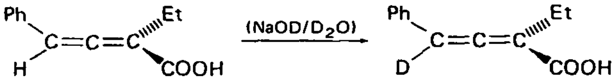


FIGURE 4. Atomic charges from STO-3G calculations in units of 10^{-3} electrons.

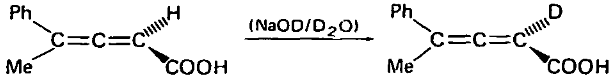
The high bonding polarity and C–H acidity in allenes make possible prototropic allene–acetylene rearrangements and H/D exchange reactions[36]. Such reactions are facilitated for allenes with acceptor groups, such as COOH or CN, but also for phenylallenes. (Note the extreme short C–H bond length in penta-2,3-dienedioic acid, **20**.) In this way, penta-2,3-dienoic acid (**31**) rearranges easily in NaOD/D_2O to deuterated pent-3-ynoic acid, which is in equilibrium with deuterated **31**[43], and the phenylallene carboxylic acids **32** and **33** give deuterated compounds[44].



(31)



(32)



(33)

In Table 2 structural data for ketenes, ketene imines, carbodiimides and thioketenes are summarized.

Generally, the ketene moiety is linear. With the exception of the bis(trimethylgermyl)ketene (**38**) the C=C bond lengths in ketenes are identical with those in allenes within experimental error. The C=O bond lengths of 1.16 Å in ketenes are shorter than the standard C=O bond length of 1.22 Å observed for aldehydes or ketones[67]. This is expected from consideration of the hybridization of the atoms involved in the different C=O bonds. The ketenic C=O bond length corresponds to that of carbon dioxide O=C=O.

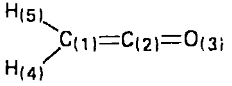
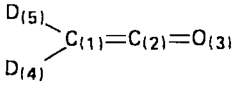
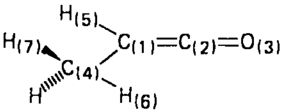
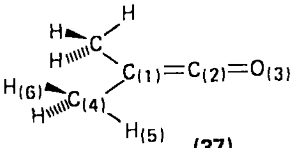
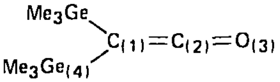
The amount of C=O bond shortening (0.06 Å) in ketenes relative to carbonyl compounds indicates an increased 'triple-bond' character for the C=O unit in ketenes and thus stresses the relative importance of the resonance form **B** for the description of ground states of ketenes. This has also been inferred from infrared[45]

(A) (B)

and ^{13}C-n.m.r. data[53]. Resonance form **B** partly accounts for the extreme high-field position of the ^{13}C chemical shift of the terminal carbon atom in ketene (**34**) ($\delta_{C(1)} = 2.5$, $\delta_{C(2)} = 194.0$ p.p.m., relative to TMS)[53]. The central carbon atom in **34** exhibits a resonance in a similar low-field position as is observed for allene (**7**).

The C–H bond length in ketene [r(C–H) = 1.079 Å] is only somewhat shorter

TABLE 2. Bond lengths and bond angles in ketenes, ketene imines, carbodiimides and thioketenes

Molecule	Bond length, r		Bond angle, α			
	Bond	r (Å)	Angle	α (deg.)	Method[a]	Reference
 (34)	$C_{(1)}=C_{(2)}$	1.314	$H_{(4)}C_{(1)}H_{(5)}$	122.3	MW	45, 46
		1.314		122.2	MW	47
	$C_{(2)}=O_{(3)}$	1.161				45, 46
		1.161				47
	$C_{(1)}-H_{(4)}$	1.079				45, 46
		1.071				47
 (35)	$C_{(1)}-D_{(4)}$	1.0775	$D_{(4)}C_{(1)}D_{(5)}$	122.3	I.r., R	48
 (36)	$C_{(1)}=C_{(2)}$	1.306	$C_{(2)}C_{(1)}C_{(4)}$	122.6	MW	49
	$C_{(2)}=O_{(3)}$	1.171	$C_{(2)}C_{(1)}H_{(5)}$	113.7		
	$C_{(1)}-C_{(4)}$	1.518	$C_{(4)}C_{(1)}H_{(5)}$	123.7		
	$C_{(1)}-H_{(5)}$	1.083				
	$C_{(4)}-H_{(6)}$	1.083				
	$C_{(4)}-H_{(7)}$	1.11				
 (37)	$C_{(1)}=C_{(2)}$	1.314	$C_{(1)}C_{(4)}H_{(5)}$	111.9	MW	50
	$C_{(2)}=O_{(3)}$	1.171	$C_{(1)}C_{(4)}H_{(6)}$	110.5		
	$C_{(1)}=C_{(4)}$	1.505				
	$C_{(4)}-H_{(5)}$	1.088				
	$C_{(4)}-H_{(6)}$	1.093				
 (38)	$C_{(1)}=C_{(2)}$	1.274	$Ge_{(4)}C_{(1)}Ge_{(5)}$	127.6	ED	51
	$C_{(2)}=O_{(3)}$	1.160				
	$C_{(1)}-Ge_{(4)}$	1.946				
	C–H	1.131				

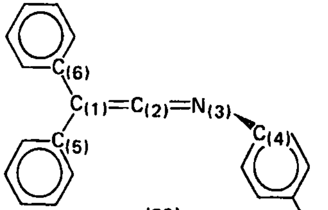
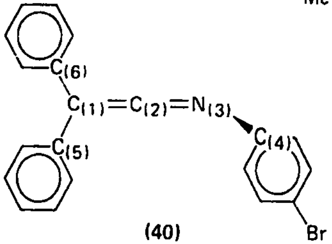
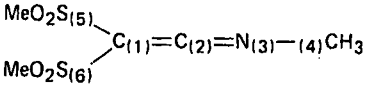
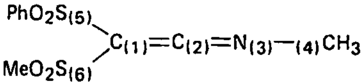
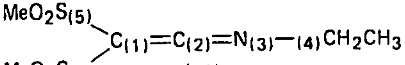
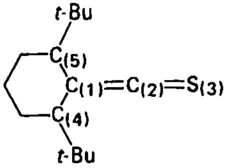
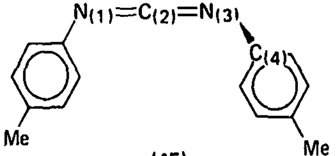
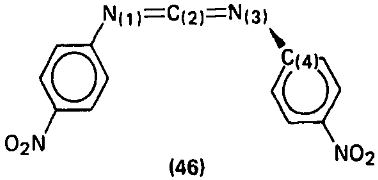
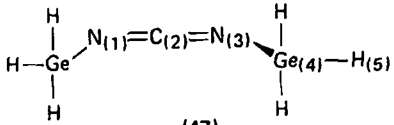
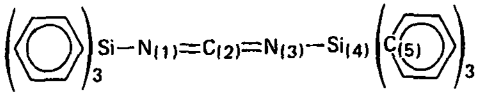
 (39)	$C_{(1)}=C_{(2)}$	1.331	$C_{(1)}C_{(2)}N_{(3)}$	173.7	X	52
	$C_{(2)}=N_{(3)}$	1.206	$C_{(2)}N_{(3)}C_{(4)}$	124.6		
	$N_{(3)}-C_{(4)}$	1.427	$C_{(5)}C_{(1)}C_{(6)}$	123.1		
 (40)	$C_{(1)}=C_{(2)}$	1.330	$C_{(1)}C_{(2)}N_{(3)}$	172.4	X	52
	$C_{(2)}=N_{(3)}$	1.240	$C_{(2)}N_{(3)}C_{(4)}$	123.1		
	$N_{(3)}-C_{(4)}$	1.441	$C_{(5)}C_{(1)}C_{(6)}$	122.7		
 (41)	$C_{(1)}=C_{(2)}$	1.342	$C_{(1)}C_{(2)}N_{(3)}$	180	X	54
	$C_{(2)}=N_{(3)}$	1.154	$C_{(2)}N_{(3)}C_{(4)}$	180		
	$N_{(3)}-C_{(4)}$	1.426	$S_{(5)}C_{(1)}S_{(6)}$	122.6		
	$C_{(1)}-S_{(5)}$	1.726				
 (42)	$C_{(1)}=C_{(2)}$	1.354	$C_{(1)}C_{(2)}N_{(3)}$	177.0	X	55
	$C_{(2)}=N_{(3)}$	1.148	$C_{(2)}N_{(3)}C_{(4)}$	170.6		
	$N_{(3)}-C_{(4)}$	1.382	$S_{(5)}C_{(1)}S_{(6)}$	122.4		
	$C_{(1)}-S_{(5)}$	1.735	$C_{(2)}C_{(1)}S_{(5)}$	118.5		
	$C_{(1)}-S_{(6)}$	1.723	$C_{(2)}C_{(1)}S_{(6)}$	118.9		
 (43)	$C_{(1)}=C_{(2)}$	1.356	$C_{(1)}C_{(2)}N_{(3)}$	173.3	X	56
	$C_{(2)}=N_{(3)}$	1.165	$C_{(2)}N_{(3)}C_{(4)}$	144.5		
	$N_{(3)}-C_{(4)}$	1.465	$C_{(2)}C_{(1)}S_{(5)}$	121.8		
	$C_{(1)}-S_{(5)}$	1.739	$S_{(5)}C_{(1)}S_{(6)}$	121.5		
	$C_{(1)}-S_{(6)}$	1.741				
 (44)	$C_{(1)}=C_{(2)}$	1.290	$C_{(1)}C_{(2)}S_{(3)}$	177.8	X	57
	$C_{(2)}=S_{(3)}$	1.569	$C_{(4)}C_{(1)}C_{(5)}$	111.5		
	$C_{(1)}-C_{(4)}$	1.536				

TABLE 2 – *continued*

Molecule	Bond length, *r*		Bond angle, α		Method[a]	Reference
	Bond	*r* (Å)	Angle	α (deg.)		
 (45)	$N_{(1)}{=}C_{(2)}$ $N_{(3)}{-}C_{(4)}$	1.223 $(1.204)^b$ 1.432 (1.428)	$N_{(1)}C_{(2)}N_{(3)}$ $C_{(2)}N_{(3)}C_{(4)}$	170.4 128.4 $(127.2)^b$	X	62
 (46)	$N_{(1)}{=}C_{(2)}$ $N_{(3)}{-}C_{(4)}$	1.219 $(1.203)^b$ 1.406 (1.392)	$N_{(1)}C_{(2)}N_{(3)}$ $C_{(2)}N_{(3)}C_{(4)}$	169.7 129.6 $(134.4)^b$	X	63
 (47)	$N_{(1)}{=}C_{(2)}$ $N_{(3)}{-}Ge_{(4)}$ $Ge_{(4)}{-}H_{(5)}$	1.184 1.813 1.505	$N_{(1)}C_{(2)}N_{(3)}$ $C_{(2)}N_{(3)}Ge_{(4)}$	180 138	ED	64
 (48)	$N_{(1)}{=}C_{(2)}$ $N_{(3)}{-}Si_{(4)}$ $Si_{(4)}{-}C_{(5)}$	1.164^c 1.696 1.846	$N_{(1)}C_{(2)}N_{(3)}$ $C_{(2)}N_{(3)}Si_{(4)}$ $N_{(3)}Si_{(4)}C_{(5)}$	180 180 108.2	X	65
$Me_3Sn{-}N_{(1)}{=}C_{(2)}{=}N_{(3)}{-}{}_{(4)}SnMe_3$ (49)	$N_{(1)}{=}C_{(2)}$ $N_{(3)}{-}Sn_{(4)}$	1.24 2.47	$N_{(1)}C_{(2)}N_{(3)}$ $C_{(2)}N_{(3)}Sn_{(4)}$	180 117.6	X	66

[a] Cf. Table 1.
[b] Values for the symmetry-related structural units.
[c] Mean bond lengths and mean bond angles.

than that of allene (r(C–H) = 1.086 Å), which is also reflected by a slightly larger one-bond carbon–proton coupling constant [$^1J(^{13}$C–H) = 171.5 Hz for **34**]^{53}. The most remarkable difference between the H_2C=C= structural units in both kinds of molecules is the enlarged HCH bond angle in **34** (122.3°) relative to that of **7** (118.2°). This difference between the methylene groups in allene and ketene is manifested qualitatively in significantly different two-bond proton–proton spin–spin coupling constants [^2J(H–H) = –9.0 Hz for **12**, ^2J(H–H) = –15.8 Hz for **34**]^{68}. Generally, the HCH bond angle α_{HCH} in methylene systems H_2C=X may be related to the difference $\Delta\tilde{\nu}$(C–H) between the antisymmetric and the symmetric combination of the methylene group C–H stretching modes^{41} (Figure 5).

A short C=C bond length is also observed in the thioketene **44**, where the cumulenic moiety may be regarded as being essentially linear. The C=S bond length in **44** (1.569 Å) is somewhat shorter than that of thioformaldehyde H_2C=S [r(C=S) = 1.611 Å]^{58} and comparable with that of carbon disulphide S=C=S [r(C=S) = 1.554 Å]^{59}. Therefore, the structural relation of thioketenes to thioaldehydes or thioketones is analogous to that between ketenes and carbonyl compounds.

The ^{13}C-n.m.r. resonance of the terminal carbon atom of t-butylthioketene, t-BuCH=C=S ($\delta_{C(1)}$ = 81.0, $\delta_{C(2)}$ = 263.3 p.p.m. relative to TMS in CCl_3F)^{60}, indicates a qualitatively similar electronic situation of this atom to the terminal carbon atom in allenes ($\delta_{C(1)}$ = 102.4, $\delta_{C(2)}$ = 207.0, $\delta_{C(3)}$ = 77.0 p.p.m. for t-BuCH=C=CH_2)^{29b}. The electronic situation of the sulphur atom in **44** may be characterized by an ESCA sulphur 2p (S_{2p}) ionization energy of 162.7 eV^{57}, which is smaller than that of S=C=O [$\epsilon(S_{2p})$ = 172 eV]^{61}. This difference is surely due to the orbital stabilizing effect of the oxygen atom in S=C=O. Quantum-chemical calculations indicate corresponding electronic situations for the sulphur atoms in thioketene H_2C=C=S and H_2C=S^{61}.

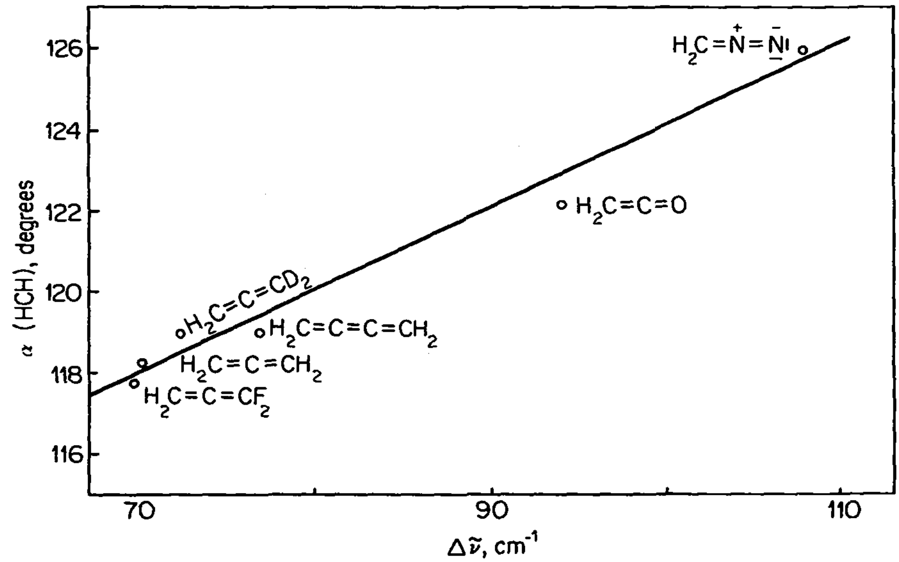


FIGURE 5. Correlation of the HCH bond angle and the difference between the antisymmetric and symmetric combination of the methylene group C–H stretching vibrations.

The triarylketene imines **39** and **40** have all allene-type configurations. The $C_{(1)}C_{(2)}N_{(3)}$ angles of the cumulenic moieties (173.7° and 172.4°, respectively) in the crystal are similar to those found in other cumulenes and probably deviate from linearity as a result of packing forces in the crystals.

The ketene imine C=C double bond (1.33 Å) seems to be slightly longer than the allenic and ketenic double bonds (1.31 Å) in molecules with mesomerically rather indifferent substituents, such as aryl groups, and thus resembles more an ethylenic double bond. This finding is unexpected with respect to the qualitatively observed intermediate position of ketene imines between allenes and ketenes, if spectroscopic properties are taken into consideration, e.g. ^{13}C-n.m.r. resonances[69] or infrared frequencies of the antisymmetric C=C=X stretching modes $\tilde{\nu}_{as}$. The infrared frequencies $\tilde{\nu}_{as}(C{=}C{=}X)$ are observed at $\tilde{\nu}_{as} \approx 1960\ cm^{-1}$ for $X = C$, $\tilde{\nu}_{as} \approx 2020\ cm^{-1}$ for $X = NH$[70] and $\tilde{\nu}_{as} \approx 2140\ cm^{-1}$ for $X = 0$[45]. On the other hand, with respect to the bond length the C=N bond in ketene imines [$r(C{=}N) = 1.21-1.24$ Å] takes a position intermediate between a usual C=N double bond ($r(C{=}N) = 1.26-1.31$ Å)[52] and a C≡N triple bond [$r(C{\equiv}N) = 1.16$ Å][67a].

A special structural situation is observed for the *N*-alkyl 2,2-disubstituted sulphonylvinylideneamines **41**–**43**. There C=C double bonds achieve values corresponding to those of typical olefins [$r(C{=}C) = 1.34-1.36$ Å], whereas the CN bonds exhibit bond lengths typical for C≡N triply-bonded systems. Most remarkable, however, is the fact that the $C_{(1)}C_{(2)}N_{(3)}C_{(4)}$ unit in *N*-methyl-2,2-dimethylsulphonylvinylideneamine (**41**) is linear. Also in the compound **42** the $C_{(2)}N_{(3)}C_{(4)}$ angle comes close to linearity (170.6°). The molecular dimensions of *N*-ethyl-2,2-dimethylsulphonylvinylideneamine (**43**) are comparable to those of **41** with the exception of the $C_{(2)}N_{(3)}C_{(4)}$ angle, which is 144.5° for **43**. Therefore, the linearity of the $C_{(1)}C_{(2)}N_{(3)}C_{(4)}$ unit in **41** seems to be bound to the methyl substituent at the nitrogen atom. The $H_3C{-}N$ bond length in **41** is identical with that in methyl isocyanide $H_3C{-}\overset{+}{N}{\equiv}\overset{-}{C}$[56]. The peculiar structures of **41**–**43** are assumed to be due to hyperconjugative effects of the *N*-alkyl groups and electronegativity effects of the sulphonyl groups[54–56]. A methyl group, attached to the nitrogen atom, may bring about complete delocalization of the lone pair, while an ethyl group cannot do so[54–56].

The diarylcarbodiimides **45** and **46** exhibit an allene-type structure, the dihedral angle between the two aryl groups being 88° for di-*p*-tolylcarbodiimide (**45**)[62]. The C=N bond lengths in conventional carbodiimides (**45**, **46**) are comparable with the C=N bond lengths in the 'normal' ketene imines **39** and **40** and phenyl isocyanate PhN=C=O [$r(C{=}N) = 1.207$ Å][71]. The $N_{(1)}C_{(2)}N_{(3)}$ angles deviate by a small amount from the idealized values of 180°, but this may be due to packing forces in the crystals. The main difference between the structures of the *p*-methyl- and the *p*-nitro-substituted diphenylcarbodiimides **45** and **46**, respectively, is observed for the $N_{(3)}{-}C_{(4)}$ bond lengths. The nitro group in the *para* position shortens this bond.

Linking an electropositive atom to the NCN carbodiimide moiety (**47**, **48**) is associated with a reduction of the C=N bond length to 1.16–1.18 Å. In contrast to digermylcarbodiimide (**47**), which is a nonlinear molecule, in the disilyl derivative **48** the SiNCNSi unit is linear. In both molecules the Ge–N bond length (1.813 Å; estimated standard bond length 1.87–1.89 Å[64]) and the Si–N bond length (1.696 Å; standard bond length 1.74 Å[67b]), respectively, provide evidence for Ge–N and Si–N π-type interactions involving vacant silicon or germanium d orbitals. The crystal structure given for the bis(trimethyltin)carbodiimide **49** refers only to the particular crystals studied in Reference 66. For this particular system the NCN grouping is linear and the trimethyltin groups are linked by NCN units to form helices. All the Sn–N links are crystallographically equivalent. The structure of $[Me_3Sn]_2NCN$ (**49**) is considered to be intermediate between carbodiimide, cyanamide and ionic structures[66].

The geometrical situations of the CNR units in carbodiimides, and probably also in ketene imines, are comparable with those in isocyanates, where sometimes linear arrangements ($H_3SiN{=}C{=}O$) and sometimes nonlinear geometries ($MeN{=}C{=}O$, $PhN{=}C{=}O$) are found[71].

As a summary, one may state that, contrary to allenes, the geometrical situation in ketene imines and carbodiimides depends sensitively upon the kinds of substituents attached to the cumulenic skeleton, especially upon the substituents attached to the nitrogen atoms. Substituents with vacant d orbitals on their directly bonded atoms (**47**–**49**) and acceptor groups (**46**) tend to increase the $C_{(2)}N_{(3)}X_{(4)}$ bond angle, i.e. they tend to favour linear CNR structures.

2. *Higher cumulenes*

Difficulties in the interpretation of experimental results for higher cumulenes are associated with the linearity (or lack of it) of the cumulenic moieties. Gas-phase structural determinations especially are complicated by out-of-linearity vibrations[73], which result in 'shrinkage effects', i.e. observed non-bonded CC distances are a trifle shorter than those calculated from the sum of the individual bond distances. In most cases, however, experimental data are reasonably interpreted, if the cumulenic skeleton is assumed to be linear.

Butatriene (**50**) as well as the simple derivatives **51** and **52** are planar molecules (Table 3). X-ray diffraction studies of **53** and **54** show that the above assumption of linear heavy atom groupings seem to be reasonable. Typically, the central C=C double bonds in butatrienes exhibit bond lengths of $r(C_{(2)}{=}C_{(3)}) = 1.26$ Å, whereas the terminal C=C bond lengths show average values of $r(C_{(1)}{=}C_{(2)}) = 1.32$ Å and thus resemble allenic double bonds. The shortening of the central $C_{sp}{=}C_{sp}$ bond in butatrienes implies some triple-bond character[76].

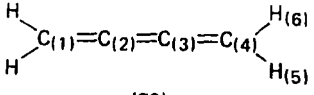
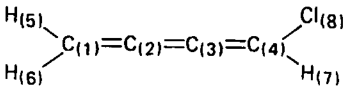
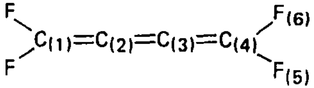
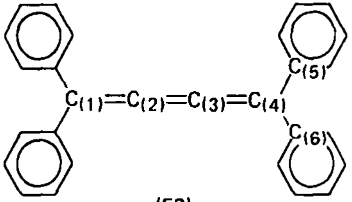
An unsymmetric substitution of the butatriene moiety, e.g. monosubstitution, such as in chlorobutatriene (**51**), does not cause any significant changes in the two terminal C=C bonds, the central C=C bond or the CCH angles[74a], contrary to ethylenes, where a corresponding substitution is associated with a slight, but significant change in the C=C bond length[74a]. This result indicates that one may look at the butatriene system as a typical structural unit with intrinsic geometrical and electronic features, i.e. it may be treated as a rigid skeleton.

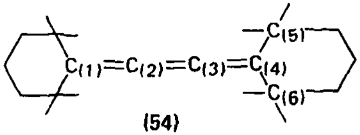
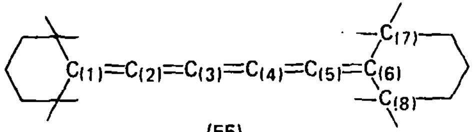
With regard to the problems of differences in experimentally determined structural data (Section II.A) one should note that chlorobutatriene (**51**) is the only cumulene where explicit comparisons of structural information obtained from microwave spectroscopy and electron diffraction studies were made[74b,c].

The bond lengths of the substituent atoms directly linked to the butatriene skeleton are comparable with those in correspondingly substituted allenes (Table 1).

The structural and electronic similarity of the $H_2C{=}$ groups in butatrienes with those in allenes are qualitatively expressed by comparable geminal proton–proton spin–spin coupling constants [$^2J(H{-}H) = -9.5$ Hz for $H_2C{=}C{=}C{=}CHOEt$[80], $^2J(H{-}H) = -9.0$ Hz for **12**[68]], comparable one-bond carbon–proton coupling constants [$^1J(^{13}C{-}H) = 163.0$ Hz for *trans*-*t*-$BuHC{=}C{=}C{=}CHBu$-*t*[81], $^1J(^{13}C^*{-}H) = 158.0$ Hz for $EtC^*H{=}C{=}CH_2$[82]) and comparable differences $\Delta\tilde{\nu}(C{-}H)$ between the asymmetric and the symmetric CH_2 stretching modes (Figure 5).

TABLE 3. Bond lengths and bond angles in higher cumulenes

Molecule	Bond length, r		Bond angle, α		Method[a]	Reference
	Bond	r (Å)	Angle	α (deg.)		
 (50)	$C_{(1)}{=}C_{(2)}$	1.309	$C_{(1)}C_{(2)}C_{(3)}$	180	I.r., R	72[b]
		1.318		170	ED	73
		(1.3270)[c]		(180)[c]		
	$C_{(2)}{=}C_{(3)}$	1.284	$H_{(5)}C_{(4)}H_{(6)}$	119.0		72
		1.283		116		73
		(1.2572)[c]		(115)[c]		73
	$C_{(4)}-H_{(5)}$	1.085				72
		1.083				73
		(1.0834)[c]				
 (51)	$C_{(1)}{=}C_{(2)}$	1.326	$C_{(1)}C_{(2)}C_{(3)}$	180	ED	74a
	$C_{(3)}{=}C_{(4)}$	1.326	$C_{(2)}C_{(3)}C_{(4)}$	180		
	$C_{(2)}{=}C_{(3)}$	1.260	$C_{(3)}C_{(4)}Cl_{(8)}$	122.2		
	$C_{(4)}-H_{(7)}$	1.082	$C_{(3)}C_{(5)}H_{(7)}$	119.5		
	$C_{(4)}-Cl_{(8)}$	1.733	$C_{(2)}C_{(1)}H_{(5)}$	123.4		
 (52)	$C_{(1)}{=}C_{(2)}$	1.32	$C_{(1)}C_{(2)}C_{(3)}$	180	I.r., R	75
	$C_{(2)}{=}C_{(3)}$	1.28	$C_{(2)}C_{(3)}C_{(4)}$	180		
	$C_{(4)}-F_{(5)}$	1.32	$F_{(5)}C_{(4)}F_{(6)}$	110		
 (53)	$C_{(1)}{=}C_{(2)}$	1.3475	$C_{(1)}C_{(2)}C_{(3)}$	176.2	X	76
	$C_{(2)}{=}C_{(3)}$	1.2596				
	$C_{(4)}-C_{(5)}$	1.4775				

 (54)	$C_{(1)}=C_{(2)}$ $C_{(2)}=C_{(3)}$ $C_{(4)}-C_{(5)}$	1.332 1.261 1.547	$C_{(1)}C_{(2)}C_{(3)}$ $C_{(3)}C_{(4)}C_{(5)}$ $C_{(5)}C_{(4)}C_{(6)}$	179 119.7 120.5	X	77
 (55)	$C_{(1)}=C_{(2)}$ $C_{(2)}=C_{(3)}$ $C_{(3)}=C_{(4)}$ $C_{(6)}-C_{(7)}$	1.329 1.260 1.300 1.540	$C_{(4)}C_{(5)}C_{(6)}$ $C_{(3)}C_{(4)}C_{(5)}$ $C_{(5)}C_{(6)}C_{(7)}$ $C_{(7)}C_{(6)}C_{(8)}$	179.0 179.7 118.9 122.0	X	77
$O_{(1)}=C_{(2)}=C_{(3)}=C=O$ (56)	$O_{(1)}=C_{(2)}$ $C_{(2)}=C_{(3)}$	1.289 (1.2898) 1.163 (1.1655)			ED	78
$S_{(1)}=C_{(2)}=C_{(3)}=C=S$ (57)	$S_{(1)}=C_{(2)}$ $C_{(2)}=C_{(3)}$	1.56 1.28			I.r., R	79

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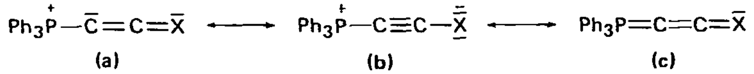
[a] Cf. Table 1.
[b] Structural data partly from Reference 72a and 72b.
[c] Values in parentheses give structural data obtained for a different molecular model.

In the hexapentaene **55** the terminal bond length $C_{(1)}{=}C_{(2)}$ and the neighbouring bond length $C_{(2)}{=}C_{(3)}$ are comparable with those in the corresponding butatriene derivative **54**. Most remarkably, the central $C_{sp}{=}C_{sp}$ double bond ($C_{(3)}{=}C_{(4)}$) is distinctly longer than the other $C_{sp}{=}C_{sp}$ bond ($C_{(2)}{=}C_{(3)}$). This shows that the C=C bond lengths in cumulated systems alternate, and, generally, this alternation will be irregular. The geometry of carbon suboxide (**56**) contains structural elements comparable with those of ketenes (Table 2), i.e. a C=O bond length of about 1.16 Å and a C=C bond length of 1.29 Å. The flexibility of this molecule, which complicates the determination of its structure in the gas phase, is a subject of current interest[83]. A similar situation is observed for carbon subsulphide (**57**). The C=C bond length is almost identical to that of **56** and the S=C bond length is identical to that in S=C=S and the thioketene **44**.

3. *Special systems*

Formally typical cumulenic subunits are involved in the triphenylphosphoranylidene molecules **58**–**60**, which may be described by the resonance structures **a**, **b** and **c**.



$$\mathrm{Ph_3\overset{+}{P}{-}\bar{C}{=}C{=}\bar{X}} \longleftrightarrow \mathrm{Ph_3\overset{+}{P}{-}C{\equiv}C{-}\underline{\bar{X}}} \longleftrightarrow \mathrm{Ph_3P{=}C{=}C{=}\bar{X}}$$

(a) (b) (c)

$\bar{X} = \bar{N}Ph$ (58)

$\bar{X} = \underline{O}|$ (59)

$\bar{X} = \underline{S}|$ (60)

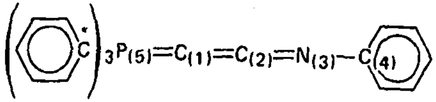
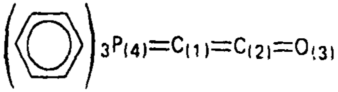
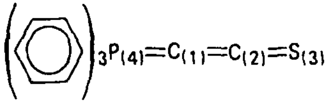
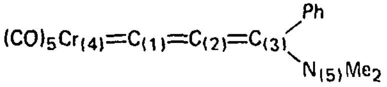
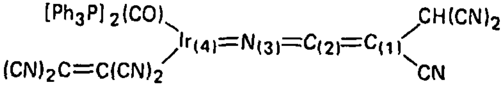
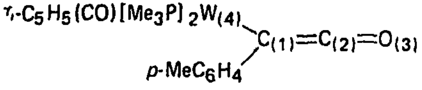
The structural data of **58**–**60** are given in Table 4. The slight departure from CCX linearity in the oxygen and sulphur derivatives **59** and **60** are certainly due to to crystal forces, whereas in the *N*-phenyl derivative **58** the $C_{(1)}C_{(2)}N_{(3)}$ angle (172.5°) shows a small, but significant, deviation from linearity.

The C=O bond length (1.185 Å), the C=S bond length (1.595 Å) and the C=N bond length (1.252 Å) in these phosphacumulenes are only a trifle longer than those in the corresponding representative cumulenes **37**, **44** and **39**. However, the C=C bond lengths in **58**–**60** are considerably shortened compared with those in the prototypical cumulenes. In **59** and **60** they achieve values of triple bonds (1.21 Å), whereas in **58** the CC bond takes an intermediate position between a double and a triple bond [r(C=C) = 1.25 Å]. This indicates the relative importance of resonance form **b** for the description of the electronic structure of the phosphacumulenes **58**–**60**. The PC bond lengths of 1.65–1.68 Å in **58**–**60** are shorter than those in $Ph_3P{=}CXY$ systems[90a], but comparable with that in $Ph_3P{=}C{=}PPh_3$ (1.624 Å)[90b]. This means that in **58**–**60** the PC bonds have considerable double-bond characteristics resulting from $p_\pi{-}d_\pi$ interactions (resonance form **c**).

The $P_{(5)}C_{(1)}C_{(2)}$ bond angle of 134.0° and the $C_{(2)}N_{(3)}C_{(4)}$ angle of 123.8° give the molecule **58** more of a ketene imine character and suggest that it should be described essentially by resonance form **a** and **b**. The $P_{(4)}C_{(1)}C_{(2)}$ angle increases in **59** and **60** and comes near to 180° in the sulphur derivative **60**, where $d_\pi{-}p_\pi$ interactions involving the two terminal atoms of the cumulenic moiety are possible.

The compounds **61**–**63** have their cumulenic skeletons directly linked to metal atoms, i.e. the cumulenic moiety is σ-bonded to a metal or there exists at least one resonance form for the description of these compounds which exhibits a metal—cumulene σ bond.

TABLE 4. Bond lengths and bond angles in special cumulated systems

Molecule	Bond length, r		Bond angle, α		Method[a]	Reference
	Bond	r (Å)	Angle	α (deg.)		
 (58)	$C_{(1)}=C_{(1)}$ $C_{(2)}=N_{(3)}$ $N_{(3)}-C_{(4)}$ $C_{(1)}=P_{(5)}$ $P_{(5)}-C^*_{ar}$	1.248 1.252 1.395 1.667 1.796	$C_{(1)}C_{(2)}N_{(3)}$ $P_{(5)}C_{(1)}C_{(2)}$ $C_{(2)}N_{(3)}C_{(4)}$	172.5 134.0 123.8	X	84
 (59)	$C_{(1)}=C_{(2)}$ $C_{(2)}=O_{(3)}$ $C_{(1)}=P_{(4)}$	1.210 1.185 1.648	$C_{(1)}C_{(2)}O_{(3)}$ $P_{(4)}C_{(1)}C_{(2)}$	175.6 145.5	X	85
 (60)	$C_{(1)}=C_{(2)}$ $C_{(2)}=S_{(3)}$ $C_{(1)}=P_{(4)}$	1.209 1.595 1.677	$C_{(1)}C_{(2)}S_{(3)}$ $P_{(4)}C_{(1)}C_{(2)}$	178.3 168.0	X	86
 (61)	$C_{(1)}=C_{(2)}$ $C_{(2)}=C_{(3)}$ $C_{(1)}=Cr_{(4)}$ $C_{(3)}-N_{(5)}$	1.236 1.372 2.015 1.322	$C_{(1)}C_{(2)}C_{(3)}$	180	X	87
 (62)	$C_{(1)}=C_{(2)}$ $N_{(3)}-Ir_{(4)}$	1.394 2.02	$C_{(2)}N_{(3)}Ir_{(4)}$	162	X	88
 (63)	$C_{(1)}=C_{(2)}$ $C_{(2)}=O_{(3)}$ $C_{(1)}-W_{(4)}$	1.24 1.21 2.27	$C_{(1)}C_{(2)}O_{(3)}$	180	X	89

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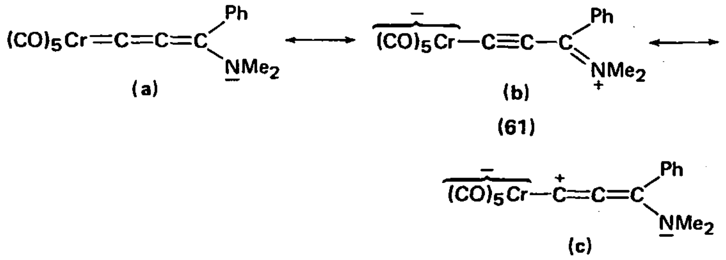
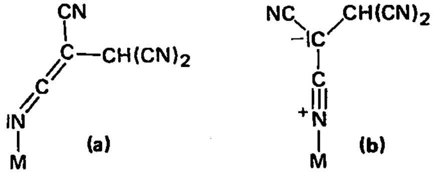
[a] Cf. Table 1.



(61)

In pentacarbonyl(3-dimethylamino-3-phenylallenylidene) chromium (**61**) the cumulenic skeleton is almost linear. The shortening of the $C_{(1)}$=$C_{(2)}$ bond and the lengthening of the $C_{(2)}$=$C_{(3)}$ bond as well as the $C_{(3)}$—$N_{(5)}$ bond length suggest resonance form **b** to be essential for the description of the electronic structure of **61**.

In a similar way, the $C_{(1)}$=$C_{(2)}$ bond length (1.394 Å) of [cyano(dicyanomethyl) keteneiminato]carbonyl(tetracyanoethylene)bis(triphenylphosphine) iridium (**62**) and the $C_{(2)}N_{(3)}Ir_{(4)}$ angle of 162° are interpreted in terms of an essential contribution of a zwitterionic structure **b** to the canonical forms of **62**. A description of **62** in terms of a ketene imine structure **a** does not seem to be adequate.



(62)

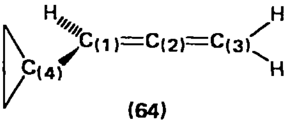
$M = (Ph_3P)_2(CO)Ir(NC)_2C{=}C(CN)_2$

In carbonyl-η-cyclopentadienyl(4-methylphenylketenyl)bis(trimethylphosphine) tungsten (**63**) the C=O bond [r(C=O) = 1.21 Å] achieves the length of a typical C=O double bond as is found in aldehydes, i.e. it is longer than in 'conventional' ketenes. On the other hand, the C=C bond is shorter than that in ketene (**34**). To sum up it can be said that linking a cumulenic moiety to a heavy metal seems to be associated with significant changes in the bond lengths of the cumulenic skeletons.

Even more drastic changes in the geometry of cumulenes are observed if the cumulenic molecules act as ligands in metal complexes where they function as π-bonded unsaturated systems. Most remarkably, the coordinated cumulenic skeleton then exhibits a distinct deviation from linearity, an average X=Y=Z angle being 140°. In most cases the formal double bonds are also lengthened with respect to the free ligand values. Metal complexes with cumulenes as ligands, whose structures have been investigated by X-ray diffraction, include carbon dioxide and carbon disulphide[91], allenes[92-96], ketene imines[97,98], ketenes[99] and butatrienes[100,101].

C. Bond Lengths and Bond Angles from Theoretical Calculations

Theoretical calculations of single-molecule gas-phase structures are largely restricted to hydrocarbon systems and simple oxygen- and nitrogen-containing compounds. The complete theoretical solution of structural problems for medium-sized chemically relevant molecules is not possible at the present time. Nevertheless, calculated structures for parent molecules, such as **7**, **34** and **50**, of the various molecular classes and simple derivatives, such as **10** and **11**, may form a basis for qualitative discussions of molecular structures, if there are no experimental data available. As has been pointed out in Section II.A experimental determinations of molecular structures often cannot yield all the parameters independently, but have to rely on some reasonably selected values. Theoretical calculations for simple molecules may then provide these necessary data. Comparisons of a large set of theoretical structures with experimental ones reveal shortcomings inherent in the different theoretical procedures and thus make it possible to choose which of them is appropriate to tackle a given structural problem. The above arguments justify a discussion of theoretical results concerning molecular structures of cumulenes, such as **64**–**75**, and their parent compounds.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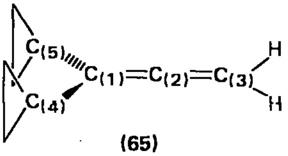
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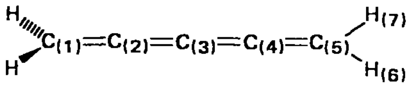
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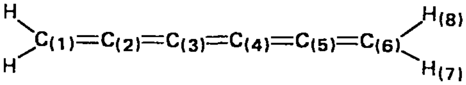
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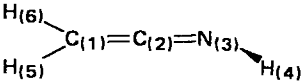
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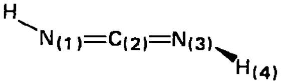
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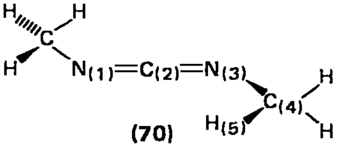
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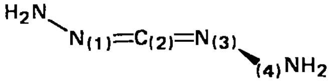
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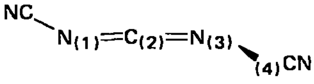
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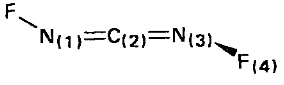
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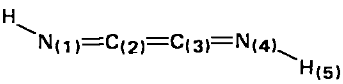
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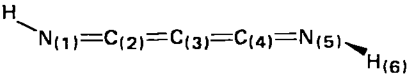

(75)

A summary of theoretically determined molecular structures or substructures from current quantum-chemical procedures, such as the EHM[102], CNDO/2 and INDO[103], MINDO/3 and MNDO[104,105] and the *ab initio* STO-3G[106] methods, is given in Table 5. Furthermore, the results of a method, which is based upon the determinations of molecular structures from empirical bond length–bond overlap linear

TABLE 5. Theoretically determined bond lengths and/or bond angles in cumulenes

	Bond length, r		Bond angle, α			
Compound	Bond	r (Å)	Angle	α (deg.)	Method	Reference
7	$C_{(1)}=C_{(2)}$	1.288	$H_{(4)}C_{(1)}H_{(5)}$	116.2	STO-3G	108
		1.311		118.4	MINDO/3	104
		1.306		114.2	MNDO	105
		1.306		117.0	IMOA	107
	$C_{(1)}-H_{(4)}$	1.083			STO-3G	108
		1.099			MINDO/3	104
		1.090			MNDO	105
		1.083			IMOA	107
10			$H_{(6)}C_{(3)}H_{(7)}$	116.2	EHM	109
			$C_{(2)}C_{(1)}H_{(5)}$	120.6	EHM	109
			$C_{(2)}C_{(1)}C_{(4)}$	124.2	EHM	109
			$C_{(2)}C_{(1)}C_{(4)}$	124.4	STO-3G	127
11	$C_{(1)}=C_{(2)}$	1.305	$C_{(2)}C_{(1)}H_{(4)}$	121.4	IMOA	107
	$C_{(2)}=C_{(3)}$	1.312	$C_{(2)}C_{(3)}H_{(6)}$	121.3		
	$C_{(3)}-C_{(7)}$	1.466	$C_{(2)}C_{(3)}C_{(7)}$	121.5		
	$C_{(1)}-H_{(4)}$	1.082				
	$C_{(3)}-H_{(6)}$	1.082				
64	$C_{(1)}=C_{(2)}$	1.3352			MINDO/3	110
	$C_{(2)}=C_{(3)}$	1.3047				
	$C_{(1)}-C_{(4)}$	1.5085				
65	$C_{(1)}=C_{(2)}$	1.3363			MINDO/3	110
	$C_{(2)}=C_{(3)}$	1.3050				
	$C_{(1)}-C_{(4)}$	1.5097				
	$C_{(1)}-C_{(5)}$	1.5107				
50	$C_{(1)}=C_{(2)}$	1.296	$H_{(5)}C_{(4)}H_{(6)}$	115.9	STO-3G	111
		1.312		110.6	MINDO/3	104
		1.310			MNDO	105
		1.307		117.0	IMOA	107
	$C_{(2)}=C_{(3)}$	1.257			STO-3G	111
		1.295			MINDO/3	104
		1.270			MNDO	105
		1.279			IMOA	107
	$C_{(4)}-H_{(5)}$	1.085			STO-3G	111
		1.100			MINDO/3	104
		1.090			MNDO	105
		1.083			IMOA	107
66	$C_{(1)}=C_{(2)}$	1.295	$H_{(6)}C_{(5)}H_{(7)}$	116.1	STO-3G	112
		1.304		111.0	MINDO/3	104
	$C_{(2)}=C_{(3)}$	1.264			STO-3G	112
		1.291			MINDO/3	104
	$C_{(5)}-H_{(6)}$	1.084			STO-3G	112
		1.097			MINDO/3	104

TABLE 5 – *continued*

	Bond length, r		Bond angle, α			
Compound	Bond	r (Å)	Angle	α (deg.)	Method	Reference
67	$C_{(1)}=C_{(2)}$	1.310	$H_{(7)}C_{(6)}H_{(8)}$	112.8	MINDO/3	104
	$C_{(2)}=C_{(3)}$	1.292				
	$C_{(3)}=C_{(4)}$	1.292				
	$C_{(6)}-H_{(7)}$	1.099				
34	$C_{(1)}=C_{(2)}$	1.310	$H_{(4)}C_{(1)}H_{(5)}$	122.5	MINDO/3	104
	$C_{(2)}=O_{(3)}$	1.167				
	$C_{(1)}-H_{(4)}$	1.086				
68	$C_{(1)}=C_{(2)}$	1.292	$H_{(5)}C_{(1)}H_{(6)}$	117.8	STO-3G	113
	$C_{(2)}=N_{(3)}$	1.242	$C_{(2)}N_{(3)}H_{(4)}$	111.0		
	$C_{(1)}-H_{(5)}$	1.079				
	$N_{(3)}-H_{(4)}$	1.048				
69	$N_{(1)}=C_{(2)}$	1.26	$C_{(2)}N_{(3)}H_{(4)}$	115	INDO	114
	$N_{(3)}-H_{(4)}$	1.07				
70	$N_{(1)}=C_{(2)}$	1.26			CNDO/2	115
		1.26	$C_{(2)}N_{(3)}C_{(4)}$	90	INDO	116
	$N_{(3)}-C_{(4)}$	1.40			CNDO/2	115
		1.40			INDO	116
	$C_{(4)}-H_{(5)}$	1.09			CNDO/2	115
71	$N_{(1)}=C_{(2)}$	1.28	$C_{(2)}N_{(3)}N_{(4)}$	123	INDO	116
	$N_{(3)}-N_{(4)}$	1.34				
72	$N_{(1)}=C_{(2)}$	1.28	$C_{(2)}N_{(3)}C_{(4)}$	90	INDO	116
	$N_{(3)}-C_{(4)}$	1.37				
73	$N_{(1)}=C_{(2)}$	1.28	$C_{(2)}N_{(3)}F_{(4)}$	118	INDO	114
	$N_{(3)}-F_{(4)}$	1.25				
74	$N_{(1)}=C_{(2)}$	1.27	$C_{(3)}N_{(4)}H_{(5)}$	113	INDO	114
	$C_{(2)}=C_{(3)}$	1.29				
	$N_{(4)}-H_{(5)}$	1.08				
75	$N_{(1)}=C_{(2)}$	1.27	$C_{(4)}N_{(5)}H_{(6)}$	117	INDO	114
	$C_{(2)}=C_{(3)}$	1.30				
	$N_{(5)}-H_{(6)}$	1.07				

relations, are given. The necessary overlap integrals or overlap populations, respectively, have been obtained from the iterative maximum overlap (IMOA) procedure[107].

Considering the most widely used quantum-chemical methods for the calculations of molecular geometries (MINDO/3 and STO-3G) one can say, at least for the cumulenic hydrocarbon systems, that MINDO/3 consistently underestimates HCH bond angles and, furthermore, reproduces the alternating C=C bond length variations in the cumulenes **7**, **50**, **66** and **67** to a lesser degree than does STO-3G. The

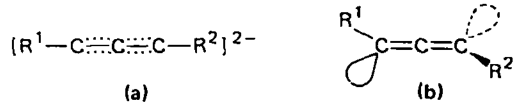
STO-3G results for ketene imine (68) essentially reflect the structural situation observed for the comparable ketene imines 39 and 40.

Concerning the theoretical results for the heterocumulenes 69–75 it seems that the C=N bond lengths are calculated to be longer than one would expect from comparisons with experimental data of similar molecules (Table 2). The most stable electronic ground state conformation of 1,4-diazabutatriene (74) is calculated to be the *trans* form.

Molecular orbital calculations may serve as useful guidelines for the prediction of geometries of molecules which are not accessible to quantitative experimental investigations. Especially interesting in this connection are the lithiated 'allenes' and allenyl anions which have been mentioned in Section II.B.1.

The structure of a 'free' allenyl anion $C_3H_3^-$ (76) has been investigated on the basis of STO-3G and STO-4.31G MO calculations[117]. Geometries and relative energies of several conformations of $C_3H_3^-$ are given in Figure 6. The structure of such a hypothetically free anion is interesting in the context of the molecular structure of cumulenes as it is isoelectronic with ketene imine (68). The most stable form of the acyclic $(H_2CCCH)^-$ system is calculated to be an 'allenyl' anion 76a, which is isosteric (isoelectronic and of the same conformation) with the ketene imine molecule (68). The propargylic systems 76b and 76c are only slightly larger in energy. Cyclic $C_3H_3^-$ systems are calculated to be of considerably more energy. 76b represents a transition state for an inversion of the allenyl anion. Owing to the above calculations allenyl anions from chiral precursors should have no configurational stability at room temperature. This is consistent with observations of Reeps[44], who has shown that chiral phenylallene carboxylic acids, such as 32 and 33, racemize in alkaline solutions (Section II.B.1).

On the other hand, CNDO/2 calculations[118] suggest that for the $(RCCCR)^{2-}$ dianion (77) a linear 'sesquiacetylene' structure (a) is more stable than a nonplanar allenic one (b).



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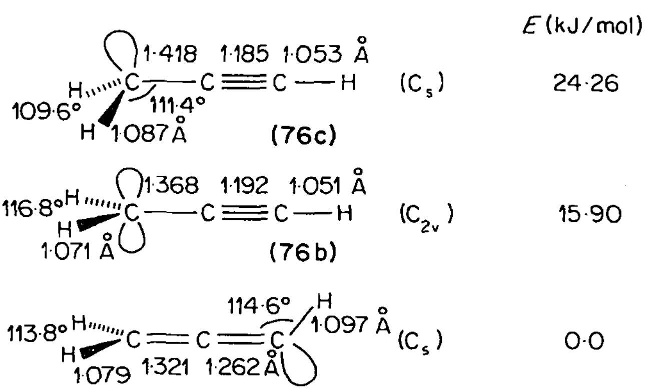
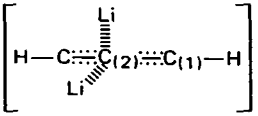


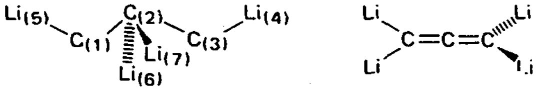
FIGURE 6. STO-3G optimized geometries and relative energies of some allenic and propargylic anions.

A corresponding result has been obtained for the dilithiated molecule [HCCCH]Li_2 (78). In 78 the most stable conformation shown involves the lithium atoms close to the central carbon atom $C_{(2)}$ with a $LiC_{(2)}Li$ angle of 90°.



(78)

A structure similar to 78 has been calculated to be the most probable arrangement of the lithiocarbon C_3Li_4, a formally tetralithiated allene 79[119]. The conformation (a) with a zig-zag LiCCCLi chain, not deviating too far from linearity, should be more stable than a typical allenic structure (b) by 79.5 kJ/mol in a 4.31G/5.21G basis. In Reference 119 many more C_3Li_4 structures have been discussed.



(C_{2v}) (D_{2d})

(a) (b)

(79)

(a) $r(C_{(1)}C_{(2)}) = 1.326$ Å
$r(C_{(1)}Li_{(5)}) = 1.794$ Å
$r(C_{(2)}Li_{(6)}) = 1.869$ Å
$\alpha(C_{(2)}C_{(1)}Li_{(5)}) = 149.3°$
$\alpha(C_{(1)}C_{(2)}C_{(3)}) = 155.7°$
$\alpha(Li_{(7)}C_{(2)}Li_{(6)}) = 93.2°$

(b) $r(C{=}C) = 1.323$ Å
$r(C{-}Li) = 1.791$ Å
$\alpha(LiCC) = 122.3°$

Generally, one can say that in theoretical structural researches of the latter type where conventional experience is no guide, it is difficult to establish with certainty that the absolute energy minimum corresponding to the most stable structure has been found.

III. ISOMERISMS OF CUMULENES AND BARRIERS TO ISOMERIZATION

A. Isomerisms of Cumulenes

The classification of cumulenes in Section I.B according to the point symmetries of their molecular skeletons allows a general discussion of isomers of a particular cumulene on a geometrical level. This level of description is based upon the conceptional dissection of the molecules into a spatially rigid skeleton and ligands attached to definite ligand sites. The molecules are then represented by certain geometrical arrangements of points in space. At this level of description the ligands R may be characterized by their gross formula or an intrinsic parameter $\sigma(R)$, which may achieve a certain numerical value. Ligands, which may be linked to the skeleton in different, nonequivalent, ways, require a statement about the particular bond involved in the link to the molecular skeleton and are treated as different groups, e.g. α-naphthyl and β-naphthyl.

The discussion of types of isomerism of cumulenes on a geometrical level may be restricted to allenes and butatrienes as prototypes of D_{2d} and D_{2h} molecules. Corresponding arguments apply also to higher cumulenes of corresponding symmetry and to the azacumulenes with appropriate restrictions resulting from the substitution of one CH unit or two CH units, respectively, in allenes or butatrienes by $\bar{N}$.

The possible types of isomeric cumulenes for both these molecular classes are illustrated in Figure 7 for the simple cases of isomeric pentadienes and hexatrienes. In Figure 7 the molecules in horizontal lines (**80**, **12**, **81a** and **82**–**84a**) are related to each other as constitutional isomers (or structural isomers) as the constituting atoms of the compounds are connected differently. The molecules arranged vertically (**81a**, **81b** and **84a**, **84b**) are stereoisomers as they differ in the position of their otherwise identically connected atoms in space.

Related to the dissection of molecules into the skeleton and the ligands the isomers **12**, **81a**, **81b**, or **83**, **84a**, **84b**, respectively, only differ by the arrangements of identical ligands on the ligand sites. All these isomers may be generated by permutations of the ligands among the fixed ligand sites. The truly different isomers of such a kind are also referred to as permutation isomers.

The stereoisomeric relation of the nonplanar D_{2d} systems **81a** and **81b** is an enantiomerism. Both these isomers are chiral and are related to each other as object and mirror image. As these enantiomers have identical scalar molecular properties (energies, refractive indices, etc.), but different pseudoscalar properties, an experimental differentiation of these chiral isomers is bound to rely on chiral properties, such as optical rotations. Prerequisite for the investigation of chiroptical properties is the isolation of the enantiomers. Chiroptical properties of cumulenes will be discussed in a separate chapter of this volume. The planar *E*-dimethylbutatriene (**84a**) and *Z*-dimethylbutatriene (**84b**) exhibit *cis–trans* isomerism (geometrical isomerism) as a special case of torsional isomerism[1b]. In principle, these last isomers differ in all their scalar molecular properties.

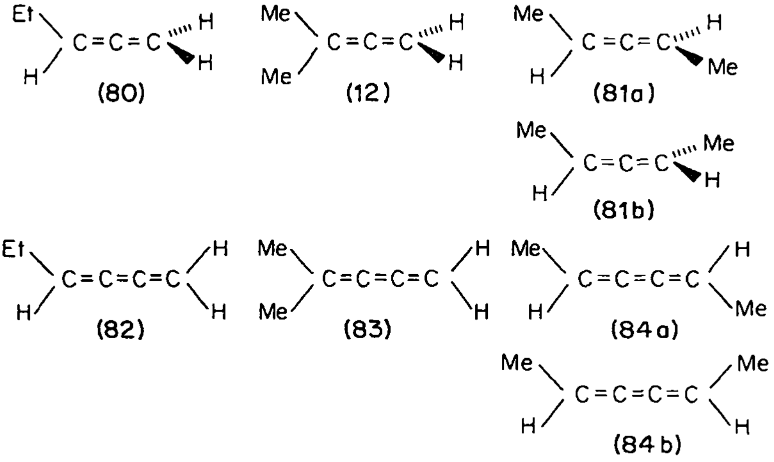


FIGURE 7. Types of isomeric cumulenes illustrated for pentadienes and hexatrienes.

So far, we have discussed the types of isomerism of cumulenes only on a geometrical level using a point model for the molecules. If one takes the pragmatic position of a practising organic chemist and differentiates isomers according to whether they may be separated by chemical or physical means under normal laboratory conditions the above geometrical description often represents a useful classification scheme. However, it is based upon an arbitrarily chosen energy barrier of about 83 kJ/mol separating isomeric molecules, which is a lower limit for facile isolation of isomers[1].

If, however, one asks for the number of isomers which can actually be observed by a given experimental method under definite conditions, one has to refer to lifetimes of particular arrangements of atoms of the molecules in space (conformation), i.e. the ratio of lifetimes of conformations to the time required to detect particular arrangements by an experimental procedure is the crucial point. Therefore, one obtains different data for conformational isomers[1b] by the various experimental methods.

The next level of describing structures of molecules then has to consider lifetimes of molecular arrangements and measuring processes. This, however, makes the definition of isomers vague. To overcome these problems, Eliel[120] has defined isomers, as far as possible, independently of the conditions under which they are observed referring to a more 'natural' barrier separating isomers. He defines a chemical species as a molecule at or very near a minimum in a potential energy hypersurface and considers two chemical species of the same molecular composition identical, if the energy barrier between them is less than kT (RT/mol, k being the Boltzmann constant and R being the gas constant, i.e. 2.475 kJ/mol at 25°C). This definition is still dependent upon temperature, but avoids problems implicit in definitions involving arbitrary barrier heights. kT is the vibrational spectroscopist's barrier and is therefore appropriate for even the fastest processes one normally observes in electronic ground states of molecules. On this basis the following discussion of the structural chemistry of cumulenes includes effects associated with *cis–trans* isomerism, enantiomerism, barriers to stereoisomerization and topics such as conformations, rotamer populations and dihedral angles. The number of isomers in this context is associated with definite methods of observation and given experimental conditions. This number is in many cases smaller than the total number of isomers (separated by energy barriers greater than kT). Eliel[120] has called this number of isomers associated with measuring conditions the number of 'residual' isomers. If this number is one, he speaks of the residual species.

B. Barriers to Stereoisomerization

1. *Barriers separating stereoisomers*

Stereoisomerization of cumulenes having a pure carbon atom skeleton occurs through rotations around the formal double bonds. Generally, quantum-theoretical calculations give more reliable results for the predictions of relative energies of isomers, including structural isomers and stereoisomers, or conformers, than for the predictions of absolute energies of molecules. Therefore, for these problems theoretical calculations are useful guidelines and give detailed information about the processes involved in such isomerizations.

Rotational barriers separating stereoisomeric cumulenes of the series $=C=(C)_n=C=$ ($n \geqslant 1$) are the subject of continuing theoretical investigations[104,121–127] using various quantum-chemical approaches. For the rotational

TABLE 6. Calculated rotational barriers ΔE for unsubstituted cumulenes $H_2C{=}(C)_n{=}CH_2$ and $H_2C{=}C{=}NH$ (68)

n	Compound	ΔE (kJ/mol) MINDO/3[104]	ΔE (kJ/mol) STO-3G[127]
1	7	196.2	383.2
2	50	157.7	309.1
3	66	127.2	
4	67	111.3	
	68[a]		97.1 (38.8)[b]

[a] From Reference 113.
[b] From STO-4.31G MO calculations.

barrier of allene (7) numerous theoretical studies are reported in the literature[104,122,124,125,128].

Nearly every calculation predicts that the rotational barrier ΔE for the parent cumulenic hydrocarbons $H_2C{=}(C)_n{=}CH_2$ should decrease monotonously with increasing n, with ΔE reaching the value zero for $n = \infty$. Numerical values obtained from the rather sophisticated semiempirical MINDO/3 procedure[104] and some values from *ab initio* STO-3G MO calculations[127] together with the barrier of ketene imine (68)[113] are summarized in Table 6.

Experimental values for rotational barriers of cumulenes, obtained under various conditions and with different procedures, are summarized in Table 7. In general, the experimental results confirm that the rotational barriers of cumulenes with a carbon atom skeleton decrease with increasing n.

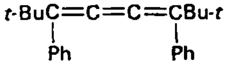
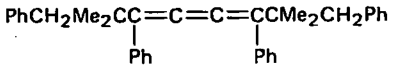
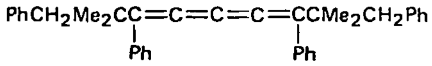
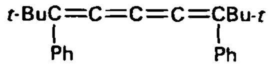
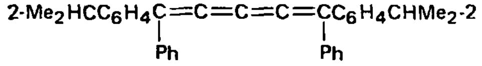
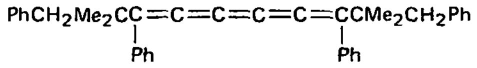
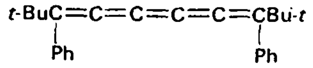
Solvent and substituent effects have only a small influence on the rotational barriers of the carbon cumulenes[131], i.e. the experimental barriers of the substituted molecules may be directly compared with the theoretical ones of the parent compounds. As a result one can say that the experimental values decrease with increasing chain length of the cumulene slightly more than has been predicted by the MINDO/3 method. The STO-3G results are in considerable error.

With respect to the question of the possibility of isolating stereoisomers for the various members of the cumulenic series ($\Delta G^{\#}$ should exceed 83 kJ/mol) one can infer that, under normal conditions, stereoisomers should be obtained only for cumulenes with $n \leqslant 4$. Consequently, enantiomers should be obtained for allenes ($n = 1$) and pentatetraenes ($n = 3$), *cis–trans* isomers should be obtained for butatrienes ($n = 2$) and hexapentaenes ($n = 4$). This has been demonstrated for allenes for a wealth of different molecules (cf. Chapter 3). In case of pentatetraenes, so far only one example, the compound **89**, for the resolution into enantiomers has been reported in the literature[133]. On the other hand, several *cis–trans* isomeric butatrienes and hexapentaenes[130,131,135–139], such as **84**[130], **86**[131,137,139], **93**[135], **94**[136], **95**[81], and **92**[131,133], have been separated.

Since allenes are configurationally stable, linking together two appropriately substituted (chiral) allenic subunits to a diallene gives rise to the existence of diastereomeric forms, a *meso* compound with a centre of symmetry and a racemic form, which may be resolved into the constituting enantiomers.

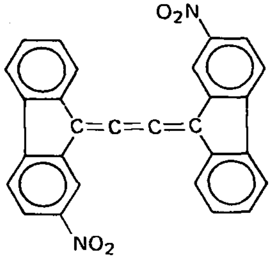
It has been shown chemically that the synthesis of the diallenes **21** and **96** lead to the *meso* forms (**21a** and **96a**, respectively)[140]. This has been corroborated by crystallographic space-group determination for **21a**[22]. Chiral forms of **21** and **96** (e.g. **21b** and **96b**) have not yet been isolated.

TABLE 7. Experimental characteristics for rotational barriers of cumulenes with carbon atom skeletons (kJ/mol)

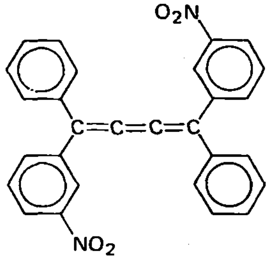
Molecule	$\Delta H_T^{\#}$	$\Delta S_T^{\#}$	$\Delta G_T^{\#}$	T(K)	Reference
$MeHC{=}C{=}CHMe$ **(81)**	188.6	+2.3	187.4	553	129
$t\text{-}BuHC{=}C{=}CHBu\text{-}t$ **(85)**	191.4	−2.4	192.8	581	129
$MeHC{=}C{=}C{=}CHMe$ **(84)**	129.7	−6.3	132.2	398	130
 $t\text{-}BuC(Ph){=}C{=}C{=}C(Ph)Bu\text{-}t$ **(86)**	113.0	−32.0	125.4	388	131
 $PhCH_2Me_2CC(Ph){=}C{=}C{=}C(Ph)CMe_2CH_2Ph$ **(87)**			125.3	388	131
 $PhCH_2Me_2CC(Ph){=}C{=}C{=}C{=}C(Ph)CMe_2CH_2Ph$ **(88)**			>106	431	132
 $t\text{-}BuC(Ph){=}C{=}C{=}C{=}C(Ph)Bu\text{-}t$ **(89)**	109.4	−18	122.5	298	133
 $2\text{-}Me_2HCC_6H_4C(Ph){=}C{=}C{=}C{=}C(Ph)C_6H_4CHMe_2\text{-}2$ **(90)**			≥96.2	410	134
 $PhCH_2Me_2CC(Ph){=}C{=}C{=}C{=}C{=}C(Ph)CMe_2CH_2Ph$ **(91)**	79.9	−20	87.5	380	131
 $t\text{-}BuC(Ph){=}C{=}C{=}C{=}C{=}C(Ph)Bu\text{-}t$ **(92)**	80	−23	86.9	298	133

Similarly, cyclic diallenes of the type 25 or 97[141] and 98[141] may exist in *meso* and chiral forms. 25 has been obtained as a *meso* compound[26], 97 and 98 could be separated into the *meso* forms (a) and the optically active chiral forms (b)[141].

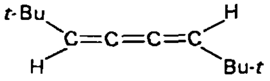
In azacumulenes, such as the ketene imines and carbodiimides, stereoisomerization may be achieved via rotation around double bonds or by inversion on nitrogen. A recent theoretical STO-4.31G MO treatment suggests that the stereoisomerization of ketene imine (68) proceeds preferentially via an inversion[113] as has also been predicted for the isoelectronic allenyl anion 76 (Section II.C). The calculated inversion



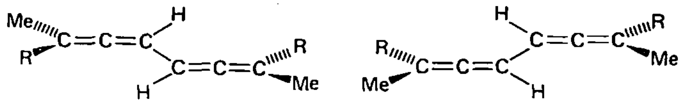
(93)



(94)



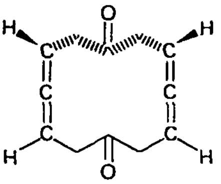
(95)



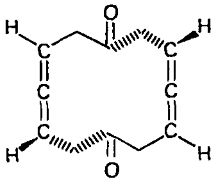
(a) (b)

R = Ph (21)

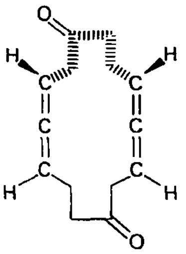
R = *t*-Bu (96)



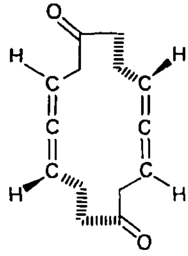
(97a)



(97b)



(98a)



(98b)

barrier of ketene imine (68) (Table 7), which gives a reasonable estimate of stereoisomerization barriers for the whole molecular class, precludes the isolation of optically active ketene imines with hydrocarbon and aryl substituents under normal conditions, the substituents being achiral. Theoretical barriers for the stereoisomerization of diazacumulenes are given in Table 8.

Generally for the diazacumulenes, inversion on both nitrogen atoms simultaneously has been calculated to involve much higher activation energy than rotation

TABLE 8. Theoretical barriers of stereoisomerization in diazacumulenes, $RN{=}(C)_n{=}NR$

Compound	*n*	R	ΔE (kJ/mol)[a]	Method	Reference
69	1	H	33.9 (32.6)	INDO	114
			35.1	IBMOL	142
70	1	Me	20.9 (18.8)	INDO	116
71	1	NH_2	77.4 (173.6)	INDO	116
72	1	CN	14.5 (14.5)	INDO	116
73	1	F	93.7 (95.4)	INDO	114
74	2	H	99.8 (183.6)	INDO	114
75	2	H	28.9 (36.0)	INDO	114

[a] Inversion barriers; rotational barriers are given in parentheses.

about double bonds or inversion on one nitrogen[114]. Stereoisomerization of carbodiimide (**69**) requires only about 34 kJ/mol. The calculation slightly favours rotation through a *trans* configuration over inversion. Taking also the results for dimethylcarbodiimide (**70**) into consideration it seems that a combination of rotation and inversion is responsible for the isomerizations of carbodiimides. Therefore, it would seem that attempts to isolate optically active carbodiimides will meet the same difficulties as were encountered with optically active ketene imines. Acceptor substituents seem to decrease the stereoisomerization barrier. On the other hand, donors tend to give the carbodiimide more configurational stability. The INDO calculations predict that, for example, difluorocarbodiimide (**73**) should be so stable that it should be possible to isolate its enantiomers. This is not unexpected comparing inversion barriers of NH_3 (25 kJ/mol) and NF_3 (230 kJ/mol)[114]. Diazapentatetraene (**75**) also exhibits a rather low isomerization barrier. Again the process is calculated to be a combination of an inversion and a rotation.

Most remarkably, the INDO calculations[114] predict configurational stability for diazabutatriene (**74**), which should allow isolation of *cis* and *trans* isomeric molecules. The isomerization by a singlet mechanism should involve an inversion on nitrogen while a rotation should be responsible for the isomerization by way of a triplet mechanism[114]. However, for the singlet mechanism there are two degenerate singlet electronic states. Therefore, configuration interaction between these two electronic configurations may lower the energy of the singlet transition state for isomerization by about 83 kJ/mol so that in this case also an extended calculation would predict the diazabutatrienes to be configurationally unstable.

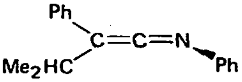
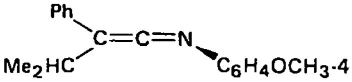
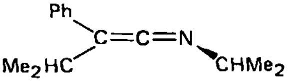
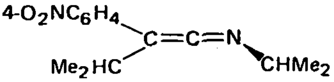
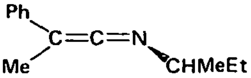
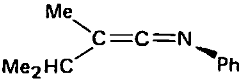
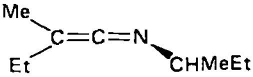
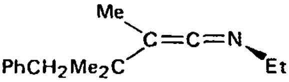
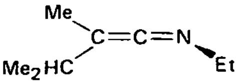
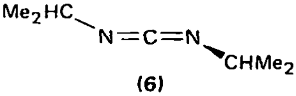
The theoretical predictions concerning stereoisomerization barriers of aza- and diazacumulenes are in agreement with experimental results, which are summarized in Table 9. Ketene imines with only alkyl substituents (**105**–**107**) have stereoisomerization barriers of about 60 kJ/mol. Introduction of a phenyl group at the nitrogen atom (**104**) reduces the barrier to about 50 kJ/mol, whereas substitution of a ketene imine at the carbon atom by phenyl (**101**, **103**) has a more pronounced effect, i.e. the barrier is reduced by about 15 kJ/mol. The substituent effects of phenyl groups on the barrier of stereoisomerization seems to be almost additive as can be seen from the barrier of the diphenylketene imine **99**, which is estimated to be about 35 kJ/mol (observed value 37.7 kJ/mol).

In contrast to the stereoisomerization barriers in carbon cumulenes, which are rather insensitive to substituent effects and involve rotations, the barrier heights in ketene imines depend markedly upon the electronic character of the substituents. As can be seen from **100** and **102** π-electron donation increases the barrier (**99** → **100**), whereas π-electron acceptance decreases it (**101** → **102**), in agreement with theoretical predictions (Table 8). Similar arguments should also hold for the carbodiimides, where the stereoisomerization barrier of alkylated molecules (**6**) is only about half of the barrier of corresponding ketene imines (**107**).

In terms of resonance structures one can say that substituents which can accept π-electron density from the π-donating ketene imine moiety[69] tend to favour resonance form **B** relative to **A**. From the flow of π-electron density from nitrogen towards the terminal carbon atom[69] one may expect that the effect is more pronounced for substitution at the carbon atom than at the nitrogen atom, in agreement with the observations for the phenyl-substituted molecules.

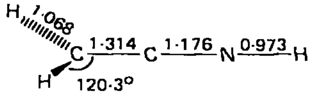
(A) (B)

TABLE 9. Experimental stereoisomerization barriers of ketene imines and carbodiimides

Molecule	ΔE (kJ/mol)	T (K)	Method	Reference
 (99)	37.7	171	^{1}H-n.m.r.	143, 145
 (100)	43.4	196	^{1}H-n.m.r.	145
 (101)	45.0	203	^{1}H-n.m.r.	145
 (102)	<32	140	^{1}H-n.m.r.	145
 (103)	43.3	201	^{13}C-n.m.r.	144
 (104)	51.1	222	^{1}H-n.m.r.	143, 145
 (105)	61.7	280	^{13}C-n.m.r.	144
 (106)	60.2	272	^{1}H-n.m.r.	145
 (107)	60.5	257	^{1}H-n.m.r.	145
 (6)	28.1	128	^{1}H-n.m.r.	146

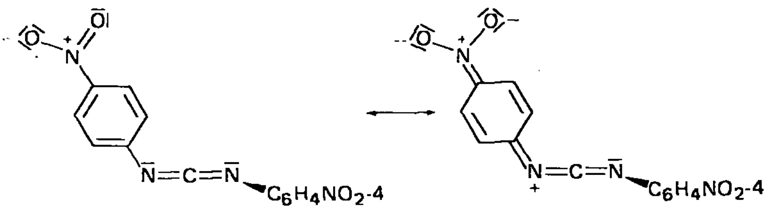
With increasing accepting character of R^1 or R^2 the CNR^3 angle is expected to become larger thus bringing together the geometries of the electronic ground state and the linear transition state for the stereoisomerization.

An STO-4.31G MO calculation characterizes the C_{2v} transition state **68a** of the inversion of ketene imine quantitatively by a short CN bond length, typical for C≡N triply-bonded systems, and a $C_{(2)}N_{(3)}H_{(4)}$ angle of 180° [113].



(68a)

With special emphasis on phenyl substituents one may argue that quinoid structures become more important, as is suggested by the $N_{(3)}$—$C_{(4)}$ bond shortening in *para*-substituted diphenylcarbodiimides, such as **46** (Table 2)[63].



(46a) (46b)

Acceptance of π-electron density from the ketene imine or carbodiimide moiety may also be achieved by d atomic orbitals of substituent atoms linked directly to the cumulenic skeleton (cf. Table 2).

π-Electron donors increase the electron repulsion between the electron densities at the terminal atoms of the cumulenic skeleton and the directly bonded atoms in the transition state. This effect is comparable to the repulsion of the lone-pair electrons in molecules like difluorocarbodiimide (**73**) and diaminocarbodiimide (**71**)[116].

2. *Magnetic nonequivalence of ^1H and ^{13}C nuclei in cumulenes*

The determinations of barriers to stereoisomerization of cumulenes, which have been reported in the preceding section, were mainly based upon n.m.r. experiments using well-known procedures[1b] in connection with equations (1) and (2), which involve the chemical shift difference $\Delta\nu$ (Hz) of corresponding nuclei in a given fixed conformation, the Boltzmann constant k, Planck's constant h and the transmission coefficient κ usually assumed to be unity. The coalescence temperature T_c then gives an upper limit for the temperature, where two (or several) different conformations may be detected. The principle of the corresponding measurements

$$k_c = \frac{\pi \cdot \Delta\nu}{\sqrt{2}} \tag{1}$$

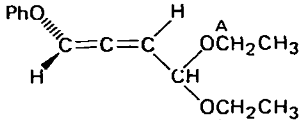
$$k_c = \kappa \frac{kT_c}{h} \exp(-\Delta G^{\#}/RT) \tag{2}$$

consists, for instance, of the observation of originally enantiotopic[1b,147] nuclei, such as the protons of a methylene group or the protons or carbon nuclei of geminal methyl groups in isopropyl substituents. Combining such types of structural units with chiral entities makes the corresponding geminal nuclei diastereotopic, i.e. magnetically nonequivalent. In particular, if the chiral unit is configurationally only stable for $T \leqslant T_c$, magnetic nonequivalencies are observable for $T \leqslant T_c$.

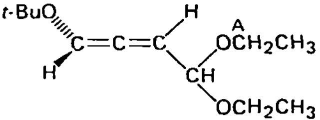
Another possibility for such kinds of measurement is exemplified in the ^{13}C-n.m.r. experiments with **103** and **105**. In these cases a chiral substituent, the *s*-butyl group, is attached to another chiral unit, which is configurationally stable for $T \leqslant T_c$. Then for $T \leqslant T_c$ diastereomeric forms (*R,R* and *S,S* vs *R,S* and *S,R*) of the corresponding molecules give rise to different n.m.r. resonances for all the now magnetically nonequivalent nuclei. Similarly, molecular systems with configurationally stable cumulenic skeletons (allenes, pentatetraenes) should exhibit magnetic nonequivalence of appropriate ^{1}H and ^{13}C nuclei under normal conditions (25°C). As geminal groups in 1,1-disubstituted allenes RRC=C=C= are enantiotopic, magnetic nonequivalencies for appropriate substitution patterns should also be observable for these groups.

Our arguments underlying the discussion of magnetic nonequivalencies in cumulenes rely essentially upon symmetry considerations. However, one must bear in mind that symmetry conditions are only necessary to detect a particular effect. They do not imply that the expected effects can be observed in any case.

Table 10 gives a summary of the different ways of achieving magnetic nonequivalency in allenes and pentatetraenes and the magnitudes of the observed effects. Further examples may be found in Reference 154. The molecules given in Table 10 all reflect situations discussed above. Formal differences are only associated with the chirality of the substituents, which involve asymmetric (tetrahedral) atoms or pyramidal chiral arrangements, such as the PhSO group. Generally, the chemical-shift nonequivalencies of allenic methylene groups depend sensitively upon the solvent polarity and/or associative power of the solvent[150]. A somewhat more complicated situation has been found for certain allenes, where double nonequivalence effects determine the n.m.r. spectra[149]. In the allenic acetals **120** and **121** the two methylene groups A and B give rise to four proton-n.m.r. signals[149]. This can be rationalized as follows. For instance, in **120** the ethoxy moieties are diastereotopic because of the absence of a symmetry plane through these groups, but additionally also the methylene groups A and B have diastereotopic protons. Consequently, there are four geometrically different protons in **120**, which then give rise to four separate n.m.r. signals.



(120)



(121)

C. Conformational Effects and Barriers Separating Conformers

After having discussed structural problems associated with isomerization processes involving the cumulenic skeleton this last topic is concerned with isomerisms resulting from rotations around single bonds. These effects include a discussion of particular arrangements of the substituent atoms, and therefore cover dihedral

TABLE 10. Magnetic nonequivalencies of ^1H and ^{13}C nuclei in allenes and pentatetraenes

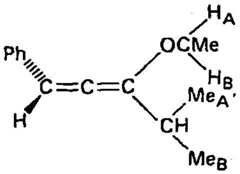
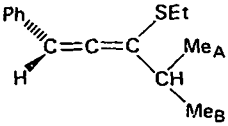
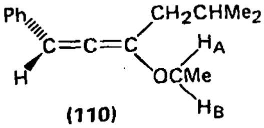
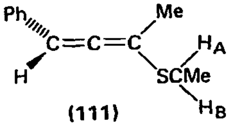
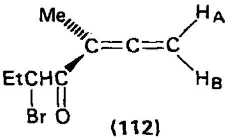
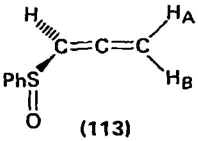
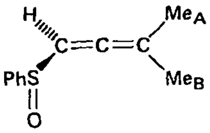
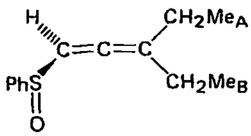
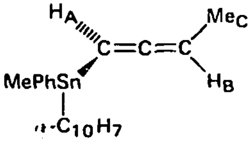
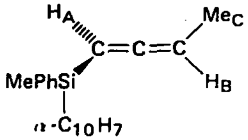
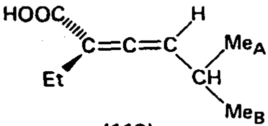
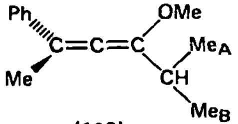
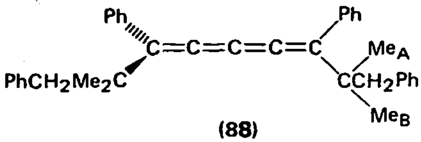
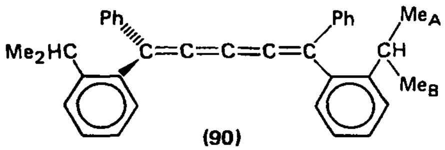
Molecule	Nucleus	$\lvert\nu_A - \nu_B\rvert$ (Hz)	Reference
 (108)	^1H ^1H	5.2 0.80	148, 149
 (109)	^1H	1.5	148
 (110)	^1H	4.0	148
 (111)	^1H	<1.0	148
 (112)	^1H	5.0	150
 (113)	^1H	0.5	151
 (114)	^1H	2.5	151
 (115)	^1H	5.0	151

TABLE 10 – *continued*

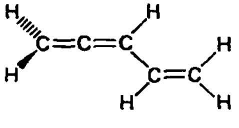
Molecule	Nucleus	$\lvert\nu_A - \nu_B\rvert$ (Hz)	Reference
 (116)	^{1}H ($\lvert\nu_A - \nu_{A'}\rvert$) ($\lvert\nu_B - \nu_{B'}\rvert$) ($\lvert\nu_C - \nu_{C'}\rvert$)	0.4[a] 0.6 0.8	152
 (117)	^{1}H ($\lvert\nu_A - \nu_{A'}\rvert$) ($\lvert\nu_B - \nu_{B'}\rvert$) ($\lvert\nu_C - \nu_{C'}\rvert$)	3.5[a] 0.2 1.4	153
 (118)	^{13}C	4.6	29[b]
 (119)	^{13}C	2.3	44
 (88)	^{1}H	7.9	132
 (90)	^{1}H ^{13}C	2.0 2.6	134

[a] Chemical shift differences of the corresponding signals of the diastereomers.

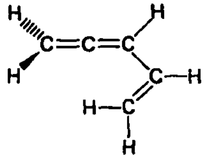
angles, relative rotamer populations, molecular conformations, and barriers to internal rotations around single bonds (conformational analysis). As in previous sections theoretical MO calculations related to the above problems are also taken into consideration.

Firstly, preferential conformations of single groups in monosubstituted cumulenes will be treated. The substituents under consideration fall into two distinct categories. One of these includes unsaturated groups, which are locally planar. The other substituents are saturated and upon rotation around single bonds may achieve molecular arrangements lacking a plane of symmetry. The unsaturated groups interact mesomerically with the cumulenic moieties thus giving preference to conformations with mirror plane symmetry.

For instance, vinylallene (**122**) is expected to have an *s-trans* (**122a**) and an *s-cis* form (**122b**) as its energetically favoured conformations. CNDO/2 calculations



(122a)

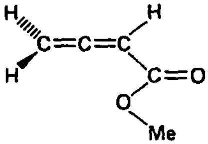


(122b)

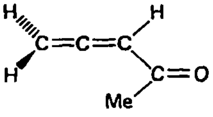
predict the *s-trans* form **122a** to be more stable than the *s-cis* form by 2.44 kJ/mol[155], which seems too low as infrared and Raman experiments[155] as well as ^{1}H-n.m.r. investigations[156] are consistent with the existence of only the *s-trans* conformer (**122a**). Similarly, electron diffraction[12] and infrared studies[157] show that diallene (**11**) prefers the *s-trans* conformation (Table 1).

The preference for the *s-trans* forms in these kinds of molecules is expected from simple analogy with the situation in 1,3-butadiene $H_2C{=}CHCH{=}CH_2$, i.e. from a general comparison of allenes $RCH{=}C{=}CH_2$ with correspondingly substituted ethylenes $RCH{=}CH_2$. However, as will be seen below, such qualitative arguments concerning preferred conformations of allenes are misleading in many cases.

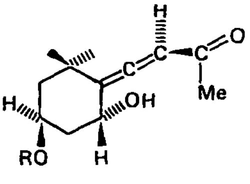
Photoelectron and u.v. absorption spectroscopic investigations[158] have revealed that carbomethoxyallene (**123**) preferentially achieves, in the gas phase and in solution, the *s-trans* form; this has also been inferred from n.m.r. experiments for acetylallene (**124**)[159]. The *s-trans* form for an allenic ketone has also been established by X-ray diffraction of the compound **125**[160]. A corresponding preference



(123)



(124)

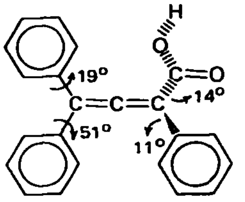


(125)

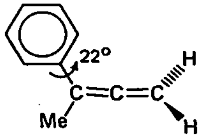
R = *p*-BrC_6H_4CO

for the *s-trans* forms has also been observed for allenic acids, such as **20** and **22** (Table 1). This finding is contrary to the situation in similarly substituted ethylenes, as these molecules (e.g. acrylic acid or methyl vinyl ketone) exhibit preferentially *s-cis* conformations[18, 158] or are mixtures of *s-cis* and *s-trans* forms[21, 161].

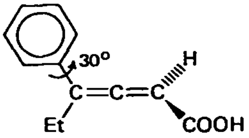
Owing to steric interactions bulky substituents geminal to mesomeric groups, such as COOH or Ph, lead to nonplanar arrangements, i.e. the planes of the substituents and the cumulenic moiety are twisted against each other by a dihedral angle θ. A methyl group geminal to the carboxyl function in **22** (Table 1) results in only a small twist of 4.2° of the planes defined by the atoms $C_{(2)}C_{(1)}C_{(4)}$ and $C_{(5)}O_{(7)}O_{(8)}$. This dihedral angle increases to $\theta = 14°$ if a phenyl ring is attached geminal to the carboxyl group as in **126**; this has been shown by X-ray investigations[162].



(126)



(127)



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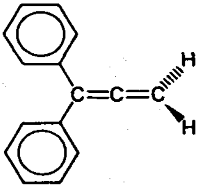


(129)

In general, substituents geminal to phenyl groups have a pronounced influence. From photoelectron and u.v. absorption spectroscopic data[163] of α-methyl-α-phenylallene (**127**) one can infer dihedral angles of $\theta = 20°$ (gas phase) and $\theta = 22°$ (in EtOH), whereas ^{13}C-n.m.r. studies give $\theta = 29°$ (in $CDCl_3$)[29b]; the former two values are in reasonable agreement with the results from the X-ray investigation of **21** ($\theta = 20.6°$)[22].

From the reduction of the u.v. absorption intensity (at ~41,000 cm^{-1}) of 4-phenylhexa-2,3-dienoic acid (**128**) relative to that in 4-phenylpenta-2,3-dienoic acid (**33**), one may estimate according to the method in Reference 163 a dihedral angle of about 30° if an ethyl group is geminal to the phenyl ring. The dihedral angle is only ~11°, if a carboxyl group is near the phenyl group.

The situation is more complex, if two phenyl rings are attached to the same terminal carbon atom as in **126** and **129**. In this case both the phenyl groups are twisted. One ring is only twisted by about 19°, thus retaining mesomeric interactions to a certain degree whereas the other ring is twisted by about 51°. Similar results have been observed for tetraphenylbutatriene (**53**) (Table 3; $\theta = 28°$ and 42°).

A CNDO/2 calculation for 1,1-diphenylallene (**129**)[164] gives an energy minimum for an angle of 40°, if the phenyl rings are symmetrically conrotated with respect to the allenic plane.

Interestingly, the angle of twist θ(Ph,R) of the phenyl group geminal to different substituents R in allenes is related via correlation (3) to the ^{13}C-n.m.r. chemical shift parameter τ(Ph,R), which is essential for the semiempirical calculations of the ^{13}C chemical shifts of the allenic central carbon atoms δ_{C_Z} (Figure 8) according to equation (4)[29b]. In equation (4) $\sigma(R_i)$ represent ligand-specific parameters for the groups R attached to the ligand sites i, and the $\tau(R_j,R_k)$ are pair terms for the geminal substituents R^1,R^2 and R^3,R^4.

Methyl-group conformations in the cumulenes **10**, **12** and **36**, **37** confirm the usual observations that methyl groups prefer to eclipse unsaturated linkages[111b], i.e. the corresponding molecules achieve conformations of C_s symmetry with one hydrogen eclipsing the double bonds. The preferred conformations of methylallenes and methylketenes are displayed in Table 1 and Table 2, respectively.

$$\tau(\text{Ph,R}) = 3.59 \sin 2\theta(\text{Ph,R}) \qquad (3)$$

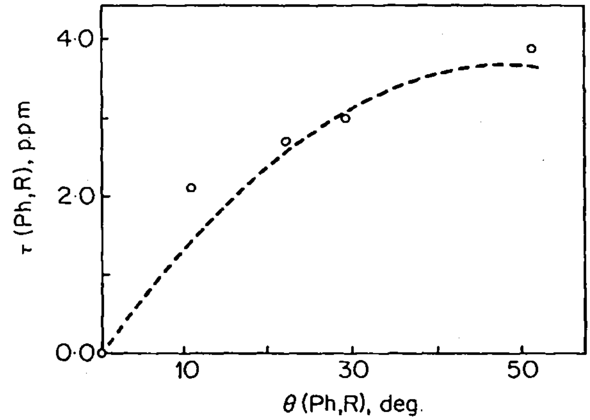


FIGURE 8. Relation between the ^{13}C-n.m.r. chemical shift parameter for the calculation of the ^{13}C chemical shifts of the allenic central atoms of phenylallenes and the angle of twist of the phenyl group.

$$\delta_{C_Z} = \rho + \sum_{i=1}^{4} \sigma(R_i) + \tau(R^1,R^2) + \tau(R^3,R^4) \qquad (4)$$

The experimental and theoretical barriers of rotation around single bonds for these single rotors (**10**, **36**) and double rotors (**12**, **37**) are summarized in Table 11. Taking also the rotational barriers of propene MeCH=CH$_2$ (V = 7.272 kJ/mol)[11] and isobutene Me$_2$C=CH$_2$ (V = 9.244 kJ/mol)[11] into consideration, one can see that the rotational barriers V increase roughly with decreasing π-donating character of the molecular skeletons, the effects for the single rotors being more pronounced than those for the double rotors. Pople and coworkers[165] have shown that, in general, the difference $\Delta V = V^2 - V^1$ between the barriers of the single rotors MeCH=X (V^1) and double rotors Me$_2$C=X (V^2) should be related to the π-electron donating character of the groups C=X. This can be seen from the correlation of ΔV of such systems (including the pair MeCH=O and Me$_2$C=O)[165] with the ^{13}C-n.m.r. resonances of the *para* carbon atoms in PhXMe systems[35,69] (X = C=C=O, C=C=CH$_2$, C=CH$_2$, C=O). The *para*-carbon resonances in PhR are usually regarded as measures of the π-donating character of the substituent R (Figure 9).

TABLE 11. Rotational barriers around single bonds in allenic and ketenic hydrocarbons

Compound	Exp. V (kJ/mol)	Reference	Calc. V (kJ/mol)	Reference
10	6.65	9	5.64, 5.86	127
			5.59	109
			5.44	102
12	8.47	11	9.79	163
36	4.92	44	4.90	109
37	8.64	45[a]		
80	2.36[a]		13.57	158

[a] Cf. text.

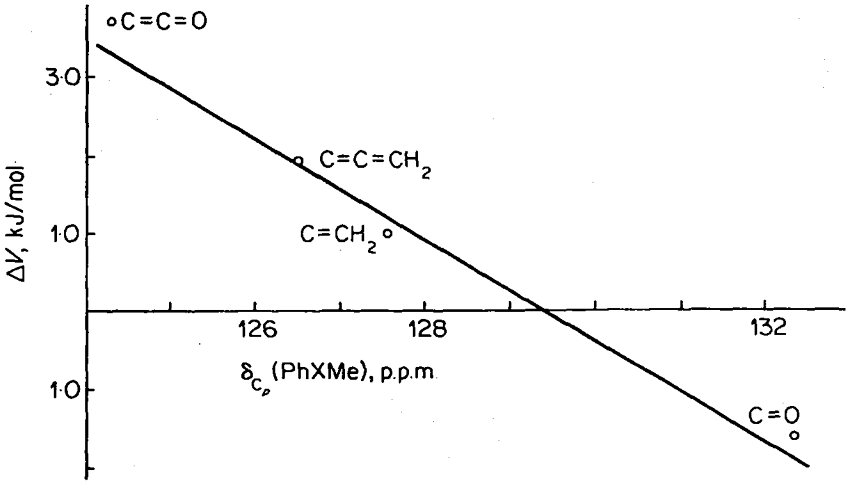
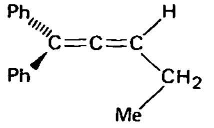


FIGURE 9. Correlation of the differences ΔV in rotational barriers of double and single rotors ($Me_2C{=}X$ and $MeHC{=}X$) with the *para*-carbon atom ^{13}C chemical shifts of PhXMe systems.

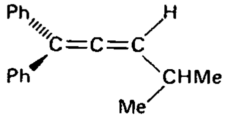
The situation in ethylallene (**80**) may be used to discuss the conformation of cumulenes as related to the variation of the two bond angles α and β (Figure 10)[158]. Ethylallene may serve as a model for other $H_2C{=}C{=}CHYMe$ systems, such as methoxyallene (**17**) and thiomethylallene (**18**) (Table 1) and other cumulenes with an ethyl group as a substituent.

For ethylallene (**80**) a *syn* conformation of C_s symmetry with the $C_{(5')}$ carbon atom and its hydrogen atom eclipsing the allenic bond ($\alpha = 0°$, $\beta = 0°$; Figure 10) has been calculated to be the preferred form[158]. The rotational barrier for a transformation of this conformation into the most stable *anti* conformation with $\alpha = 180°$ and $\beta = 60°$ (Figure 10) has been calculated to be $V = 13.57$ kJ/mol. This last *anti* form is also less stable than another C_s *syn* conformation with $\alpha = 0°$ and $\beta = 60°$ by about 5 kJ/mol. These theoretical results concerning ethyl group conformations in cumulenes are qualitatively confirmed for the 1,1-diphenylallenes **130** and **131**, where corresponding *syn* conformations are more stable than *anti* conformations by 2.36 kJ/mol and 2.72 kJ/mol, respectively[166].



(130)

V = 2·36 kJ/mol



(131)

V = 2·72 kJ/mol

The preference for a *syn* C_s conformation has also been established for methoxyallene (**17**) by electron diffraction and by the magnitude of the vicinal $^{13}C{-}H$ spin–spin coupling constant involving the methoxy carbon atom[82]. On the other hand, electron diffraction data for thiomethylallene (**18**)[19] give evidence that a *syn* C_s conformation and a nonplanar *gauche* conformation are of similar energy.

The conformational preference of C_s *syn* forms for allenes $H_2C{=}C{=}CHYMe$ is

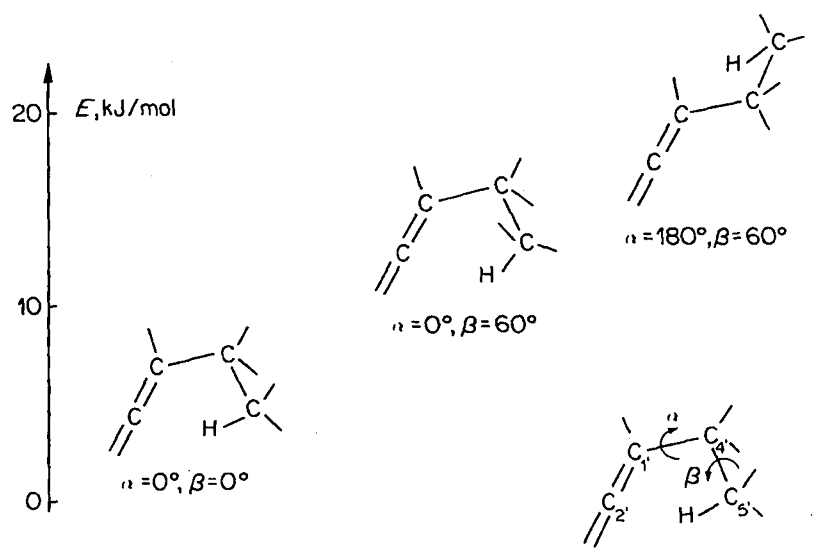
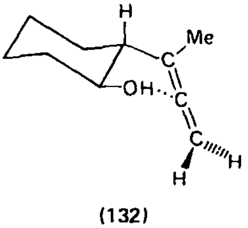


FIGURE 10. Some conformations of ethylallene with respect to the variation of the dihedral angles $\alpha(C_{(2')}C_{(1')}C_{(4')}C_{(5')})$ and $\beta(C_{(1')}C_{(4')}C_{(5')}H)$. Taken from J. Kroner, W. Kosbahn and W. Runge, *Ber. Bunsenges. Phys. Chem.*, 81, 826 (1977), and reproduced by permission of Verlag Chemie, GmbH, Weinheim.

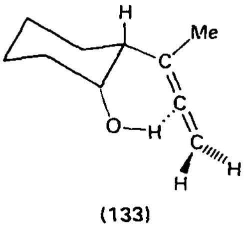
comparable with the situation in corresponding carbonyl compounds $O{=}CHYMe$ and propargylic systems $HC{\equiv}CYMe$ where sp carbon atoms or oxygen atoms with perpendicular p atomic orbitals (lone pairs) are also involved in (secondary) interactions with the YMe groups[1b,167]. In similar ethylenes $H_2C{=}CHYMe$ *gauche* conformations are largely preferred.

Conformational differences are also observed in 4-chloro-1,2-butadiene (**19**) and 3-chloropropene $H_2C{=}CHCH_2Cl$, which exists in the gas phase in two rotameric forms, a C_s conformation with the chloro group *syn* to the ethylenic moiety and a *gauche* conformation[20]. According to microwave spectroscopy[20] the allene **19** seems to exist in only one *gauche* form, which is displayed in Table 1. Infrared and Raman spectral data are also in agreement with this finding[168].

The conformational stability of allenes with substituents which possess β-hydroxy groups, such as CH_2CH_2OH, may be discussed qualitatively taking the hydrogen-bonding ability of the allenic central carbon atom into consideration[169,170], and giving preference to hydrogen-bonded cyclic arrangements. Hydrogen bonds for β-hydroxy groups with the allenic moiety have been demonstrated by infrared spectroscopy for cyclic allenes such as **132** and **133**[170].



(132)



(133)

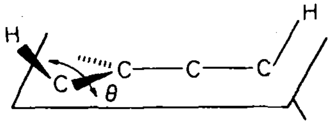


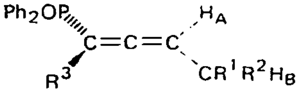
FIGURE 11.

Investigations of five-bond proton–proton coupling constants ^5J(H–H) of such cyclic systems[170] have resulted in the suggestion of an empirical equation (5) relating ^5J(H–H) (Hz) in allenes to the dihedral angle θ defined in Figure 11.

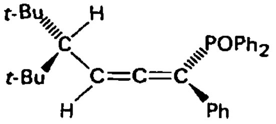
$$^5J(\mathrm{H{-}H}) = 2.25 \sin^2\theta + 1.18 \tag{5}$$

Assuming the existence of only one preferred conformation for the allenes **80**, **122** and **19**, equation (5), with appropriate averaging for the different hydrogen atom orientations of the groups, gives values for ^5J(H–H) from the experimental bond angles, which are in reasonable agreement with those from n.m.r. spectroscopy (Table 12).

A conformational analysis of allenes of the type

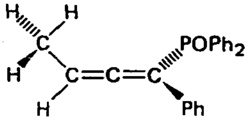


on the basis of vicinal couplings $^3J(\mathrm{H_A{-}H_B})$ has been performed[173] using values of $^3J(\mathrm{H_A{-}H_B}) = 11$ Hz $= {}^3J_t$ for $\mathrm{H_B}$ *trans* to $\mathrm{H_A}$ and $^3J(\mathrm{H_A{-}H_B}) = 4.3$ Hz $= {}^3J_g$ for *gauche* arrangements. The values for ^3J_t and ^3J_g have been obtained from the experimental coupling constants $^3J_{\mathrm{exp}}$ of the compounds **134** and **135**.



(134)

$^3J_{\mathrm{exp}} = {}^3J_t = 11$ Hz



(135)

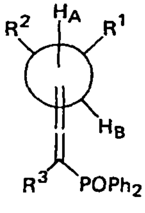
$^3J_{\mathrm{exp}} = 1/3[{}^3J_t + 2\,{}^3J_g] \approx 6{\cdot}5$ Hz

$^3J_g = 4{\cdot}3$ Hz

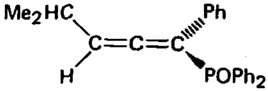
Then the percentage x for the conformation A of these kinds of molecules is obtained from the observed coupling constants $^3J_{\mathrm{obs}}$ according to equation (6). The relative contribution of conformation A to the rotamer population of a great number of phosphoryl allenes is given in Reference 173. Interestingly, for compound **136**, x has been found to be $x = 0.34$, in agreement with the observation for

TABLE 12. Calculated (equation 5) and experimental five-bond proton–proton coupling constants in allenes (Hz)

Compound	^5J(H–H) (calc.)	^5J(H–H) (exp.)	Reference
80	3.14	3.50	171
122	1.18	1.09	156
19	2.16	2.24	172



(A)

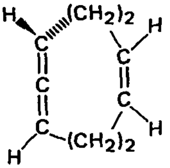


(136)

131, where a conformation with a *gauche* arrangement of the corresponding H_A and H_B atoms has been found to be more stable than one corresponding to A.

$$^3J_{\text{obs}} = x\,^3J_t + (1-x)\,^3J_g \qquad (6)$$

Dynamic ^{13}C-n.m.r. spectroscopy[38] of the cyclic allene 1,2-cyclononadiene (**26**) has revealed that this compound exists in solution as a 2:1 mixture of two (one symmetrical and one unsymmetrical) conformations, having a free energy difference of 0.753 kJ/mol. These findings have been corroborated by force-field calculations and define the conformations found experimentally in structural terms. For instance, the $C_{(1)}C_{(2)}C_{(3)}$ angles in these conformations are calculated to be 170° and 165°, respectively. The major conformation lacks symmetry, whereas the symmetrical one achieves a time-averaged C_2 symmetry. The ^{13}C-n.m.r. data for 1,2,6-cyclononatriene (**137**) reveal the presence of a single conformation, which



(137)

lacks symmetry. The n.m.r. data for 1,2,6,7-cyclodecatetraene (**25**) are consistent with a single conformation in solution having either C_2 or C_i symmetry. Force-field calculations of **25** give as the most stable conformation the C_i arrangement, in agreement with X-ray diffraction results (Table 1).

IV. ACKNOWLEDGEMENT

Support by the 'Deutsche Forschungsgemeinschaft' is gratefully acknowledged.

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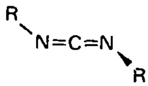
Note Added in Proof

A recent *ab initio* investigation on the molecular structure of methyl allenyl sulphide (**18**)[174] has revealed that the two C=C double bonds in **18** have almost identical bond lengths, as is observed for the other allenes. There is no immediate answer for the discrepancy of these theoretical results and the electron diffraction data in Table 1. Considering all the structural data of allenes in Table 1 a refinement of the electron diffraction data of **18** should be taken into account.

Furthermore, the theoretical investigation[174] predicts that the *syn* form of **18** is the most stable and that the first rotational transition state for *syn–anti* interconversion occurs at a dihedral angle of 65–70°. According to STO-44-31G calculations the *syn* form would go to a *gauche* form through a barrier of about 5 kJ/mol. According to the MO calculations under normal conditions a *gauche* form may be found as a second stable conformer of **18**. The *gauche* form of **18** should be less stable than the *syn* form by about 3.3 kJ/mol[174].

With respect to conformational analysis of allenes it has been shown experimentally that propargylallene $HC{\equiv}CCH_2CH{=}C{=}CH_2$ (**138**) exists in the gas phase in a single preferred *gauche* conformation which is more stable than the *syn* or *anti* form by more than 8.4 kJ/mol[175a]. This has been predicted on the basis of semiempirical MO calculations[175b]. With respect to its conformations **138** exhibits a close analogy to 4-chloro-1,2-butadiene (**19**) (Table 1).



R = p-MeOC$_6$H$_4$ (**139**)
R = Ph$_2$CH (**140**)

Recent X-ray investigations of the carbodiimides **139** and **140**[176] have shown that aliphatic substituents also do not affect the C=N bond lengths markedly [r(C=N) = 1.215 Å in **140**, r(C=N) = 1.220 Å in **139**][176]. The substituents in **139** and **140** are located in almost perpendicular planes. However, the NCN angle deviates about 10° from a linear arrangement, as is also observed for the carbodiimides **45** and **46** (Table 2). In Reference 176 it has been suggested that this deviation from linearity of the NCN arrangement is a molecular characteristic of carbodiimides rather than a result from packing forces in the crystals.

The Chemistry of Ketenes, Allenes and Related Compounds
Edited by Saul Patai

CHAPTER **3**

Chirality and chiroptical properties*

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I. INTRODUCTION

Spectroscopic properties of chiral molecules, i.e. their optical activity as measured by the specific or molar rotation at a definite wavelength, preferentially the

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*This chapter is dedicated to the memory of R. Kuhn (1900–1967), Nobel prize laureate and pioneer in the field.

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wavelength of the sodium D line, the optical rotatory dispersion (ORD) and the circular dichroism (CD) are usually referred to as 'chiroptical properties'[1].

Stereochemical and synthetic aspects of optically active allenes together with a discussion of their molar rotations have been summarized in References 2a and 2b. The latter also includes a compilation of naturally occurring allenes and their optical rotations.

It is the intention of the present chapter to present the various aspects associated with chirality and chiroptical properties of cumulated systems. For reasons to be discussed below this contribution is largely restricted to allenes.

For a consistent treatment of chiroptical properties for different classes of molecules new concepts[3–7] emerging from the 'Theory of chirality functions' by Ruch and Schönhofer[4] have proven to be extremely useful and have vigorously entered into the discussions of the quantitative aspects of the optical activity of allenes[8–11]. In order to envisage their scope and limitations, pertinent features of these new theoretical concepts will be summarized with special emphasis on allenes.

Chiroptical properties of molecules are pseudoscalar in character, i.e. the experimental measurements of numerical values of molecules (or mixtures thereof) give the value zero if the objects are achiral (or the mixtures are racemic), and give identical values with opposite signs if the molecules or the mixtures are enantiomeric, regardless of the orientations of the molecules in space[3–6]. Such experiments with chiral molecules are referred to as 'chirality observations'[3–6]. So far, chirality observations based upon spectroscopic properties (optical rotation, circular dichroism) have been regarded primarily as useful tools for structural chemistry because of their extraordinary sensitivity to configuration and conformation. Therefore, optical activity was mainly a topic for structural chemists or stereochemists. For their purposes the relationship of measured values to the influences and characteristics of particular parts (subunits) of the molecule, their interactions and spatial arrangements are required. For stereochemical purposes qualitative arguments often suffice, e.g. the sign of a particular chirality observation may suffice to deduce structural information about the relative arrangements of atoms and groups of a molecule. Thus an empirical rule, proposed by Lowe[12] and further extended by Brewster[13], for the deduction of the absolute configuration of allenes from the sign of the rotation and the screw pattern of the (average) polarizabilities of the substituents has had widespread applications.

The discussion of the optical rotation of allenes on the basis of chirality functions also covers such a topic, since the theoretical predictions of absolute configurations are an implicit result of an adequate quantitative description of chirality observations.

Structural information (absolute configurations) may also be obtained from the circular dichroism, provided that one has enough knowledge about the electronically excited states which give rise to particular optically active electronic bands, i.e. one has to know what kinds of electronic transitions are involved in the excitations. Conversely, using known absolute configurations (and optical purities) makes circular dichroism spectroscopy an integral part of molecular spectroscopy for the study of electronically excited states[14]. The usefulness of CD spectroscopy for the detection and assignment of electronic bands of allenes has been demonstrated only recently[15,16].

Covering both the stereochemical and the spectroscopic aspects of circular dichroism will link the molecular structure of cumulenes to their electronic structure.

II. THEORETICAL

Optical activity is associated with the interaction of chiral molecules with linearly polarized light. When passing through an optically active medium linearly polarized light is subjected to two characteristic effects. Firstly, the linear polarization changes into an elliptic polarization. The corresponding observable phenomenon is known as circular dichroism. Secondly, the major axis of the emergent elliptically polarized light is rotated relative to the plane of the incident linearly polarized light. This effect is the (circular) birefringence. Both phenomena may be treated quantitatively if the linearly polarized light is regarded as a superposition of two coherent left and right circularly polarized light waves of identical frequency and intensity. Then (circular) birefringence results from the different phase velocities of transmission for the left and right circularly polarized light beams in the optically active medium, i.e. it results from different refractive indices n_l and n_r of the left and the right circularly polarized light waves.

$$\Delta n = \frac{\pi}{\lambda}(n_l - n_r) \tag{1}$$

In equation (1) λ is the wavelength of the incident light. The birefringence Δn is characterized by the temperature-dependent molar rotation $[\phi]_\lambda^T$ (or specific rotation $[\alpha]_\lambda^T$)^{1,14}.

The circular dichroism as measured by the ellipticity θ results from the different absorptions k_l and k_r of the two kinds of circularly polarized light beams in the optically active medium.

$$\theta = \frac{\pi}{\lambda}(k_l - k_r) \tag{2}$$

The molecular ellipticity $[\theta]$ is linearly related to the molar circular dichroism $\Delta\epsilon$ (equation 3), i.e. the difference between the molar extinction coefficients for left and right circularly polarized light.

$$\Delta\epsilon(\lambda) = \epsilon_l - \epsilon_r \tag{3a}$$

$$[\theta] = 3300\,\Delta\epsilon(\lambda) \tag{3b}$$

Both the chiroptical properties $\Delta\epsilon(\lambda)$ and $[\phi]_\lambda^T$ depend upon the wavelength λ of the incident light. The wavelength dependency of the molar rotation is the optical rotatory dispersion (ORD). Therefore, circular dichroism and optical rotatory dispersion have the same electronic origin as the usual u.v. absorption phenomena and may be discussed on the basis of the same model concepts.

Absorption of light is associated with electronic excitation of the molecule from one state $|0\rangle$ with energy E_0 into a state $|i\rangle$ with energy E_i in a definite 'chromophore'. In most cases vibrational and rotational aspects of circular dichroism are negligible. Usually, $|0\rangle$ is the electronic ground state. Then for a single electronic transition $|0\rangle \rightarrow |i\rangle$ a plot of the circular dichroism $\Delta\epsilon$ versus the wavelength $\lambda = c/\nu$ gives the wavelength dependency of $\Delta\epsilon$ to a good approximation as a symmetric Gaussian band (Figure 1). The maximum of the band is related to the excitation energy $E_i - E_0 = h\nu_{0i}$, i.e. the CD curve is nonzero only for the absorption region of the molecule around $h\nu_{0i}$, depending upon the half-width Δ_{0i}. In the region where no absorption of light by the optically active medium occurs, the optical rotatory dispersion is a monotonous curve, i.e. within the transparent region there is no change of sign of the ORD curve. However, inside the absorption region ORD

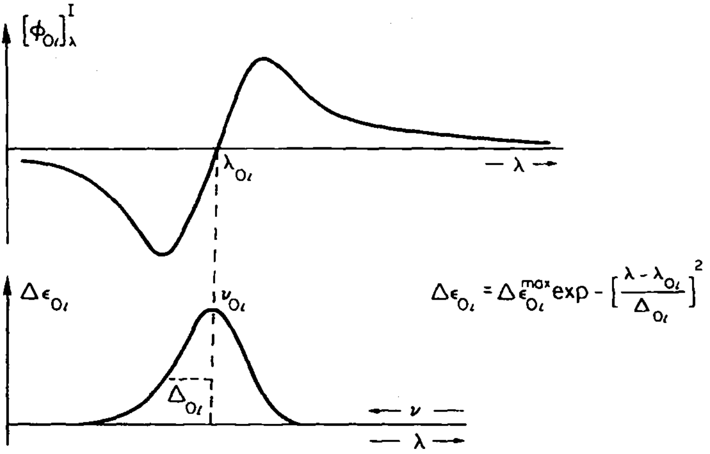


FIGURE 1. Optical rotatory dispersion $[\phi_{0i}]_\lambda^T$ and circular dichroism $\Delta\epsilon_{0i}$ associated with one electronic transition.

will be anomalous. There will be an inversion of sign. The combined effect of CD and anomalous ORD inside the absorption region is called the Cotton effect (Figure 1). With respect to the same electronic transition $|0\rangle \rightarrow |i\rangle$ ORD and CD are related formally by the Kronig–Kramers relations (4) and (5)[14].

$$[\phi_{0i}]_\lambda{}^T = \frac{2}{\pi} \int_0^\infty [\theta_{0i}]_{\lambda'}{}^T \frac{\lambda'}{\lambda^2 - \lambda'^2} d\lambda' \tag{4}$$

$$[\theta_{0i}]_\lambda{}^T = -\frac{2}{\pi\lambda} \int_0^\infty [\phi_{0i}]_{\lambda'}{}^T \frac{\lambda'^2}{\lambda^2 - \lambda'^2} d\lambda' \tag{5}$$

Therefore, the complete knowledge of one effect determines the other and the same kind of information may be deduced from either ORD or CD.

Optical rotation for spectral regions well removed from all absorption maxima of the molecule may be described quantum-theoretically by the Rosenfeld equation (6)[14].

$$[\phi]_\lambda{}^T = \sum_i [\phi_{0i}]_\lambda{}^T = \frac{96\pi N_L}{hc} \frac{n_\lambda{}^2 + 2}{3} \sum_i \left(\frac{\nu^2}{\nu_{0i}{}^2 - \nu^2}\right) R_{0i} \tag{6}$$

In equation (6) ν is the frequency of the incident light, N_L is Avogadro's number, h is Planck's constant, c is the velocity of light and n_λ is the refractive index of the dispersive medium for the incident light of wavelength λ. The factor $(n_\lambda{}^2 + 2)/3$ is the Lorentz correction for the local electric field of the solvent cavity in which the solute molecule is enclosed.

While CD may effectively only be measured in regions of absorption, under certain circumstances, for single electronic transitions, ORD curves have long tails outside the regions of absorption, which result from a superposition of contributions $[\phi_{0i}]_\lambda{}^T$ of all the different electronic transitions of the molecule.

The Rosenfeld equation (6) relates the molar rotation of a molecule to a fundamental molecular quantity, the rotatory strength R_{0i}. The rotatory strength is defined as the imaginary part of the scalar product of the molecular electric transition dipole moment μ and the magnetic transition dipole moment m for the electronic transition $|0\rangle \rightarrow |i\rangle$ under consideration.

$$R_{0i} = \mathrm{Im}\ \langle 0|\mu|i\rangle \cdot \langle i|m|0\rangle \tag{7}$$

Circular dichroism is also governed by the rotatory strength, which is experimentally related to the area of the curve $\Delta\epsilon/\lambda$ (equation 8).

$$R_{0i} = 0.23 \times 10^{-38} \int \frac{\Delta\epsilon(\lambda)}{\lambda}\, d\lambda\ \text{(cgs)} \tag{8}$$

The rotatory strength plays a role formally comparable to the one of the dipole strength D_{0i} (equation 9) for ordinary absorption and refraction[14].

$$D_{0i} = \mathrm{Re}\ \langle 0|\mu|i\rangle \cdot \langle i|\mu|0\rangle = 0.92 \times 10^{-38} \int \frac{\Delta\epsilon(\lambda)}{\lambda}\, d\lambda\ \text{(cgs)} \tag{9}$$

The rotatory strength R_{0i} characterizes the ith electronic transition and fixes the sign and the magnitude of the Cotton effect. As R_{0i} obeys a sum rule (equation 10) all the quantities R_{0i} cannot have the same sign.

$$\sum_i R_{0i} = 0 \tag{10}$$

The sum rule (10) has an important consequence for the molar rotation in the transparent region. Because of the factor ν_{0i} in the denominator of the Rosenfeld equation (6) transitions in the far-ultraviolet will be of less importance than transitions of comparable rotatory strength in the near-ultraviolet and additionally the contributions from the far-ultraviolet absorption bands will tend to cancel out, since the several values for R_{0i} will, according to equation (10), not be of the same sign. In many cases the resultant optical rotations will only be due to some few bands nearest the visible spectral region ($\bar{\nu} \leqslant 50{,}000\ \mathrm{cm}^{-1}$).

Generally, CD spectroscopy gives the same information as u.v. absorption spectroscopy. However, since CD bands may be positive or negative, CD is much more powerful in resolving overlapping absorption bands. Therefore, circular dichroism is especially appropriate for the detection of electronically excited states associated with weak u.v. absorption bands. A useful parameter in the combined use of CD and u.v. absorption spectroscopy for the characterization of a given electronic transition is the 'g-factor' (equation 11), $\cos(m,\mu)$ being the angle between the electric and the magnetic transition dipole moment.

$$g_{0i} = 4\frac{R_{0i}}{D_{0i}} = 4\,\frac{|\langle 0|m|i\rangle|}{|\langle 0|\mu|i\rangle|}\cos(m,\mu) \tag{11}$$

The order of magnitude of g_{0i} gives an insight into the nature of the electronic transition under consideration. In the extreme case of a transition with a large electric and magnetic transition moment parallel to each other g_{0i} is about 10^{-3}. For most transitions large magnetic moments will be accompanied by small electric moments and vice versa. A typical value of g_{0i} for a strong electric dipole allowed transition is 10^{-5}–10^{-6}, whereas strong magnetic dipole transitions will exhibit values of $g_{0i} \approx 10^{-2}$–10^{-1} [14].

Using the quantum-theoretical expression for the rotatory strength (equation 7) it should be possible to calculate the rotatory strengths directly, and via the Rosenfeld equation (6) to calculate the optical rotatory dispersion in the transparent region, provided the electronic wave functions for the particular molecule are known. Apart from numerical difficulties, in most cases such a procedure cannot give any better insight into the origin of the optical activity than can an experimental investigation. The origin of the optical activity is concerned with the relationship of the properties of the whole molecule with the properties of appropriate subunits of the molecule, with the spatial arrangements of these subunits, and with the interactions between them.

Optical rotation and circular dichroism depend sensitively upon structural features of the molecules. In particular, structural aspects of chirality phenomena are covered favourably by the 'Theory of chirality function'[4].

III. ELEMENTS OF CHIRALITY AND OPTICAL ACTIVITY

A. Chirality and Chirality Functions

Chirality is a property which differentiates an object from its mirror image and, therefore, is related to the concept of symmetry.

Mathematically, symmetry can be defined in terms of a 'symmetry group', i.e. a set of transformations giving rise to no detectable change in the object. Then, an object is termed achiral if the position in space only is altered on reflection or rotation–reflection, but chiral if a different object is generated, i.e. one that is not superimposable onto its mirror image by rotation (and/or translation). Ruch[7b] has called the symmetry of an object 'chiral' if its symmetry group does not contain reflection operations, and otherwise 'achiral'. Objects related to each other as image and mirror image are referred to as enantiomers[1].

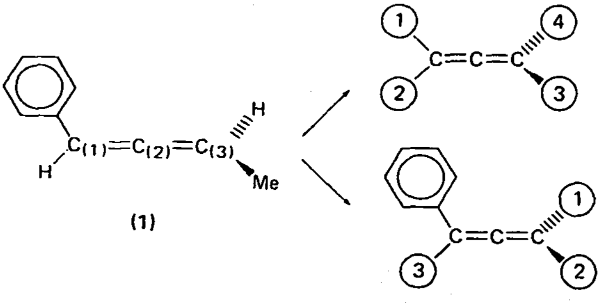
Concerning the molecular level, the geometrical description of chirality starts from the conceptional dissection of the molecule into an (achiral) skeleton or frame with n ligand sites to which the (achiral) ligands (substituents) are attached. The ligands may be atoms or groups of atoms and may be characterized by 'substituent constants'. These parameters allow a differentiation of molecules according to a statement about the skeleton, the ligands and their spatial arrangements.

The molecular skeletons may be monocentric, corresponding to the valence state of atoms (sp^3, dsp^2, d^2sp^3, etc.), such as the methane skeleton consisting of the carbon atom with its four tetrahedrally directed bonds, or polycentric, such as the allenic frame with the ligand sites in perpendicular planes.

Chirality associated with monocentric systems is called 'centrochirality'[1], whereas for the allenes one speaks of 'axial chirality'[1].

With respect to the quantitative treatment of particular molecular properties a given molecule may be dissected conceptionally in different ways according to the specific invariants (frames) and variables (ligands) for the description of the phenomenon under consideration. For instance, 3-methyl-1-phenylallene (1) may be thought of as a four-site allenic skeleton with one phenyl group, one methyl group and two hydrogen ligands with respect to the ^{13}C-n.m.r. chemical shift $\delta_{C(2)}$ of the allenic central carbon atom or the molar rotation $[\phi]_D^{25}$ at the wavelength of the sodium D line (Section IV). Alternatively, 1 may be viewed as a three-site skeleton with one methyl group and two hydrogen atoms, if the u.v. and CD spectra of phenylallenes near 40,000 cm^{-1} are discussed (Section V).

If the molecular skeleton itself is achiral, then chiral properties of molecules may



(1)

arise from the different nature (and perhaps the spatial orientation, the conformation) of the ligands and their arrangements on the various ligand sites. A natural and evident problem associated with chiral properties of molecules, therefore, is the establishment of good models and concepts to account for the observable facts for a definite set of molecules in terms of differences in various properties (or parameters) of the ligands.

The first level of describing molecules by models, which allows the introduction of a geometrical structure for the phenomenon of interest, concerns the skeleton. The restriction to a spatially rigid skeleton makes possible a systematic treatment of chirality for idealized objects and facilitates the representation of the complex problem of chiroptical properties on the basis of symmetry arguments, even for molecules with chemically different skeletons, provided the number of ligand sites and their arrangements in space are identical.

The symmetry of the skeleton, i.e. the point symmetry group G of the arrangement of the ligand sites, defines a class of molecules, which may be characterized by a geometrical figure. The individual members of the class are determined by a specification of the ligands at the various sites. In this way, methane derivatives are representatives of a molecular class, where the skeleton has the symmetry T_d of a regular tetrahedron. Allenes and pentatetraenes may be viewed as representatives for the molecular class with the skeletal symmetry D_{2d} of an irregular tetrahedron. In short, methane derivatives are representatives of 'T_d molecules' and allenes and pentatetraenes of 'D_{2d} molecules' (Figure 2).

Symmetry operations on the molecular skeleton subject the molecules to rotations or rotation–reflections by which the skeleton is brought into coincidence with itself. Such operations (from the symmetry group G) on a rigid skeleton may be represented as interchanges of the ligands, i.e. permutations (from a permutation group S) of the ligands among the sites. In general, a permutation of the ligands gives a different isomer, but there may be some permutations whose effect is the same as simply rotating the molecule and/or replacing it by its mirror image. The truly different isomers produced in this way are called 'permutation isomers'.

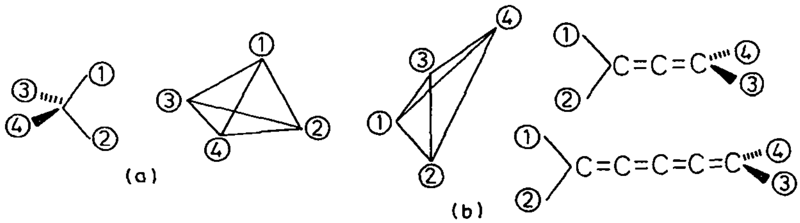


FIGURE 2. Enumeration of ligand sites for molecules with (a) a T_d skeleton and (b) a D_{2d} skeleton.

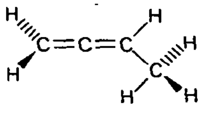
The further level of analytical description of chirality is concerned with the ligands and the permutation operations with the ligands. The nature of the ligands determines the overall symmetry of a molecule if the symmetry arrangement of the ligand sites is not influenced by the ligands or by certain types of ligands, i.e. the site symmetry has to be retained. In case of the allenes (or pentatetraenes) this means that the mirror planes of the cumulenic skeleton must be identical with the mirror planes of the ligands at the particular sites. In this way, the geometrical model imposes a constraint on the set of real molecules whose chiralities can be investigated by means of the model theory. Situations which will affect the above conditions include any deformations of valence and dihedral angles by neighbouring ligands, and changes of conformation, or rotamer populations if particular ligands are arranged in a definite manner relative to the positions of other ligands.

Furthermore, since most investigations on chiroptical properties are performed in solution, steric hindrances of solvation or other solvent effects (hydrogen-bonding effects) have also to be taken into consideration, if chirality observations for real experimental situations are to be discussed.

If more than one orientation of a ligand on a site in the molecule is possible this means that in relation to the time-scale of the experimental investigation of chiroptical properties, one of the following must hold:

(*a*) the ligand must possess sufficient symmetry to make all properties of interest invariant under rotations,
(*b*) the properties of interest refer to time- or ensemble-averages to which all orientations contribute equally, or
(*c*) for a given distribution of ligands, a single orientation is strongly preferred.

Information as to whether the above restricting conditions are met for a particular ligand R may be obtained from structural data of the corresponding monosubstituted molecules, e.g. from monosubstituted allenes $RCH{=}C{=}CH_2$. In case of allenes it is known (cf. Chapter 2) that methylallene (2), ethylallene (3) and methoxyallene (4) exist in solution in only one preferred conformation of C_s symmetry.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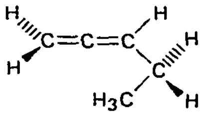
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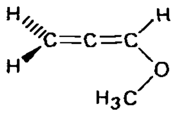
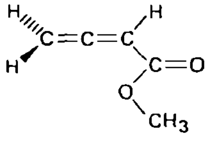

(4)

Similarly, for carbomethoxyallene (5) and acetylallene (6) and their derivatives the *s-trans* conformation is largely preferred.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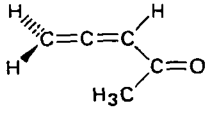

(6)

On the basis of the geometrical model, which represents the ligands as points of a particular quality, any molecular property *P* will depend upon intrinsic properties $\lambda(R_i)$ of the ligands R on the various sites *i*, and thus can be thought of as a function $F[\lambda(R_1), \ldots, \lambda(R_n)]$ of the ligands or parameters thereof. Related to a particular molecular skeleton the (scalar) ligand characteristic $\lambda(R)$ is a 'substituent constant' with a fixed numerical value for a given experiment. If the $\lambda(R)$ parameters are numerically well fixed, one may hope to find another set of substituent constants $\sigma(R)$, which represents a definite physical property and thus, when linearly related to the $\lambda(R)$ parameters, yields an interpretation of the $\lambda(R)$ parameters. Such substituent constants $\sigma(R)$ are adequately determined from molecular properties of monosubstituted compounds.

According to Ruch[3-5,7] a function of the ligands or of certain ligand parameters for the description of a chiral molecular property for a class of molecules with a common achiral skeleton is called a 'chirality function'.

At this level of describing molecular properties a molecular skeleton is a spatial arrangement of points (sites) and the particular molecule is an indexed set, where definite numbers are assigned to the sites. A permutation of the ligands corresponds to a reassignment of the ligand sites by numbers.

Molecules with exclusively identical ligands have the symmetry G of the molecular skeleton. Any other selection of ligands gives rise to another symmetry of the molecule. The different possibilities of arrangement of ligands (like and different) on the n sites of the skeleton may be illustrated by 'partition diagrams'[4-7], which represents mathematically the various possibilities of decomposing the integer n into a sum of numbers $m \leqslant n$. In the case of skeletons with four sites, specifically the T_d and D_{2d} cases, five partitions are obtained as displayed in Figure 3.

In Figure 3 (a) represents the case of four like ligands, (b) the case of three like ligands and one different, (c) that of two different pairs of identical ligands,

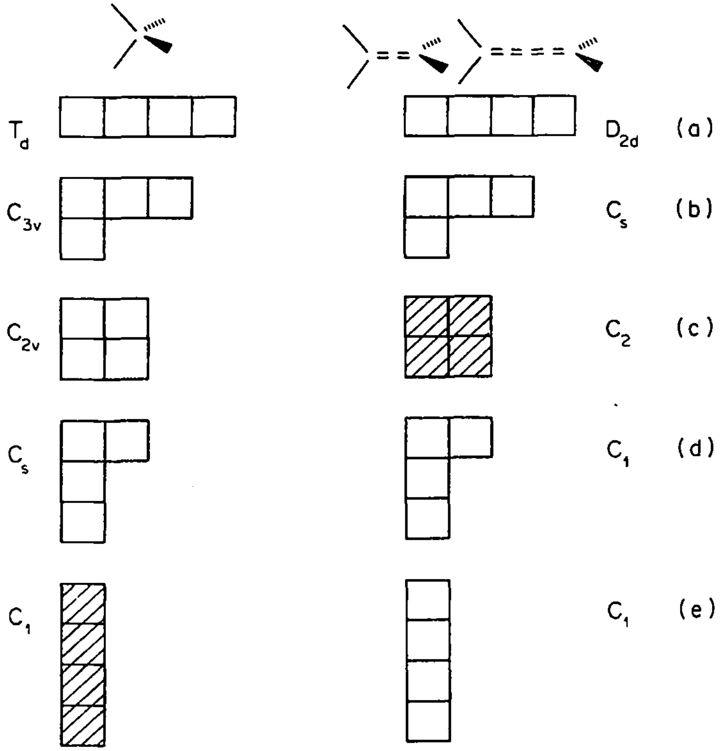
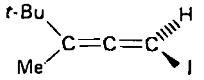


FIGURE 3. Partition diagrams for T_d and D_{2d} molecules.

(d) that of one pair of identical ligands and two other ligands and (e) that of four different ligands. Conventionally, the boxes are arranged in such a way that longer horizontal lines are positioned above shorter ones. All the different allowed permutations of the ligands present are represented in a single diagram.

If we now look with the help of the partition diagram for the molecule which has the maximum number of identical ligands and yet is chiral owing to its symmetry, we see that in case of the T_d molecules all the four ligands have to be different ('asymmetric atoms'), whereas in the case of the allenes or pentatetraenes two pairs of like ligands can lead to chiral molecules. The corresponding diagrams are shaded. If arranged in the manner given in Figure 3 all the diagrams below the one representing chiral molecules with a maximum number of identical ligands also represent chiral molecular arrangements[4-7].

The configurational nomenclature of the enantiomers of the cumulenes according to Cahn, Ingold and Prelog[1c] essentially uses the geometrical description of molecules outlined above, referring in particular to the special situation of the existence of enantiomers with two identical ligands for these axially chiral molecules. For instance, the enantiomer 7 should be viewed along the cumulenic axis. Since, according to the sequence rules[1c], the front substituents in an appropriate projection (located on the vertical projection axis of 7) have precedence over the rear groups (located on the horizontal axis in the above projection of 7), the precedence order is *t*-Bu > Me > I > H, and the enantiomer 7 has the (*S*) configuration. In a similar way, the configurational nomenclature of the enantiomers 8 and 9 of 1,2-cyclononadiene and cyclonona-2,3-dienone-1, respectively, may be established as (*R*).



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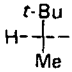

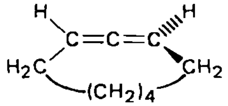

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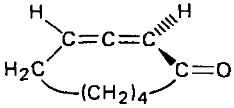


(9)

The maximum number *o* of identical ligands which may occur for chiral molecules is the 'chirality order'[4-7]. This is characteristic for the chirality phenomenon of a given molecular class with *n* ligand sites. It yields as an immediate consequence the minimum number of ligands $N = (n - o)$, which according to their simultaneous contributions are necessary for the description of a chiral property.

In the case of D_{2d} molecules we have $o = 2$ and consequently a chirality function χ must involve at least pair terms $\omega(R_i,R_j) = \omega(R_j,R_i)$: $N = n - o = 4 - 2$

$$\chi(R^1,R^2,R^3,R^4) = \sum_{i \neq j} \omega(R_i,R_j) \tag{12}$$

On the other hand, for T_d molecules ($o = 1$) at least triple terms have to be taken into consideration: $N = 4 - 1$

$$\chi'(R^1,R^2,R^3,R^4) = \sum_{i \neq j \neq k} \omega(R_i,R_j,R_k) \tag{13}$$

If we assign one ligand-specific parameter $\mu'(R_i)$ to each ligand R attached to the site i of the tetrahedral T_d skeleton (Figure 2), the chirality function χ' (equation 14) may or may not accurately describe an interesting chiral property of methane derivatives; it does, however, possess the necessary transformation properties for doing so. It is invariant under rotations of tetrahedral molecules, but changes sign if the molecule is replaced by its mirror image.

$$\chi'(R^1,R^2,R^3,R^4) = [\mu'(R^1) - \mu'(R^2)]\,[\mu'(R^2) - \mu'(R^3)]\,[\mu'(R^3) - \mu'(R^1)] \\ \times [\mu'(R^1) - \mu'(R^4)]\,[\mu'(R^2) - \mu'(R^4)]\,[\mu'(R^3) - \mu'(R^4)] \quad (14)$$

On the other hand, the function (15), which results from (16) with $\omega(R_i,R_j) = \lambda(R_i)\lambda(R_j)$, possesses all the symmetry requirements for the description of a chirality observation of allenes (or pentatetraenes), $\lambda(R_i)$ again being a ligand-specific parameter for the ligand R at site i (Figure 2).

$$\chi(R^1,R^2,R^3,R^4) = [\lambda(R^1) - \lambda(R^2)]\,[\lambda(R^3) - \lambda(R^4)] \quad (15)$$

$$\chi(R^1,R^2,R^3,R^4) = \omega(R^1,R^3) - \omega(R^1,R^4) - \omega(R^2,R^3) + \omega(R^2,R^4) \quad (16)$$

The problem of whether such functions are sufficiently general to completely describe the actual physical situation is solved by Ruch and Schönhofer[4] in terms of the concept of 'qualitative completeness'. In their theory the crucial role is played by the transformation properties of the chirality function, not just under the point-group of the skeleton ($G \simeq S$), but under the larger group of all permutations of the ligands among the n sites of the skeleton (the symmetric group S_n). This group generates not only all orientations of a molecule and its mirror image which leave the constitution invariant, but all constitutional isomers (permutation isomers) as well. For allenes with four different ligands it is easily seen that the group S_4 (with $4! = 24$ elements) produces three different constitutional isomers.

The concept of 'qualitative completeness' emerges from the assumption that, apart from accidental cases, any ensemble of chiral molecules gives a nonzero chirality observation, regardless of whether this ensemble contains only chiral molecules of one kind or is a mixture of (nonenantiomeric) chiral constitutional isomers.

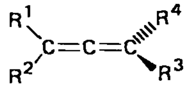
B. Chirality Functions for D_{2d} Molecules

Summarizing some aspects of the 'Theory of chirality functions'[4] with emphasis on D_{2d} molecules, and especially allenes, will not only facilitate the possibility of seeing the relationship of this theory to experiments with allenes, but may help to illustrate and clarify the background of the general theory.

The important aspect of this theory is that it may be developed in terms of expressions for chirality functions which have a particularly simple mathematical form and which, furthermore, meet the chemist's way of thinking in terms of 'substituent effects'. The general theory provides expressions containing, for instance, only formally defined elements, such as ligand-specific parameters $\lambda(R)$, $\mu(R)$, etc. which may be experimentally determined in form of numerical values from a restricted set of chiral molecules and then used to predict chirality observations for other molecules. The parameters may also be obtained on the basis of a quantum-mechanical theory and may then be physically interpreted.

The quantitative description of a chirality observation, e.g. the molar rotation $[\phi]_D^{25}$, naturally guarantees the theoretical determination of the absolute configuration of the molecule.

As well as measuring the pseudoscalar properties of molecules of one kind in an achiral solvent one may also be interested in the corresponding properties of a permutation isomer. Additionally, one may study the relationship between the



chirality observations of different (nonenantiomeric) constitutional isomers. In case of the allenes, which are represented by irregular tetrahedrons of symmetry D_{2d} and ligands at the corners of the tetrahedron (Figure 2), one may be interested in mixtures of the type (a) or (b) in Figure 4. The mixture of type (b) summarizes all possible constitutionally isomeric molecules if the four ligands are different.

The (equimolar) mixtures in Figure 4 are nonracemic and therefore one may expect that corresponding chirality observations of these mixtures will not be zero. It is then quite natural to assume that a chirality function which describes the particular chirality observation for such a mixture, e.g. the one for the mixture (b), should also be nonzero. Formulated for the general case the requirement that sufficiently general chirality functions have to obey to describe observable phenomena is just the property of 'qualitative completeness'. In general, a qualitatively complete chirality function χ is a sum of several components, which differ in their transformation properties under the full permutation group S_n. The different components describe different contributions to the observable chiral properties, and these contributions are independent of each other. The theory does not state that 'qualitatively incomplete functions', e.g. a single one of all the components, do not exist or do not suffice for the description of an observable chiral property. The point is that their existence cannot be predicted *a priori* on the basis of any (group-theoretical and/or quantum-theoretical) arguments or criteria. Their existence, specifically their usefulness in predicting chiral properties, can only be realized

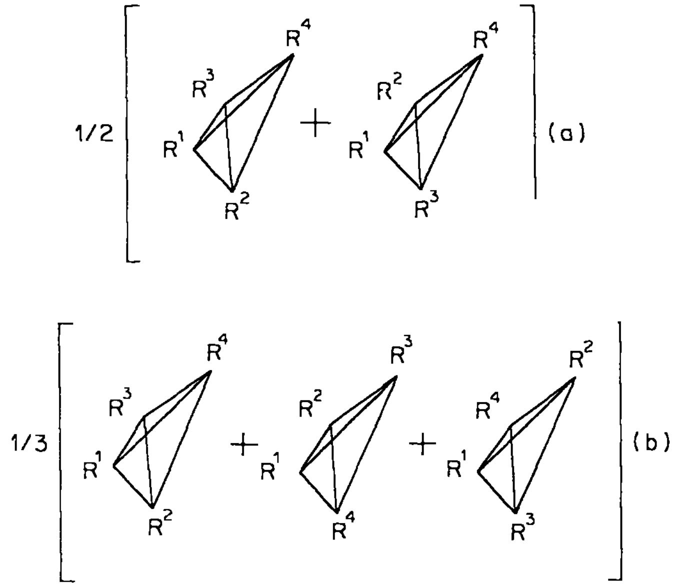


FIGURE 4. Reproduced with permission from W. Runge and G. Kresze, *J. Amer. Chem. Soc.*, 99, 5597 (1977).

a posteriori. 'Qualitatively incomplete functions' ('shortened expressions') may suffice for numerical purposes for some kinds of measurements, for certain molecular classes or for a restricted set of ligands among an enlarged set of interesting ligands within a particular molecular class.

In case of the allenes (and pentatetraenes) the qualitatively complete chirality function χ is made up additively of two components ϕ_1 and ϕ_2 (with different structures). If χ is developed in terms of polynomials of the lowest degree in ligand-specific parameters $\lambda(R_i)$ and $\mu(R_i)$ the corresponding expression is given by equation (17).

$$\chi(R^1,R^2,R^3,R^4) = \phi_1(R^1,R^2,R^3,R^4) + \phi_2(R^1,R^2,R^3,R^4) \tag{17a}$$

$$\begin{aligned}\chi(R^1,R^2,R^3,R^4) = {} & \epsilon_1[\lambda(R^1) - \lambda(R^2)]\,[\lambda(R^3) - \lambda(R^4)] \\ & + \epsilon_2[\mu(R^1) - \mu(R^2)]\,[\mu(R^2) - \mu(R^3)]\,[\mu(R^3) - \mu(R^1)] \\ & \times [\mu(R^1) - \mu(R^4)]\,[\mu(R^2) - \mu(R^4)]\,[\mu(R^3) - \mu(R^4)]\end{aligned} \tag{17b}$$

In equation (17b) the coefficients $\epsilon_i = \pm 1$ $(i = 1, 2)$ are sign factors which may be determined experimentally or by quantum-mechanical theory. Both the components ϕ_1 and ϕ_2 have characteristic features. From equation (17b) one can easily see that for chiral allenes with two identical ligands the μ term vanishes, i.e. for molecules of the type shown in Figure 5 which are known to exhibit pronounced optical activity.

For this kind of molecule ϕ_1, i.e. the λ term, represents the qualitatively complete chirality function and we may infer that for allenes (or pentatetraenes) with two identical ligands a shortened expression like that of equation (15) strictly describes the chiroptical properties. Therefore, among all the molecules of interest there exists a subset of molecules (having two identical ligands) with a particularly simple chirality function. This set is characterized by the fact that all the chiral members are only related to each other by an enantiomerism. Permutation of ligands only generates achiral constitutional isomers of symmetry C_{2v} $(R^2 = R^3)$ or C_s, respectively.

The whole set of interesting molecules contains species where, additionally, a constitutional isomerism is superimposed onto the enantiomerism and therefore effects associated with the constitutional isomerism of allenes are not covered by the shortened expression (15), i.e. the λ term ϕ_1. For such situations the further com-

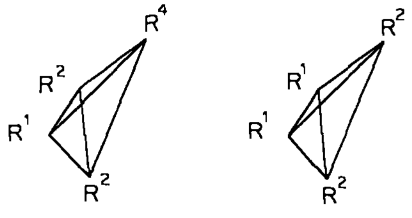


FIGURE 5. Reproduced with permission from W. Runge and G. Kresze, *J. Amer. Chem. Soc.*, 99, 5597 (1977).

ponent ϕ_2 is relevant. The function ϕ_1 satisfies the zero identity (18), regardless of the nature of the ligands.

$$\phi_1(R^1,R^2,R^3,R^4) + \phi_1(R^1,R^3,R^4,R^2) + \phi_1(R^1,R^4,R^2,R^3) = 0 \tag{18}$$

Therefore it does not contribute to the expression (19) which describes the (nonzero) chirality observation of the nonracemic isomer mixture of type (b) in Figure 4.

$$\begin{aligned}
&1/3\ [\chi(R^1,R^2,R^3,R^4) + \chi(R^1,R^3,R^4,R^2) + \chi(R^1,R^4,R^2,R^3)] \\
&\quad = \epsilon_2/3\,[\mu(R^1) - \mu(R^2)]\,[\mu(R^2) - \mu(R^3)]\,[\mu(R^3) - \mu(R^1)] \\
&\quad \times [\mu(R^1) - \mu(R^4)]\,[\mu(R^2) - \mu(R^4)]\,[\mu(R^3) - \mu(R^4)]
\end{aligned} \tag{19}$$

In this way, one can see that either of the functions ϕ_1 and ϕ_2 by itself is incapable of giving a sufficiently general description of a chiral property of D_{2d} molecules. Each vanishes identically in situations where there is no reason from symmetry why it should, i.e. no reason inherent in the definition of chirality functions or in experiences with chiral properties of molecules. The isomer mixture of type (b) in Figure 4 essentially relates chirality observations of constitutional isomers to each other and this relation is determined by the component ϕ_2 of the qualitatively complete chirality function. On the other hand, the isomer mixture of type (a) in Figure 4 also involves constitutional isomers, where only two ligands R^2 and R^3 are interchanged. However, in this case the corresponding μ terms cancel and the chirality observation for an isomer mixture of type (a) only depends upon one component ϕ_1, the λ term.

$$\begin{aligned}
&1/2\ [\chi(R^1,R^2,R^3,R^4) + \chi(R^1,R^3,R^2,R^4)] \\
&\quad = \epsilon_1/2\ \{[\lambda(R^1) - \lambda(R^2)]\,[\lambda(R^3) - \lambda(R^4)] \\
&\quad + [\lambda(R^1) - \lambda(R^3)]\,[\lambda(R^2) - \lambda(R^4)]\}
\end{aligned} \tag{20}$$

This situation, exemplified on the basis of definite expressions for the qualitatively complete chirality function for D_{2d} molecules, stresses that the different components ϕ_1 and ϕ_2 represent physically independent components of the observable phenomenon and consequently, have been developed in terms of different parameters λ and μ.

The situation for allenes of the type shown in Figure 5 and isomer mixtures of type (b) (Figure 4) gives experimental arrangements, which allow the determination of the parameters λ and μ independently.

With respect to the isomer mixture of type (b) (Figure 4) of D_{2d} molecules and equations (18) and (19) the concept of qualitative completeness is easily identified as the mathematical concept of 'linear independencies' of chirality observations for constitutional isomers. If one assumes that the chirality observations are strictly described by the component ϕ_1 only, equation (18) would mean that one has only to measure the chiral properties of two constitutionally isomeric allenes to know the exact value for the third. However, such a situation with permutation isomers is not met in the physical reality apart from some accidental cases. Numerically, equation (18) may show approximate linear dependencies between molecular properties of permutation isomers, but one cannot predict for what situations this will be the case.

The concept of linear independencies of functions describing molecular properties of permutation isomers has also been successfully applied to the general treatment of scalar molecular properties of allenes, such as ^{13}C-n.m.r. chemical

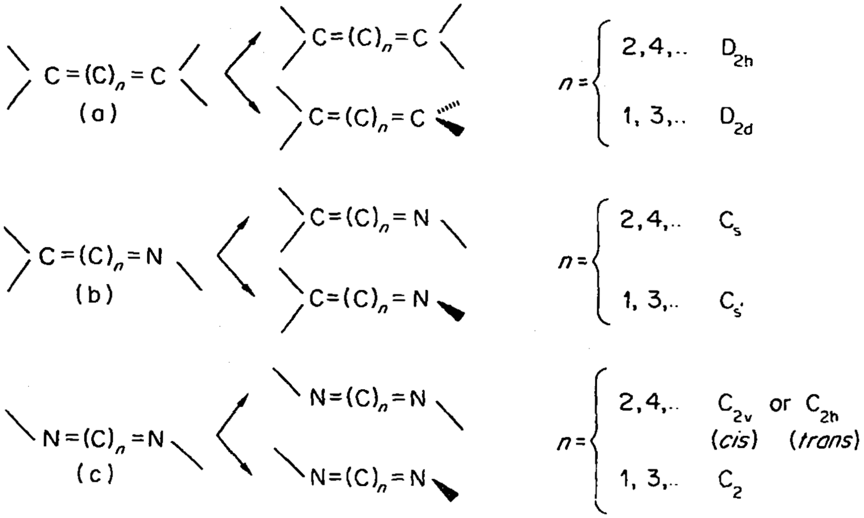


FIGURE 6. Geometries of cumulenes and azacumulenes according to the number of their inner carbon atoms.

shifts[17], ^{1}H-n.m.r. chemical shifts[18] and electron densities[19] of the allenic carbon and hydrogen atoms.

C. Elements Inducing Optical Activity in Cumulenes

The discussion so far on a geometric level has covered only one, albeit especially important, aspect associated with the chirality of cumulenes. Generally, it has been restricted to acyclic molecules. On the geometric level of description chirality and chiroptical properties result from an inherent effect of the arrangement of points at the cumulenic D_{2d} functionality. These types of allenes (or pentatetraenes) may be called 'inherently chiral', a term which is also used to classify molecules with a chiral skeleton[20] and must not be confused within the different contexts. In a similar way, the chirality of other cumulenes may be discussed starting from the symmetries of the corresponding molecular skeletons which are given in Figure 6. Structural chemistry predicts that, apart from the planar ketenes (and thioketenes), the carbon cumulenes (a) and the azacumulenes (b) and (c) (Figure 6) with a linear cumulene moiety are nonplanar for odd *n* and planar for even *n*. For the nonplanar cumulenes the substituents are expected to lie in perpendicular planes[1].

In the nonplanar molecules (a) and (b) chirality may result from an appropriate arrangement of (achiral) substituents, whereas in the nonplanar diazacumulenes (c) each ligand combination yields a chiral molecule. The planar cumulenes are 'inherently symmetric', i.e. the corresponding skeletons cannot give rise to chirality through an appropriate arrangement of (achiral) ligands. Chirality can only be introduced if the cumulene moiety is chirally perturbed by the environment, i.e. by chiral ligands. In a similar way chirality may of course be introduced into nonplanar cumulenes. For instance, Table 1 gives a summary of allenes **10**–**13**, which are chirally perturbed by ligands, together with their molar rotations.

From these examples one can see that a chiral perturbation in the position α to the allenic skeleton has a more pronounced effect than a perturbation in the β-position. The remarkable difference in optical activity of the two comparable

$\mathrm{EtMe\dot{C}HHC{=}C{=}CH_2}$

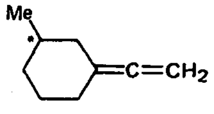
(10)

$\mathrm{EtMe\dot{C}HCH_2HC{=}C{=}CH_2}$

(11)

$^{-}\mathrm{OOC\dot{C}H(\overset{+}{N}H_3)CH_2HC{=}C{=}CH_2}$

(12)



(13)

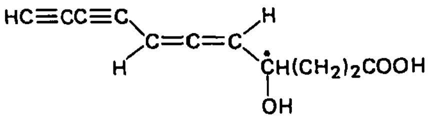
TABLE 1. Allenes whose chirality results from a chiral environment

Compound	$[\phi]_D$ (deg.)	Solvent	Reference
10	+62.8	Neat	2b, 21, 22
11	+ 4.8	Neat	2b, 21, 22
12	0[a]	–	23
13	+60.0	Isooctane	2b, 21, 22

[a] 12 is a naturally occurring allene, which when isolated is inactive at the wavelength of the sodium D line, but dextrorotatory at short wavelengths.

allenes 11 and 13 with the chiral perturbator in the β-position may be attributed to a more pronounced conformational rigidity in the cyclic allene 13 and the preference of one form in the rotamer population[21,22].

The chiral allenic hydrocarbons 10, 11 and 13 may be obtained by conventional methods of allene chemistry[24] starting from compounds of known absolute configuration and optical purity. The dextrorotatory 10, 11 and 13 have the (*S*) configuration for the chiral ligands. If in a monosubstituted allene with a chiral ligand one hydrogen atom of the methylene group is substituted by another (achiral) ligand, we have a combination of two elements for the induction of chirality. In this case interchange of geminal ligands at the allenic skeleton does not give an enantiomer as is the case for only achiral ligands, but gives a diastereomer with different chemical and physical properties. Some allenes of this type are found in nature, e.g. the compounds 14–17, whose rotations are given in Table 2. For all these molecules the absolute configurations are not known and only one of the possible diastereomeric forms has been isolated.



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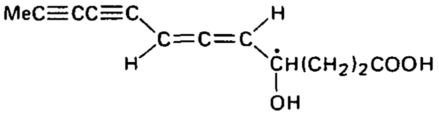
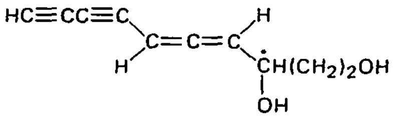
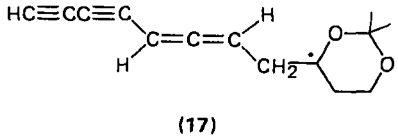


(15)



(16)



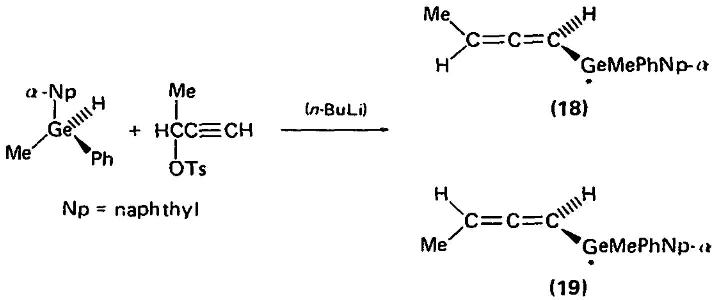
(17)

TABLE 2. Allenes whose chirality is due to the allenic axial chirality and a chiral ligand

Compound	$[\phi]_D$ (deg.)[a]	Reference
14	+723	25
15	+735	25
16	−341	26
17	−454	26

[a] In ethanol.

The detection of two optically active diastereomeric allenes of the above type was achieved with ^{1}H-n.m.r. spectroscopy[27] when (R)-(+)-α-naphthylphenylmethylgermane via its lithium derivative was reacted with the tosylate of but-3-yn-2-ol.

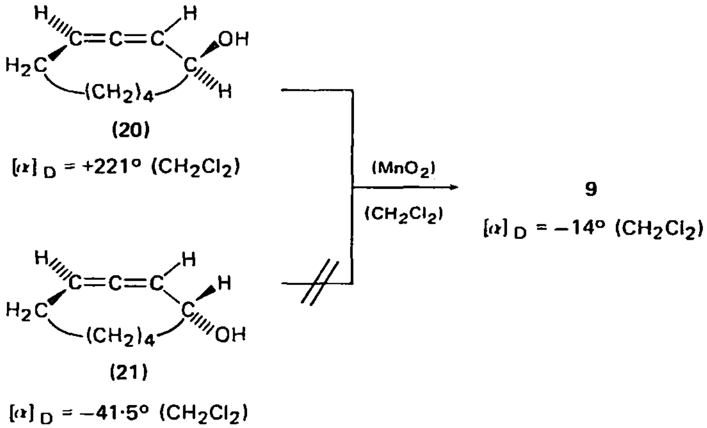


(18)

(19)

Two diastereomers were obtained in the ratio 65/35 with a rotation of $[\alpha]_D = +25°$ for their mixture. From the rotation of the 50/50 mixture ($[\alpha]_D = +5.5°$) one may conclude that the particular diastereomer in excess has a positive rotation. The configuration of the allenic subunit of the dextrorotatory diastereomer has been tentatively assigned as (*S*) (**18**). The configuration of the germyl group is not known, because of possible inversion during the course of the reaction. For instance, if the tosyl group is replaced by bromine, a corresponding reaction proceeds with inversion at the germyl group.

Similar structural situations may also be observed for cyclic allenes, such as the cyclonona-2,3-diene-ols-1 **20** and **21**, with an endocyclic allenic functionality. These diastereomers behave chemically quite differently. When oxidized with manganese dioxide only **20** was converted into cyclonona-2,3-dienone-1 (**9**), whereas **21** was largely unaffected by this reagent[28].



(20)

$[\alpha]_D = +221°$ (CH_2Cl_2)

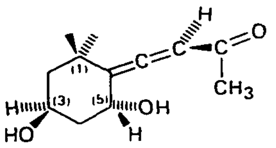
(21)

$[\alpha]_D = -41{\cdot}5°$ (CH_2Cl_2)

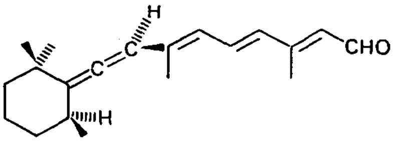
9

$[\alpha]_D = -14°$ (CH_2Cl_2)

As an example for the combination of asymmetric perturbation and the allenic axial chirality, the allenic functionality being exocyclic, an allenic ketone **22**[29] may be cited; it is structurally related to naturally occurring allenic carotenoids, such as fucoxanthin, neoxanthin, etc., whose optical rotations may be found in Reference 2b. The absolute configuration of **22** has been established by X-ray crystallographic analysis of the $C_{(3)}$ *p*-bromobenzoate[29]. Structurally related to **22** is an all-*trans* allenic retinal **23**, which is used as an artificial rhodopsin analogue[30]. The CD spectra of such artificial rhodopsins in the range of $300 \leqslant \lambda \leqslant 600$ nm are comparable with that of 9-*cis*-rhodopsin (isorhodopsin)[30].

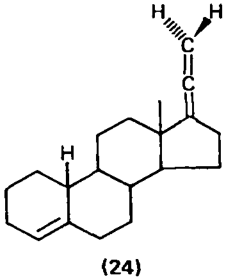


(22)



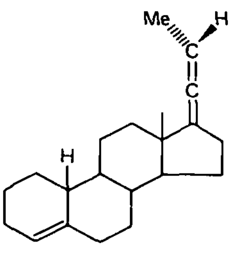
(23)

The rotations of the cyclic allenes **20** and **21** show the effect which occurs when the chirality of the substituent is reversed by interchanging two groups of the formal ligand. The rotations of the allenic steroids **24**–**27**[31] and **28**, **29**[32] give an idea of the effect when the chirality is changed in the allenic subunit.



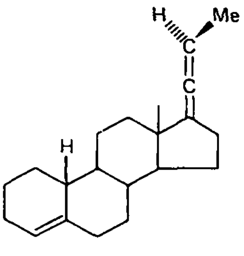
(24)

$[\alpha]_D^{20} = +109°$ (CH_2Cl_2)



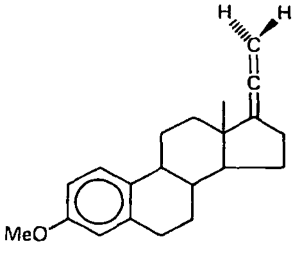
(25a)

$[\alpha]_D^{20} = +151{\cdot}7°$ (CH_2Cl_2)



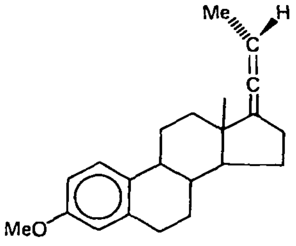
(25b)

$[\alpha]_D^{20} = +61{\cdot}3°$ (CH_2Cl_2)



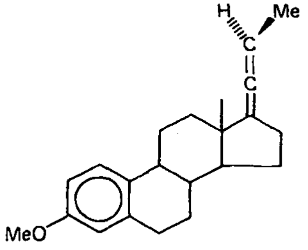
(26)

$[\alpha]_D^{20} = +41{\cdot}2°$ (CH_2Cl_2)



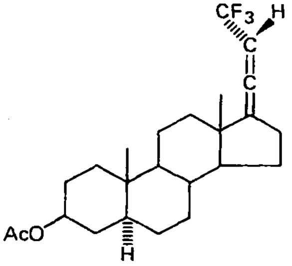
(27a)

$[\alpha]_D^{20} = +84°$ (CH_2Cl_2)



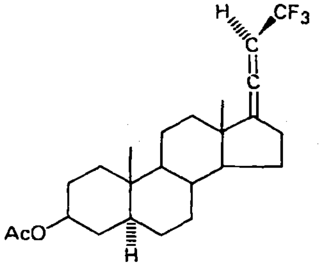
(27b)

$[\alpha]_D^{20} = -15{\cdot}5°$ (CH_2Cl_2)



(28)

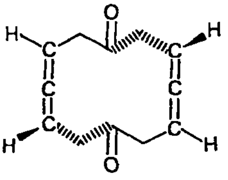
$[\alpha]_D = +7°$



(29)

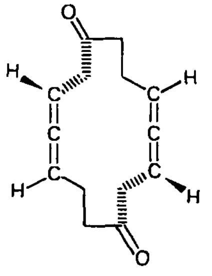
$[\alpha]_D = +51°$

If two chiral allenic subunits are combined, such diallenes exist in diastereomeric forms, which may be optically active or not. The combination retaining a centre of inversion gives an achiral *meso* form. Optically active diallenes, the cyclic compounds **30** and **31**, have been obtained by Sondheimer and coworkers[33].



(30)

$[\alpha]_D = +55{\cdot}5°$ (EtOH)

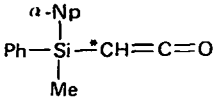


(31)

$[\alpha]_D = +34{\cdot}1°$ (EtOH)

D. Chiral Cumulenes other than Allenes

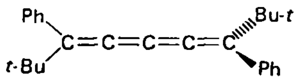
Cumulenes of the type (a) and (b) with an even *n* (Figure 6) as well as ketenes (or thioketenes) can only become optically active through chiral perturbation. Until now, only one example of an optically active molecule with a ketene functionality has been reported[34]. It is the α-naphthylphenylmethylsilylketene (**32**).



$$\mathrm{Ph{-}\underset{Me}{\overset{\alpha\text{-}Np}{Si}}{-}{}^{*}CH{=}C{=}O}$$

(32)

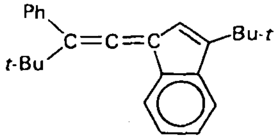
So far, only the structural implications for chirality of cumulenes have been considered. However, in order to investigate chiroptical properties under normal laboratory conditions one has to isolate chiral molecules which must be configurationally stable under normal conditions. Therefore, the energy barrier, which is necessary to transform one chiral molecule into its enantiomer must exceed 84 kJ/mol[1]. The configurational stability of allenes is a well-known fact. The separation of enantiomeric pentatetraenes in optically pure forms was achieved only recently for 1,3-diphenyl-1,3-di-*t*-butylpentatetraene (33)[35]. The treatment of optical activity of allenes based upon chirality functions (Section IV) suggests that dextrorotatory 33 of symmetry C_2 has the (*S*) configuration. A claim to have isolated optically active 33 after dehydration of a dialcohol with *d*-camphorsulphonic acid[36] was later shown to be in error[37]. The isolated product was an indenoallene 34, which is obtained from 33 under the acidic conditions of the dehydration reaction.



(33)

$[\alpha]_D = +336{\cdot}6^\circ$ ($CHCl_3$)

$[\alpha]_D = -336{\cdot}0^\circ$ ($CHCl_3$)



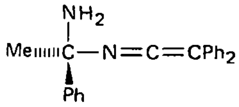
(34)

$[\alpha]_{546} = +11^\circ$

D_{2d} cumulenes of type (a) with $n \geqslant 5$ (Figure 6) are configurationally not stable under normal conditions.

In the case of (acyclic) ketene imines and carbodiimides [n = 1 for (a) and (b) in Figure 6] the energy barriers separating enantiomers have been determined to be in the range of 30–70 kJ/mol (cf. Chapter 2). For these reasons, attempts to separate enantiomers and to demonstrate the chirality of ketene imines and carbodiimides via chiroptical properties should not be successful for molecules with 'conventional' substituents. Schlögl and Mechter[38] report partial resolution of diferrocenylcarbodiimide. However, as the observed optical rotation, $[\alpha]_D = -4.8^\circ$ (benzene), is very small, the rotation is probably due to an impurity[39].

On the other hand, induction of optical activity in the azacumulenes by chiral substituents represents no difficulties. Thus, (*S*)-(–)-diphenyl-*N*-(1-phenylethylamine)ketene imine (35) has been synthesized by conventional procedures without any measurable racemization[40].



$$\mathrm{Me\underset{Ph}{\overset{NH_2}{C}}{-}N{=}C{=}CPh_2}$$

(35)

$[\alpha]_D^{25} = -35{\cdot}3^\circ$ (CCl_4)

IV. SEMIEMPIRICAL CALCULATION OF OPTICAL ROTATIONS OF ACYCLIC ALLENES

A. Molar Rotations

1. Allenes with ligands bonded via carbon to the molecular skeleton

Section III established the possibility of a semiempirical treatment of the molar rotation $[\phi]_D^{25}$ of allenes at the wavelength of the sodium D line as well as the optical rotatory dispersion $[\phi]_\lambda^{25}$ in the transparent region, provided a sufficiently great number of optically pure molecules of known absolute configurations is available[8-11].

In Table 3 a summary of molar rotations of acyclic allenes fitting the above requirements is given. In all cases the rotations correspond to molecules of (*S*) configurations. Sometimes the optical purities have not been established by chemical or physical means, but are only highly probable values. The compounds include allenic hydrocarbons (36, 37), phenylallene carboxylic acids and alkylallene carboxylic acids as well as their methyl esters and sodium salts (38–62), α- and β-allenic alcohols with alkyl groups (63–66) or diyne groups (70–74) and allenes with an α-naphthyl group (76–78). So far, the rotations of only three optically pure allenes with hetero substituents have been reported in the literature.

One of the inherent difficulties in a quantitative treatment of optical rotations for a molecular class is the extreme sensitivity of optical activity towards solvent effects[11]. Generally, one may distinguish forces which are independent of any orientations of the solvent and solute molecules and those forces which, e.g. via hydrogen bonds, lead to special arrangements of solvent and solute molecules and thus may introduce additional contributions to chirality observations. The first kind of solvent effects may be accounted for using the Lorentz factor $(n_D^2 + 2)/3$ (equation 6).

In order to treat the molar rotations of allenes consistently and to rule out possible influences of the solvent on chirality observations the conditions for measuring rotations have to be as similar as possible. For this purpose ethanol, methanol or acetonitrile have been proposed as 'standard solvents'[11]. Chloroform and methylene chloride may exert considerable solvent effects, especially if molecules with protic groups, such as COOH, CH_2OH, etc., are studied[11]. For nonpolar allenes hydrocarbon solvents are appropriate.

The 'shortened' expression (15) of the qualitatively complete chirality function (17), i.e. the λ term, suffices for a numerically adequate description of the molar rotations of phenylallenes and alkylallene carboxylic acids[9,11]. For such types of allene, when substituted by four different ligands, the component ϕ_2, i.e. the μ term, does not seem to contribute essentially to the chirality observations. According to the general theory this result has to be regarded as accidental. It cannot be predicted by any arguments and therefore it is not clear whether the λ term also suffices for the prediction of the rotations of allenes, which are not of the above two molecular types, and which additionally are not of the type shown in Figure 5. However, this problem is without relevance for the present discussion of the optical rotations of the allenes 36–81. If the allenes under consideration are not phenylallenes or alkylallene carboxylic acids, they have at least two identical ligands and therefore the μ term vanishes identically for these molecules. Consequently, the rotations of all the allenes 36–81 may be discussed on the basis of equation (15), the λ term, which may then serve for the prediction of absolute configurations and optical purities.

TABLE 3. Molar rotations of acyclic allenes $R^1R^2C{=}C{=}CR^3R^4$ having the (*S*) configuration

Compound	R^1	R^2	R^3	R^4	$[\phi]_D$ (deg.)		Reference
36	Me	H	Me	H	+ 53.3	(neat)	2b, 11
37	Ph	H	Ph	H	+1958	(EtOH)	41, 11
38	Ph	H	COOH	H	+673	(MeOH)	42, 11
39	Ph	Me	COOH	H	+515	(EtOH)	42, 43, 11
40	Ph	Et	COOH	H	+496	(EtOH)	42, 43, 11
41	Ph	Me	COOH	Me	+280	(EtOH)	43, 44, 11
42	Ph	Et	COOH	Et	+ 88.8	(EtOH)	43, 44, 11
43	Ph	Et	COOH	Me	+253	(EtOH)	43, 44, 11
44	Ph	Me	COOH	Et	+103	(EtOH)	43, 44, 11
45	Ph	H	COOH	Me	+374	(EtOH)	43, 11
46	Ph	H	COOH	Et	+157	(EtOH)	43, 11
47	Ph	*i*-Pr	COOH	H	+416	(MeOH)	42, 11
48	Ph	*t*-Bu	COOH	H	+383	(MeOH)	42, 11
49	Ph	Et	COOMe	Et	+124	(EtOH)	43, 11
50	Ph	Et	COOMe	Me	+300	(EtOH)	43, 11
51	Ph	Me	COOMe	Et	+154	(EtOH)	43, 11
52	Ph	Et	COONa	Et	+211	(EtOH)	43, 11
53	Ph	Et	COONa	Me	+354	(EtOH)	43, 11
54	Ph	Me	COONa	Et	+249	(EtOH)	43, 11
55	Et	Me	COOH	H	+124	(EtOH)	45, 11
56	Me	H	COOH	Et	+ 34.4	(EtOH)	43, 11
57	Et	H	COOH	Me	+100	(EtOH)	43, 11
58	Et	H	COOH	Et	+ 74.9	(EtOH)	43, 11
59	Me	H	COOH	Me	+ 63.5	(EtOH)	43, 11
60	*n*-Hex	H	COOH	H	+244	[a]	46, 11
61	Me	H	COOH	*n*-Bu	+ 47.2	($CHCl_3$)	47, 11
62	Et	Me	COOMe	H	+111	($CHCl_3$)	45. 11
63	Me	H	CH_2OH	H	+ 76	(MeOH)	48
64	Me	H	CMe_2OH	H	+113	(MeOH)	48, 11
65	Me	H	CH_2CH_2OH	H	+ 84	(MeOH)	48, 11
66	*n*-Und[b]	H	CH_2CH_2OH	H	+194	(neat)	49
67	*n*-Und	H	$(CH_2)_3COOMe$	H	+139	(EtOH)	50
68	CH_2OAc	H	$(CH_2)_3COOMe$	H	+ 84.9	(CH_2Cl_2)	51
69	CH_2OAc	H	$(CH_2)_4OAc$	H	+ 86.0	(CH_2Cl_2)	51
70	$HC\equiv CC\equiv C$	H	CH_2OH	H	+448	(CH_2Cl_2)	26, 11
71	$HC\equiv CC\equiv C$	H	CH_2CH_2OH	H	+475	(EtOH)	52, 11
72	$HC\equiv CC\equiv C$	H	$(CH_2)_3OH$	H	+350	(EtOH)	26, 52
73	$HC\equiv CC\equiv C$	H	$(CH_2)_4OH$	H	+288	(EtOH)	26, 52
74	$MeC\equiv CC\equiv C$	H	CH_2CH_2OH	H	+496	(EtOH)	26, 52
75	$HC\equiv CC\equiv C$	H	CH_2COOMe	H	+456	(EtOH)	26, 52
76	α-Np[c]	Ph	α-Np	Ph	+1559	(cyclohexane)	53
77	α-Np	Ph	COOMe	Ph	−187	(benzene)	54
78	α-Np	Ph	$COOCH_2COOH$	Ph	−113	(MeCOOEt)	54, 55
79	Ph	Et	NCO	Me	+152	(isooctane)	56
80	*t*-Bu	H	$POCl_2$	*t*-Bu	+168	(dioxane)	57
81	*t*-Bu	H	$PO(OH)_2$	*t*-Bu	+103	(Me_2CO)	57

[a] The solvent for the measurement is not given.
[b] *n*-Und = $CH_3(CH_2)_{10}$.
[c] Np = Naphthyl.

For the determination of the numerical values of the $\lambda(R)$ parameters only some of them need to be evaluated from chirality observations of particular molecules[9,11]. They are given in Table 4 in the first column using the convention $\lambda(H) = 0$ $(\epsilon_1 = +1)$[11]. The compounds whose rotations in ethanol have been used to evaluate the corresponding $\lambda(R)$ parameters are given in the second column of Table 4. Rotations, which have been measured in other solvents, have been converted to the ethanol standard using the Lorentz factor.

These 'primary' $\lambda(R)$ parameters exhibit linear correlations with the ^{13}C-n.m.r. chemical shift parameters $\sigma(R)$ (Figure 7), which are used for the semiempirical calculations of the ^{13}C chemical shifts $\delta_{C(2)}$ of the allenic central carbon atoms according to equation (21)[17].

$$\delta_{C(2)} = \rho + \sum_{i=1}^{4} \sigma(R_i) + \tau(R^1,R^2) + \tau(R^3,R^4) \qquad (21)$$

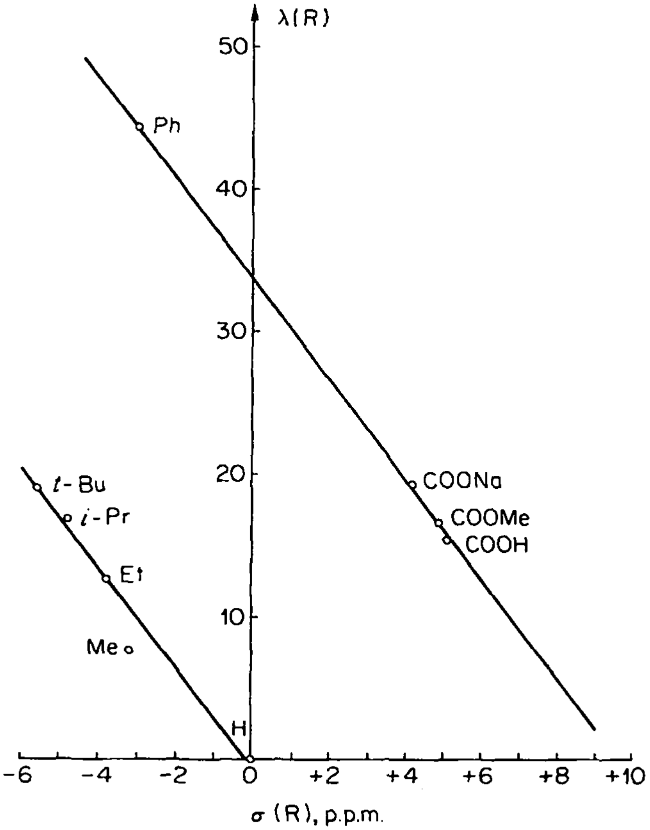


FIGURE 7. Correlation of the $\lambda(R)$ parameters and the ^{13}C chemical shift parameters $\sigma(R)$, which are used for the calculation of the ^{13}C shifts of the allenic central atoms. Taken from W. Runge and J. Firl, *Ber. Bunsenges. Phys. Chem.*, 79, 913 (1975) and reproduced by permission of Verlag Chemie, GmbH, Weinheim.

In equation (21) the $\sigma(\mathrm{R}_i)$ are ligand-specific parameters for the substituents attached to the ligand sites i, the τ are interaction parameters for the geminal substituents $\mathrm{R}^1,\mathrm{R}^2$ or $\mathrm{R}^3,\mathrm{R}^4$, respectively. The parameters $\sigma(\mathrm{R})$ have been determined from monosubstituted allenes $\mathrm{RCH{=}C{=}CH_2}$[17]. The pair terms τ are necessary to differentiate constitutionally isomeric allenes.

Two correlations, equations (22a) and (22b), with almost equal slopes have been obtained by a linear regression[11]. Equation (22a) is valid for σ-inductive alkyl groups including hydrogen and equation (22b) for mesomeric substituents bonded via a carbon atom to the allenic skeleton.

$$\lambda(\mathrm{R}) = -3.47\,\sigma(\mathrm{R}) - 0.85 \qquad \text{for inductive groups} \qquad (22a)$$

$$\lambda(\mathrm{R}) = -3.53\,\sigma(\mathrm{R}) + 33.76 \qquad \text{for mesomeric groups} \qquad (22b)$$

As the ^{13}C chemical shifts of the allenic central carbon atoms or the ^{13}C chemical shift parameters $\sigma(\mathrm{R})$, respectively, are related to the π-electron densities $P_{\mathrm{C}(2)}{}^{\pi}$ (CNDO/S) at the central carbon atom of monosubstituted allenes[11], there are also correlations of the $\lambda(\mathrm{R})$ parameters with the π-electron densities (equations 23a and 23b), which have been obtained from quantum-chemical CNDO/S calculations[19].

$$\lambda(\mathrm{R}) = 190.3\,P_{\mathrm{C}(2)}{}^{\pi}(\mathrm{CNDO/S})(\mathrm{RHC{=}C{=}CH_2}) - 173.0 \qquad \text{for inductive groups} \qquad (23a)$$

$$\lambda(\mathrm{R}) = 344.0\,P_{\mathrm{C}(2)}{}^{\pi}(\mathrm{CNDO/S})(\mathrm{RHC{=}C{=}CH_2}) - 269.3 \qquad \text{for mesomeric groups} \qquad (23b)$$

TABLE 4. $\lambda(\mathrm{R})$ parameters for the calculation of molar rotations of allenes

Primary parameters	Compound used	Secondary parameters	Method used
$\lambda(\mathrm{H}) = +0$[11]		$\lambda(n\text{-Pr}) = +7.7$	Equation (22a)[11]
$\lambda(\mathrm{Ph}) = +44.3$	37[11]	$\lambda(n\text{-Bu}) = +12.6$	Equation (22a)[11]
$\lambda(\mathrm{COOH}) = +15.4$	38[11]	$\lambda(n\text{-Pe}) = +7.7$	Equation (22a)[11]
$\lambda(\mathrm{Me}) = +7.7$	41[11]	$\lambda(n\text{-Hex}) = +12.6$	Equation (22a)[11]
$\lambda(\mathrm{Et}) = +12.6$	42[11]	$\lambda(p\text{-MeC}_6\mathrm{H}_4) = +42.3$	Equation (22a)[11]
$\lambda(i\text{-Pr}) = +16.9$	47[11]	$\lambda(p\text{-ClC}_6\mathrm{H}_4) = +44.3$	Equation (22a)[11]
$\lambda(t\text{-Bu}) = +18.9$	48[11]	$\lambda(\mathrm{CH_2SMe}) = +7.7$	Equation (22a)[11]
$\lambda(\mathrm{COOMe}) = +16.5$	49[11]	$\lambda(\mathrm{(CH_2)_2OH}) = +12.6$	Equation (22a)[11]
$\lambda(\mathrm{COONa}) = +19.3$	52[11]	$\lambda(\mathrm{CH_2OH}) = +9.5$	Equation (23a)[11]
$\lambda(\mathrm{CMe_2OH}) = +14.7$	64[11]	$\lambda(\mathrm{HC{\equiv}CC{\equiv}C}) = +37.5$	Equation (23b)[11]
$\lambda(\alpha\text{-Np}) = +82.9$	76[a]	$\lambda(\mathrm{MeC{\equiv}CC{\equiv}C}) = +37.5$	*a, b*
$\lambda(\mathrm{NCO}) = +12.4$	79[a]	$\lambda(\mathrm{CH_2OAc}) = +9.5$	*a, c*
$\lambda(\mathrm{POCl_2}) = +27.5$	80[a]	$\lambda(\mathrm{CH_2COOMe}) = +9.5$	*a, c*
$\lambda(\mathrm{PO(OH)_2}) = +24.5$	81[a]	$\lambda(n\text{-Und}) = +15.4$	66[a]
		$\lambda(\mathrm{(CH_2)_3OH}) = +9.3$	72[a]
		$\lambda(\mathrm{(CH_2)_4OH}) = +7.7$	73[a]
		$\lambda(\mathrm{(CH_2)_3COOMe}) = +9.3$	*a, d*
		$\lambda(\mathrm{(CH_2)_4OAc}) = +7.7$	*a, e*

[a] This work.
[b] Estimated from $\lambda(\mathrm{MeC{\equiv}CC{\equiv}C}) = \lambda(\mathrm{HC{\equiv}CC{\equiv}C})$.
[c] Estimated from $\lambda(\mathrm{CH_2OH}) = \lambda(\mathrm{CH_2OAc}) = \lambda(\mathrm{CH_2COOMe})$.
[d] Estimated from $\lambda(\mathrm{(CH_2)_3COOMe}) = \lambda(\mathrm{(CH_2)_3OH})$.
[e] Estimated from $\lambda(\mathrm{(CH_2)_4OAc} = \lambda(\mathrm{(CH_2)_4OH})$.

The correlations (22) and (23) may be used to derive further $\lambda(R)$ parameters without any reference to chirality observations[11]. The 'secondary' $\lambda(R)$ parameters obtained in this way are given in third column of Table 4. Notes in the fourth column of Table 4 show what method was used to evaluate the corresponding $\lambda(R)$ parameter, i.e. from correlations (22) or (23), or in some cases from the molar rotation of a particular compound, relying on parameters evaluated from the empirical correlations. The great differences between the numerical values of the $\lambda(R)$ parameters of the methyl, ethyl, *i*-propyl and *t*-butyl groups are remarkable. Usually, it is assumed that such alkyl groups exhibit similar influences on optical activity. A quantum-mechanical theory of the optical rotation of (*S*)-1,3-dimethylallene (**36**)[58], which has given the physical interpretation of the $\lambda(\mathrm{Me})$ parameter, claims that this parameter is related to the difference in the group polarizabilities concerning the major axes of the =C—Me bond, $\Delta\alpha(\mathrm{Me}) = \alpha_{rr}(\mathrm{Me}) - \alpha_{tt}(\mathrm{Me})$, the anisotropic polarizability, and a factor κ (Me), which reflects the polarity of the C_{sp^2}—C_{sp^3} bond between the allenic terminal carbon atom and the ligand carbon atom (equation 24).

$$\lambda(\mathrm{Me}) = G\kappa(\mathrm{Me})\Delta\alpha(\mathrm{Me}) \tag{24}$$

G is a geometrical factor depending upon the symmetry of the molecular skeleton.

Since the group anisotropic polarizabilities for alkyl groups such as Me and *t*-Bu are almost identical[11], the large variations of the $\lambda(R)$ parameters for the alkyl groups should be due to the factor κ (R), i.e. the bonding polarities. This is established by the linear correlation of the $\lambda(R)$ parameters with the group moments $|\mu(R)|$[11] (Figure 8).

This finding, i.e. the polarity influence on the $\lambda(R)$ parameters for inductive groups, may be used for the estimation of some parameters in Table 4. As the Taft inductive substituent constants σ^*[59] are almost identical for the groups CH_2X

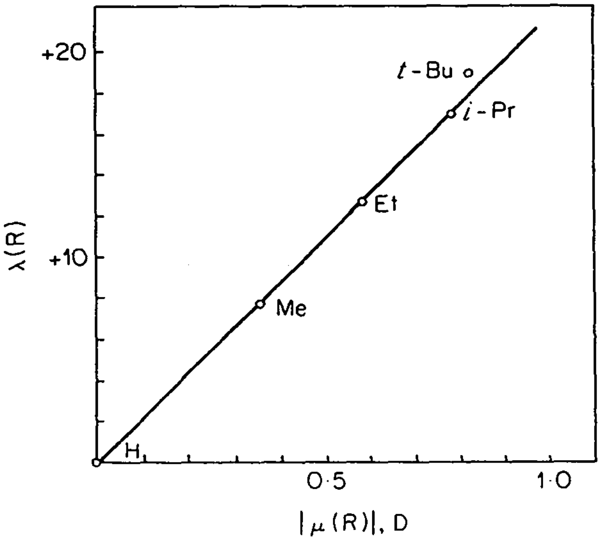


FIGURE 8. Correlation of the $\lambda(R)$ parameters of inductive substituents and the group moments $|\mu(R)|$. Reproduced with permission from W. Runge and G. Kresze, *J. Amer. Chem. Soc.*, 99, 5597 (1977).

TABLE 5. Experimental and calculated (equation 15) molar rotations of allenes having the (*S*) configuration

Compound	$[\phi]_D^{25}$ (deg.) (exp.)	χ (deg.) (calc.)
36	+53.3 (neat)	+62.3 (neat)[b]
39	+515 (EtOH)	+564 (EtOH)
40	+496 (EtOH)	+488 (EtOH)
43	+253 (EtOH)	+244 (EtOH)
44	+103 (EtOH)	+102 (EtOH)
45	+374 (EtOH)	+342 (EtOH)
46	+157 (EtOH)	+124 (EtOH)
50	+300 (EtOH)	+279 (EtOH)
51	+154 (EtOH)	+143 (EtOH)
53	+354 (EtOH)	+368 (EtOH)
54	+249 (EtOH)	+256 (EtOH)
55	+124 ($CHCl_3$)	+77.7 ($CHCl_3$)[c]
56	+34.4 (EtOH)	+21.6 (EtOH)
57	+100 (EtOH)	+97.0 (EtOH)
58	+74.9 (EtOH)	+35.3 (EtOH)
59	+63.5 (EtOH)	+59.3 (EtOH)
60	+244[a]	+194 (EtOH)
61	+47.2 ($CHCl_3$)	+45.6 ($CHCl_3$)[d]
62	+111 ($CHCl_3$)	+83.3 ($CHCl_3$)
63	+76 (MeOH)	+72.4 (MeOH)[e]
65	+84 (MeOH)	+97.0 (MeOH)
67	+139 (EtOH)	+143 (EtOH)
68	+84.9 (CH_2Cl_2)	+91.0 (CH_2Cl_2)[f]
69	+86.0 (CH_2Cl_2)	+75.3 (CH_2Cl_2)
70	+448 (CH_2Cl_2)	+366 (CH_2Cl_2)
71	+475 (EtOH)	+473 (EtOH)
74	+496 (EtOH)	+473 (EtOH)
75	+456 (EtOH)	+356 (EtOH)
77	−187 (benzene)	−1180 (benzene)[g]

[a] The solvent for the measurement is not given.
[b] χ(neat) = 1.05 χ(EtOH).
[c] χ($CHCl_3$) = 1.03 χ(EtOH).
[d] Cf. reference 11.
[e] χ(MeOH) = 0.99 χ(EtOH).
[f] χ(CH_2Cl_2) = 1.03 χ(EtOH).
[g] χ(benzene) = 1.10 χ(EtOH).

(X = OH, OMe, COMe), it seems reasonable to assume $\lambda(CH_2OH) = \lambda(CH_2OAc) = \lambda(CH_2COOMe)$ as well as $\lambda((CH_2)_4OH) = \lambda((CH_2)_4OAc)$ and $\lambda((CH_2)_3OH) = \lambda((CH_2)_3COOMe)$.

In order to demonstrate the relevance of the treatment of the molar rotations of allenes on the basis of chirality functions in Table 5 a comparison between experimental and calculated (χ) rotations is given. For this comparison only the rotations of molecules which have not been used to evaluate $\lambda(R)$ are taken into consideration.

At first, it is seen that for the molecules whose rotations have been measured under standard conditions the agreement between observed and experimental rotations is excellent. Only four compounds (46, 56, 58 and 75) exhibit larger deviations and it has been argued that the discrepancies for **46**, **56** and **58**, which characteristically have an ethyl group geminal to the carboxylic functionality, result from solvent and conformational effects[11]. Conformational effects surely play a decisive role in case of laballenic acid ester **75**. Solvent effects for these kinds of molecules often become smaller if acetonitrile is used instead of ethanol. Chloroform and methylene chloride exhibit pronounced solvent effects on the molar rotation of allenes, especially if protic groups are present in the molecules (e.g. **55**)[11]. Therefore, the agreement between calculated and observed rotations is not so good for these solvents, though the deviations generally do not exceed 25%. A similar deviation is also observed for 1,3-dimethylallene (**36**), whose rotation has been measured on the neat liquid, so that intermolecular interactions may influence the optical activity. A serious discrepancy is observed for **77** only, but this is a special case, which will be discussed in Section III.A.3.

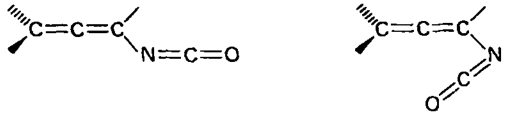
Obviously, special expressions of chirality functions involving ligand-specific parameters and their quantum-theoretical interpretations form a sound basis for an adequate description of optical rotations of allenes. The correlation of the $\lambda(R)$ parameters with other substituent constants or other physical quantities assure the accuracy of the selected numerical values of these parameters, which may be masked sometimes by solvent, conformational and other effects. The linear correlation of the $\lambda(R)$ parameters with the ^{13}C chemical shift parameters $\sigma(R)$ (equation 22) gives explicitly an idea as to how far the λ term (equation 15) is 'incomplete' with respect to the description of the molar rotation of allenes. According to equation (21) the $\sigma(R)$ parameters do not suffice to differentiate constitutionally isomeric allenes (such as **39** and **45**, **40** and **46**, **43** and **44**, or **55**, **56** and **57**) on the basis of the ^{13}C chemical shifts of the allenic central carbon atoms. The calculation of $\delta_{C(2)}$ using only one-particle functions $[\sigma(R)]$ gives the same value for all the constitutional isomers, which is contrary to experimental observation[17]. Constitutionally isomeric allenes can only be differentiated by ^{13}C n.m.r. resonances due to the existence of (measurable) pairwise interactions (τ). The correlation of the $\lambda(R)$ and $\sigma(R)$ parameters therefore shows that equation (15) cannot account for any effects associated with constitutional isomerism. Alternatively, one can say that the molar rotation of allenes does not seem to depend essentially upon effects resulting from the possibility of constitutional isomerism of allenes.

2. *Allenes with hetero substituents*

So far, only rotations of allenes with ligands bonded via a carbon atom to the cumulenic skeleton have been considered. It is also important to have a set of $\lambda(R)$ parameters for hetero substituents since there are various methods for the syntheses of optically active allenes with hetero substituents. In all cases, however, it is rather difficult to determine the absolute configurations and optical purities of such molecules.

In these cases the λ formula (15) for the calculation of molar rotations in connection with empirical correlations of the $\lambda(R)$ parameters and quantum-chemical indices is very useful. Three $\lambda(R)$ parameters for hetero substituents have already been evaluated (Table 4). If their numerical values are to be related to theoretically determined indices, there arises the immediate question about the rotamer populations of the corresponding molecules, or the preferred conformations of the corresponding monosubstituted molecules $RHC{=}C{=}CH_2$ with these ligands.

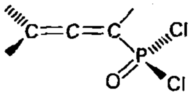
For instance, for the allenyl isocyanate **79** it is not known whether the *s-trans* or the *s-cis* form is more stable.



(79)

It has been shown[60] that the corresponding ethylene derivatives, e.g. acrylic acid derivatives, where the *s-cis* form is largely preferred, give preferentially *s-trans* isocyanates. As in allene carboxylic acids the carboxyl group has the *s-trans* conformation (cf. Chapter 2), it seems reasonable to assume that the transformation of an allenic acid into an allenyl isocyanate, as performed for the synthesis of **79**[56], gives mainly the *s-cis* allenyl isocyanate.

Concerning the dichlorophosphonylallene **80**, one may assume that as a result of the chemical synthesis[57] **80** achieves an *s-cis* conformation of symmetry C_s.



(80)

If now the parameters $\lambda(\text{NCO})$ and $\lambda(\text{POCl}_2)$ of the hetero substituents (Table 4) are also taken into consideration the correlation of the $\lambda(\text{R})$ parameters with the π-electron densities $P_{\text{C}(2)}{}^{\pi}$ remains only qualitatively valid. However, there exists an excellent correlation (equation 25) of the $\lambda(\text{R})$ parameters with the orbital densities $c_{(2)\pi}{}^2$ at the allenic central atoms in the highest occupied π orbital (π HOMO) of monosubstituted allenes, calculated within the CNDO/S scheme[19,61] (Figure 9). *$c_{(2)\pi}$ is the CNDO/S LCAO MO coefficient for the central atom in the π HOMO.* For this correlation only $\lambda(\text{R})$ parameters have been used, which have been evaluated from chirality observations.

$$\lambda(\text{R}) = -\ 379.6\ c_{(2)\pi}{}^2(\text{CNDO/S}) + 121.6 \qquad (25)$$

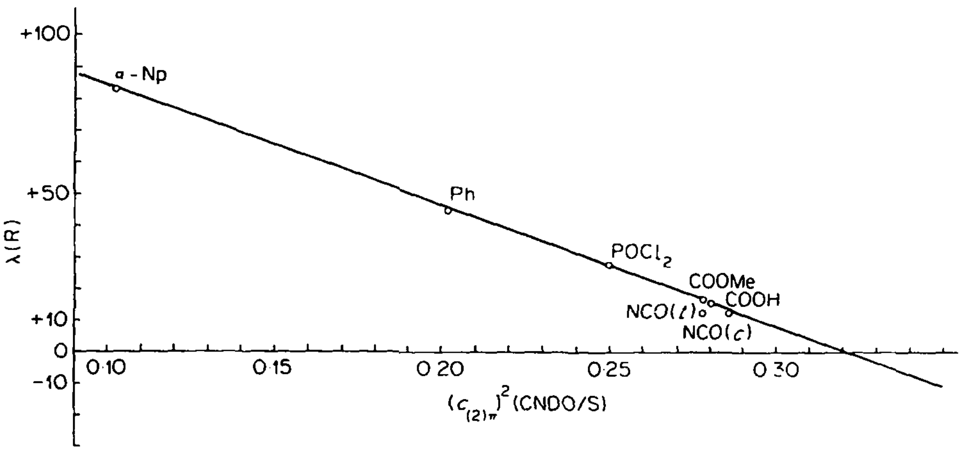


FIGURE 9. Correlation of the $\lambda(\text{R})$ parameters and the orbital densities of the central atoms of monosubstituted allenes in the highest-occupied π orbital.

TABLE 6. π-Orbital densities $c_{(2)\pi}{}^2$ and λ(R) parameters for various substituents obtained from equation (25)

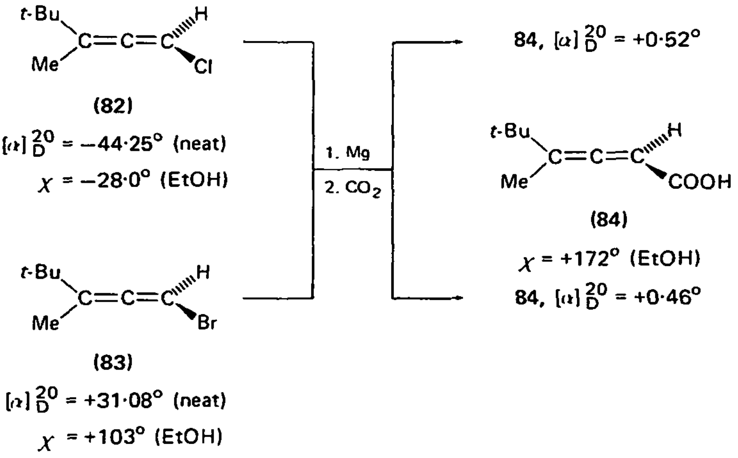
Ligand R	$c_{(2)\pi}{}^2$(CNDO/S)	λ(R)
NCO	0.286[a]	+12.4
	0.278[b]	+16.0
$POCl_2$	0.250[c]	+27.5
HC≡C	0.263	+21.8
$H_2C{=}CH$	0.253[b]	+25.6
MeC=O	0.293[b]	+10.4
CN	0.270	+19.1
F	0.366	−17.3
Cl	0.327[c]	−2.5
Br		+9.2[d]
MeO	0.376	−21.1
MeS	0.296[c]	+9.2
$MeSO_2$	0.279[c]	+15.8

[a] *s-cis* Conformation.
[b] *s-trans* Conformation.
[c] Calculation including d atomic orbitals.
[d] Estimated from λ(Br) = λ(MeS), as Br and MeS have identical ^{13}C shift parameters $\sigma(R)^{17b}$, similar electronegativities and similar resonance integrals B_{CR} for the calculation of π ionization energies[62].

The point for a *s-cis* isocyanate NCO(*c*) falls on the regression line, in agreement with the above arguments concerning the preferred orientation of the NCO group, whereas the point for *s-trans* isocyanate NCO(*t*) shows a larger deviation.

In Table 6 π-orbital densities $c_{(2)\pi}{}^2$ and λ(R) parameters for hetero substituents evaluated via correlation (25) are summarized. These parameters must be regarded as tentative, since there exist no experimental data to test the numerical accuracies.

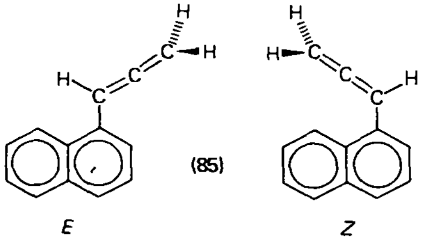
Interestingly, some of the hetero substituents, the strong π-donor groups MeO, F and Cl, have negative λ(R) parameters, whereas all ligands bonded via carbon to the allenic skeleton have positive λ(R) parameters (only hydrogen has the value zero). Furthermore, the ligand-specific parameters λ(Cl) and λ(Br) have opposite signs, whereas in general the chloro and the bromo group have almost identical substituent constants (σ_p, σ^+, R , etc.)[59] for most scalar properties. Qualitatively, opposite signs for λ(Cl) and λ(Br) may be easily demonstrated. Both laevorotatory (*S*)-1-chloro-3,4,4-trimethyl-penta-1,2-diene (**82**) and dextrorotatory 1-bromo-3,4,4-trimethylpenta-1,2-diene (**83**) give, via Grignard reactions, dextrorotatory 4,5,5-trimethyl-hexa-2,3-dienoic acid (**84**) of (*S*) configuration, and therefore **83** also has the (*S*) configuration[63]. The absolute configurations of all three molecules **82**–**84** are predicted correctly by the λ formula (15). The optical purities of **82**–**84** have not yet been determined experimentally. Consequently, the chloroallene **82** and the bromoallene **83** are heterochirally[7] related to each other, whereas the bromoallene is related homochirally[7] to the allene carboxylic acid **84**. This means that with respect to their substituent effects on the molar rotations of allenes the bromo and the carboxyl group are more similar than the bromo and the chloro group.



3. *Conformational chirality effects*

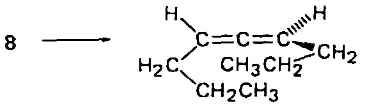
Since the calculation of the molar rotation of allenes with the λ formula (15) gives reasonable agreement with experimental values, serious deviations may provide valuable chemical information concerning solvent effects, specific ligand interactions, conformational effects, etc. Conformational effects seem to be involved in chirality observations of allenes with ethyl groups geminal to carboxyl groups[11].

In the case of the allene 77 there is an extreme discrepancy between experimental and predicted rotation. As 77 has two identical ligands (two phenyl groups), the μ term of the qualitatively complete chirality function (17) vanishes identically. An explanation of the above discrepancy in terms of a noncompetence of the λ term for the prediction of the molar rotation of 77 is ruled out. Therefore, one may consider conformational effects associated with the chirality of allenes like 77 or 76. As a result of steric interactions it may be assumed that for the α-naphthylallene (85) the '*E*-like' conformation is more stable than the '*Z*-like' conformation. This is corroborated by the fact that the π-orbital density $c_{(2)\pi}{}^2$ (= 0.102) of *E*-85 falls on the regression line (25), if λ(α-Np) is evaluated from the molar rotation of 76 (Table 4).


(85)

In 76 and 77 the geminal aryl groups are of course twisted. The results of Section IV.A.1, however, show that the calculation of the molar rotation of allenes with the λ formula (15) is not influenced by such effects. Predictions of rotations of phenylallenes do not depend upon whether the phenyl ring is twisted by geminal methyl or ethyl groups or not twisted. Therefore, another explanation for the deviation of predicted from observed rotations of 77 is likely. The bulky α-naphthyl group prevents rotation of its own plane and of the adjacent phenyl group with respect to the allenic skeleton. This inhibited rotation should lead, e.g. for α-NpPhC=C=CH_2, to a pair of enantiomers (owing to atropisomerism*)[64]. On the basis of statistical arguments it may be assumed that in the case of 1,3-di-α-naphthyldiphenylallene (**76**) there is an equal *a priori* probability for the existence of enantiomeric molecules (RS vs SR and RR vs SS) with the subunits α-NpPhC= in **76** so that the contributions to the optical rotation of the molecular ensemble of **76** owing to atropisomerism effects should cancel. On the other hand, in the case of 2,4-diphenyl-4-α-naphthylbuta-2,3-dienoic acid ester (**77**) such cancellations of atropisomerism effects are not possible, and the observed rotation of **77** probably reflects this kind of conformational effect.

Generally, a rough estimate of the contribution of conformational and other chirality effects to observed rotations may be obtained in the following way. The rotations are calculated with the λ term (15) and the difference between observed and predicted rotation is interpreted as an additional contribution to the experimentally observed chirality observation. As an example of such a procedure consider the rotation of (*R*)-(+)-1,2-cyclononadiene (**8**) ($[\phi]_D = +214°$ (CH_2Cl_2) for optically pure **8**)[65]. It may be assumed that the overall rotation is determined by the intrinsic allenic axial chirality, described by equation (15), and by chirality effects resulting from the conformation of the hydrocarbon chain as well as a ring strain, which gives **8** a nonlinear C=C=C moiety (cf. Chapter 2). The contribution from the allenic axial chirality for (*R*)-**8** is estimated relating **8** to (*R*)-1,3-di-*n*-propylallene (**86**), whose rotation (χ) is calculated to be $-61.1°$ (CH_2Cl_2). The



(86)

difference $+275°$ [$= 214° - (-61°)$] gives an estimate for the conformational and ring-strain contribution to the observed rotation of **8**. This means that the two last effects far exceed the axial chirality contribution. Similar effects are also expected for cyclonona-2,3-dienone-1 (**9**).

B. Optical Rotatory Dispersion

The semiempirical treatment of the molar rotation $[\phi]_D^{25}$ of allenes on the basis chirality functions is easily extended to the optical rotatory dispersion $[\phi]_\lambda^{25}$ in the transparent region ($\lambda \geqslant 330$ nm).

The physical interpretation of the λ(R) parameters according to equation (24) implies, at least for the inductive groups, the analytical form for the description of ORD. Its wavelength dependency is determined via λ(R) by the anisotropic polarizability Δα(R). It has been shown[11] that the wavelength dependencies of the λ(R) parameters may be approximated in terms of equation (26), $[\lambda(R)]_D$ being the λ(R) parameter calculated for the wavelength of the sodium D line (Tables 4 and 6).

---

*Atropisomerism[1c] is a type of stereoisomerism resulting from hindered rotation around single bonds and allowing isolation of the particular isomers (e.g. 2,2',4,4'-tetrasubstituted biphenyls).

$$[\lambda(\mathrm{R})]_\lambda = 0.224[\lambda(\mathrm{R})]_\mathrm{D}\left(1 + \frac{1.20 \times 10^6}{\lambda^2}\right) \tag{26a}$$

R = H, alkyl, COOH, COOMe, COONa, NCO, CH_2X

$$[\lambda(\mathrm{Ar})]_\lambda = 0.100[\lambda(\mathrm{Ar})]_\mathrm{D}\left(1 + \frac{3.21 \times 10^6}{\lambda^2}\right) \tag{26b}$$

Ar = C_6H_5, p-MeC_6H_4, p-ClC_6H_4

In general, ORD curves calculated on the basis of equation (26) show deviations

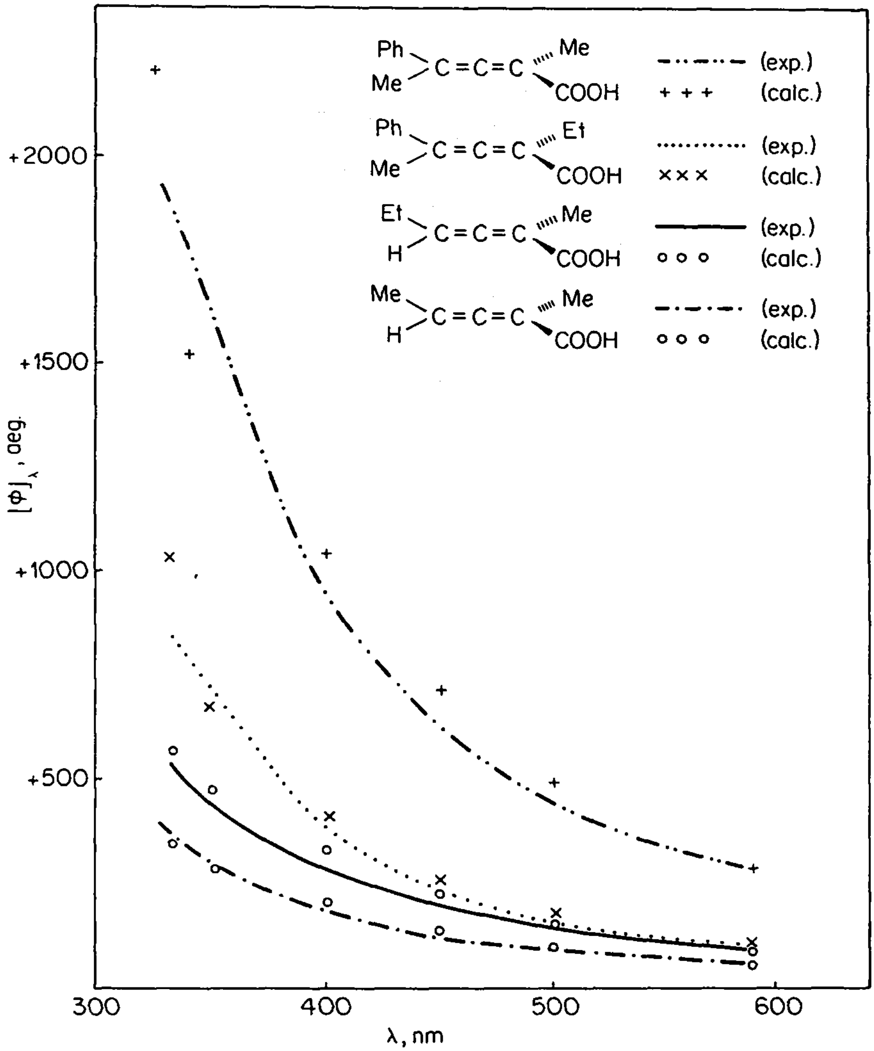


FIGURE 10. Experimental and calculated ORD curves of some allene carboxylic acids in the transparent region (in ethanol). Reproduced with permission from W. Runge and G. Kresze, *J. Amer. Chem. Soc.*, 99, 5597 (1977).

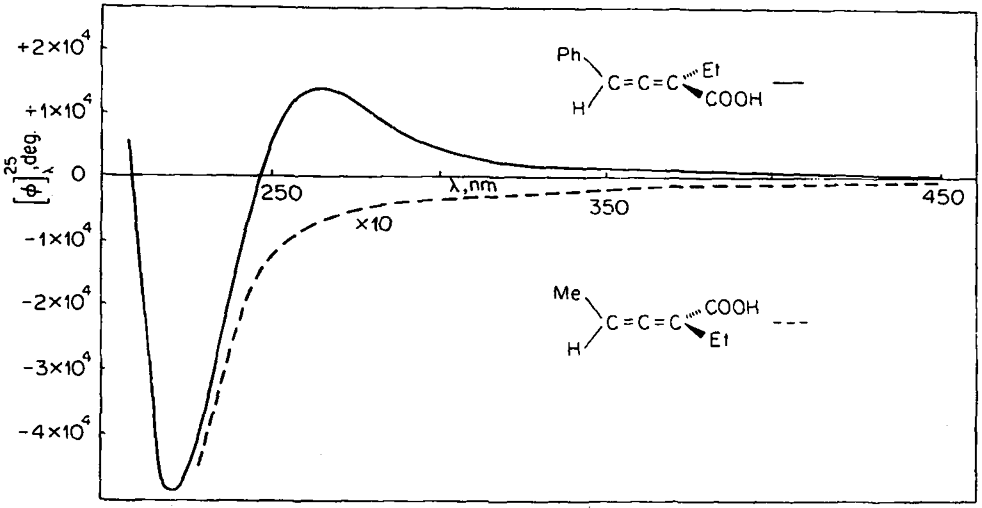


FIGURE 11. Experimental ORD curves of some allene carboxylic acids including the absorption regions (in ethanol).

from experimental ones by about 10% for $\lambda \geqslant 400$ nm and 25% for $330 \leqslant \lambda \leqslant 400$ nm.

In Figure 10 observed and calculated ORD curves in the transparent region for some alkyl- and phenyl-allene carboxylic acids are displayed. Experimental ORD curves for such molecules extending farther into the ultraviolet are given in Figure 11. ORD curves for the transparent region are also available for most of the alkyl- and phenyl-allene carboxylic acids[43,44] given in Table 3, for 8[66], 10[21,22], 68 and 69[51], 76[53], 79[58] and various open-chain allenic hydrocarbons[66].

V. SPECTROSCOPIC AND STEREOCHEMICAL ASPECTS OF CIRCULAR DICHROISM OF ALLENES

A. Excited States in Allenes

In Section IV it has been demonstrated that the molar rotation and optical rotatory dispersion of allenes may be treated quantitatively. Investigations of substituent effects have given insight into the origins of these chiroptical properties, i.e. it has been shown how observable effects in molecules are influenced by certain qualities of appropriately selected subsystems and, furthermore, how these qualities are related to other physical properties. This treatment of ORD allows the immediate application to stereochemical problems, i.e. it may be used for the prediction of absolute configurations and optical purities.

The same information (absolute configuration, molecular structure) may be obtained from the circular dichroism of a definite electronic band provided the associated electronic excited state is known. Interpretation of CD therefore requires the identification of the chromophores which are responsible for the particular electronic bands, and the electronic transitions involved in the excitations.

For the interpretation of the low-energy excited states of complex allenes the excited states are usually correlated with corresponding states of appropriately monosubstituted allenes $RHC{=}C{=}CH_2$, which then represent the 'parent chromophores'. The orbitals involved in low-energy electronic excitations correlate with

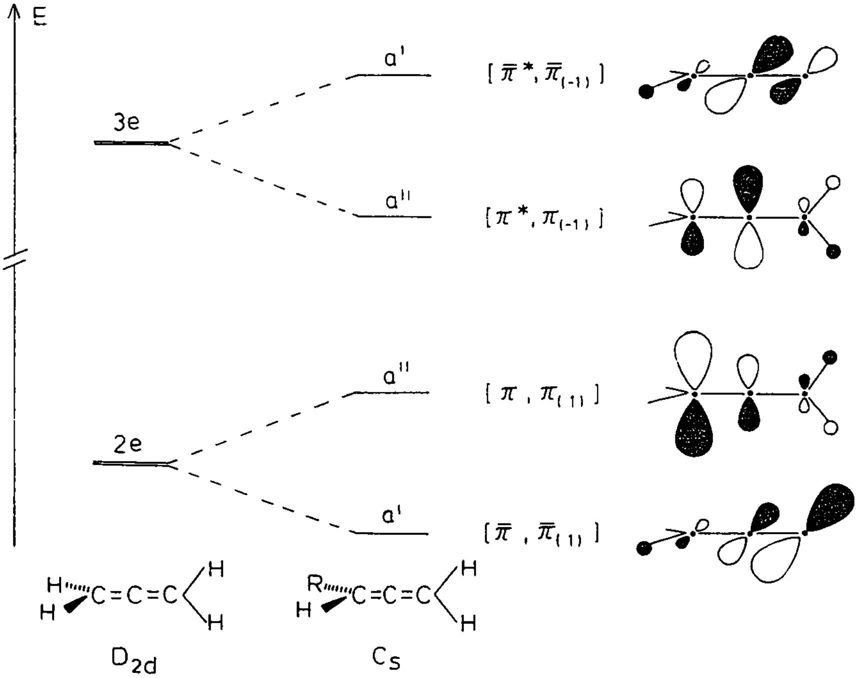


FIGURE 12. Approximate LCAO representations and correlations of the outermost π and σ orbitals of monosubstituted allenes with the degenerate allenic e orbitals.

the degenerate (highest occupied) 2e and (lowest unoccupied) 3e orbitals in allene (7) (Figure 12). Reducing the symmetry of 7 from D_{2d} to C_s in RHC=C=CH$_2$ lifts the degeneracy to give $\pi(a'')$ and $\sigma(a')$ orbitals. The σ orbitals correlating with allenic e orbitals are referred to as $\bar{\pi}(a')$ orbitals[15,16,62,67]. In monosubstituted allenes all (singlet) states are of $^1A'$ or $^1A''$ character. $^1A'$ excited states result from electric dipole allowed transitions and give strong u.v. bands, e.g. the π,π^* transitions ($\langle\pi|\mu|\pi^*\rangle \neq 0$, $\langle\pi|m|\pi^*\rangle = 0$). $^1A''$ excited states are associated with magnetic dipole allowed transitions and give weak u.v. bands, e.g. the low-energy $\pi,\bar{\pi}^*$ and $\bar{\pi},\pi^*$ transitions (($\langle\pi|\mu|\bar{\pi}^*\rangle = 0$, $\langle\pi|m|\bar{\pi}^*\rangle \neq 0$). These last excitations resemble n,π^* transitions in carbonyl compounds, as in an LCAO MO treatment they nearly correspond to p–p atomic quantum jumps[15,16,62,67]. For 1,3-disubstituted allenes with C_2 symmetry the e degeneracy of the allenic orbitals is not lifted, i.e. for C_2 allenes the resulting a and b orbitals remain accidentally degenerate[15,16] and for such systems the chromophore comprises the whole molecule. In allene (7), which represents the parent chromophore of symmetry D_{2d}, the one-electron (singlet) excitation 2e → 3e results in four excited states $^1A_2$, $^1B_1$, $^1A_1$, $^1B_2$, their energetic order being assumed to be $^1A_2 < {}^1B_1 < {}^1A_1 < {}^1B_2$[67–69]. However, the position of the $^1A_1$ excited state is still not clear ($^1A_1 < {}^1B_2$ or $^1A_1 > {}^1B_2$).

If the 2e and 3e orbitals of allene are described by a LCAO expansion with a minimal basis set, the components π_z and π_y of the degenerate orbitals consist to a large extent of p_z and p_y atomic orbitals, respectively (xy and xz being the D_{2d} mirror planes)[62].

The antisymmetric combination of the configurations $\pi_z \rightarrow \pi_y^*$ and $\pi_y \rightarrow \pi_z^*$ gives the $^1A_1$ (ground state) → $^1A_2$ (excited state) transition, which is magnetic dipole allowed with x polarization. Similarly, the antisymmetric combination of $\pi_z \rightarrow \pi_z^*$ and $\pi_y \rightarrow \pi_y^*$ gives the $^1B_2$ excited state with x polarization via electric dipole allowed transitions.

$^1B_1$ results from the symmetric combination of $\pi_z \rightarrow \pi_y^*$ and $\pi_y \rightarrow \pi_z^*$, $^1A_1$ from the symmetric combination of $\pi_z \rightarrow \pi_z^*$ and $\pi_y \rightarrow \pi_y^*$. These electronic states of allene (7) are only slightly perturbed by substituting alkyl groups for hydrogen. Thus, the widespread distribution of state characteristics of the allenic D_{2d} entity is largely retained in alkylallenes[67]. Therefore, the $^1A_2$ and $^1B_1$ allene parentage of the two lowest-energy 2e → 3e states of 7 persists in the $^1A''(\pi,\bar{\pi}^*)$ and $^1A''(\bar{\pi},\pi^*)$ or the $^1A_2(\pi,\bar{\pi}^*)$ and $^1A_2(\bar{\pi},\pi^*)$ excited states of monosubstituted or 1,1-disubstituted (allenylic)[67] alkylallenes, respectively, as well as in the $^1A(\pi,\bar{\pi}^*-\bar{\pi},\pi^*)$ and $^1B(\pi,\bar{\pi}^*+\bar{\pi},\pi^*)$ excited states of 1,3-disubstituted alkylallenes. The two lowest-energy excited singlet singlet states of alkylallenes, not having the symmetry of a pure rotation group, are adequately described by single configurations $\pi,\bar{\pi}^*$ or $\bar{\pi},\pi^*$, respectively[15,62,67].

B. Alkylallenes

In Figure 13 the CD and u.v. spectra of allenic hydrocarbons prototypical of systems with an allenylic C_s (or C_{2v}) chromophore[77] and an allenic D_{2d} chromophore[70,71] are displayed.

Inspection of the spectra of the 17-allenic steroid 87 reveals that the weak shoulder at about 44,000 cm^{-1} in the u.v. spectrum corresponds to two CD bands of opposite sign and comparable intensity, i.e. the circular dichrosim spectroscopy shows that the spectral region between 40,000 and 45,000 cm^{-1} comprises two electronically excited states. The longest wavelength band at 42,000 cm^{-1} corresponds to the $^1A''(\pi,\bar{\pi}^*)$ excited state in methylallene (2)[67], whereas the second band near 45,000 cm^{-1} is associated with the $^1A''(\bar{\pi},\pi^*)$ excited state[67]. An assignment of the band near 49,000 cm^{-1} has not yet been given. It can be tentatively assigned to a $\pi \rightarrow \sigma^*$ transition, where the σ^* orbital is comprised almost entirely of carbon (including the methylene carbon) 2s and hydrogen 1s atomic orbitals. This last excited state should then correlate with the $^1E(2e \rightarrow 4a_1)$ excited state in allene (7) at 185 nm[68,69].

In (*S*)-(+)-1,3-dimethylallene (36) the weak electronic band associated with the $^1A_2$ excited state and assumed to be found near 40,000 cm^{-1} for reasons of energy seems to exhibit an extremely weak circular dichroism. Under normal measurement conditions no CD for this band has been detected. The second (negative) band near 44,000 cm^{-1} corresponds to the $^1B_1$ excited state in allene. Similarly, for 1,3-di-*n*-propylallene (86) and 1,3-di-*t*-butylallene (88), only the circular dichroism of the $^1B_1$ band have been observed[66].

From the CD spectrum of (*R*)-(+)-1,2-cyclononadiene (8) (Figure 13) one can see that under certain conditions the circular dichroism of the $^1A_2$ band (near 40,000 cm^{-1}) is observable and is comparable in intensity with the $^1B_1$ CD band.

The negative CD band of 36 (Figure 13) near 53,000 cm^{-1} should correspond to the $^1A_1$ excited state of allene. However, an additional band correlating with $^1E(2e \rightarrow 4a_1)$ in 7 may also be observed in this energy region[68,69b].

In Table 7 CD data of allenic hydrocarbons are summarized. From these data some qualitative features emerge. Generally, in acyclic alkylallenes (**10**, **11**, **36**, **88**, **89**) the circular dichroism of the bands near 40,000 cm^{-1}, correlating with $^1A_2$ in

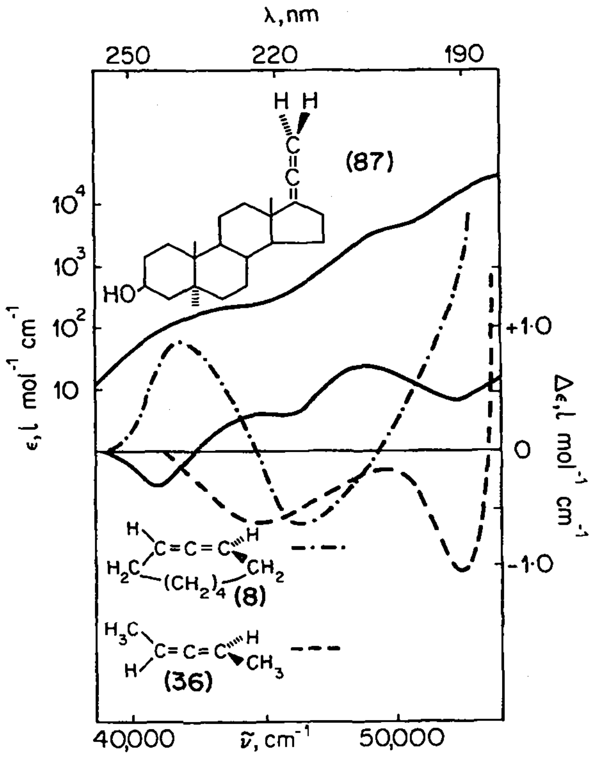


FIGURE 13. U.v. and CD spectra of allenic hydrocarbons (in isooctane). Reproduced with permission from P. Crabbé, E. Velarde, H. W. Anderson, S. D. Clark, W. R. Moore, A. F. Drake and S. F. Mason, *J. Chem. Soc., Chem. Commun.*, 1261 (1971).

allene [or $^1A''(\pi,\bar{\pi}^*)$ in methylallene (2)], seems to be very weak and probably not observable. 1,2-cyclononadiene (8) represents an exception, perhaps as a result of ring strain and twist of the allenic C=C=C entity (cf. Chapter 2). On the other hand, in chiral allenes with an exocyclic allenic functionality the circular dichroism of $^1A''(\pi,\bar{\pi}^*)$ (at 41,000 cm^{-1}) and $^1A''(\bar{\pi},\pi^*)$ (at 45,000 cm^{-1}) may be detected. The rotatory strengths of these CD bands may be of comparable magnitude.

These results seem to be supported by CNDO/S quantum-chemical calculations of reduced rotatory strengths $[R_{0i}]$ ($[R_{0i}] = 1.08 \times 10^{40} R_{0i}$) for some model allenes (Figure 14)[72] including 1,3-dimethylallene (36). The CNDO/S results for $[R_{0i}]$ are given in Table 8. Though the absolute values of such calculations are rather problematic due to the extreme sensitivity of the theoretical results towards the configuration interaction (CI) basis[73], relative orders of magnitude for the (reduced) rotatory strengths for one particular molecule seem to be reliable. Generally, the CNDO/S energies of excited states resulting from magnetic dipole allowed transitions are in error by 0.5–1.0 eV[15,62,67]. Furthermore, there remains in these calculations the degeneracy of the $^1A_2$ and $^1B_1$ excited states of allenes with the symmetry of a rotation group.

TABLE 7. CD data of allenic hydrocarbons

Compound	$[\phi]_D$ (deg.)	λ (nm)	$\Delta\epsilon$ (l mol^{-1} cm^{-1})	Reference
10	+62.8 (neat)	223	−0.12 (MeOH)	22
11	+4.8 (neat)	222	−0.09 (MeOH)	22
13	+60.0 (isooctane)	228	+1.37 (MeOH)	22
87	+100.6 (isooctane)	243	−0.28 (isooctane)	70
		225	+0.33	
		206	+0.74	
8	+155.0 (isooctane)	236	+1.22 (isooctane)[b]	70
		218	−0.63	
36	+16.5 (pentane)	223	−0.63 (pentane)[c]	70, 71
		192	−1.7	
89[a]	+52.3 (pentane)	222	−0.73 (pentane)[d]	70
88	+115.3 (pentane)	219	−1.01 (pentane)[e]	70

[a] (*S*)-EtHC=C=CHEt.
[b] Optical purity o.p. 72%.
[c] O.p. 27.8% according to equation (15).
[d] O.p. 32.9%.
[e] O.p. 32.2%.

From the results in Table 8 for (*S*)-1,3-dimethylallene (36) one sees that, indeed, the circular dichroism of the ^1A ($^1A_2$) band is much smaller than that of the ^1B($^1B_1$) band, whereas in cyclic allenes both the low-energy $^1A''$ CD bands are of comparable magnitude and of opposite sign.

The results for 1,1-dimethylallene (90), whose chirality is artificially induced by

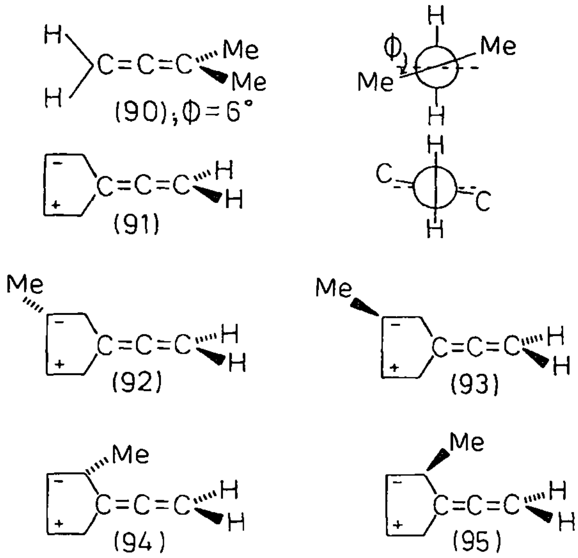


FIGURE 14. Model allenes whose rotatory strengths have been treated theoretically (+ and − denote displacements of the cyclopentyl ring atoms above and below the plane of the figure).

TABLE 8. Calculated[a] energies and reduced rotatory strengths of some allenic hydrocarbons

Compound	Excited state	ΔE (eV)	$[R_{0i}]$
36	$^1A(^1A_2)$	4.06	−0.02
	$^1B(^1B_1)$	4.05	+0.84
90	$^1A''(\pi,\bar{\pi}^*)$	3.76	+0.11
	$^1A''(\bar{\pi},\pi^*)$	4.39	+5.48
91	$^1A''(\pi,\bar{\pi}^*)$	3.88	+0.90
	$^1A''(\bar{\pi},\pi^*)$	4.54	−0.55
92	$^1A''(\pi,\bar{\pi}^*)$	3.87	+0.93
	$^1A''(\bar{\pi},\pi^*)$	4.54	−0.88
93	$^1A''(\pi,\bar{\pi}^*)$	3.86	+0.61
	$^1A''(\bar{\pi},\pi^*)$	4.54	−0.19
94	$^1A''(\pi,\bar{\pi}^*)$	3.78	+1.64
	$^1A''(\bar{\pi},\pi^*)$	4.55	−5.48
95	$^1A''(\pi,\bar{\pi}^*)$	3.78	−0.64
	$^1A''(\bar{\pi},\pi^*)$	4.54	+3.92

[a] From Reference 72.

a small twist of the methyl groups, show the extreme sensitivity of the circular dichroism of allenes with respect to twist and strain in the allenic moiety.

In open-chain alkylallenes the low-energy excited states result from excitations within the allenic D_{2d} chromophore. Therefore, a treatment of the circular dichroism or rotatory strengths, respectively, on the basis of chirality functions should involve the same arguments that have been used for the discussion of the optical rotations of D_{2d} systems (Section III.B and IV.A). With $\lambda'(R_i)$ being a ligand-specific parameter of the ligand R attached to site i (Figure 2) the rotatory strength R_Γ for an excited singlet state of irreproducible representation Γ should be described by equation (27), if only allenes with two identical ligands are taken into consideration. Again, ϵ' is a sign factor ($\epsilon' = \pm 1$; cf. equation 17).

$$R_\Gamma = \epsilon'[\lambda(R^1) - \lambda'(R^2)]\,[\lambda'(R^3) - \lambda'(R^4)] \tag{27}$$

Owing to the scarcity of CD data of appropriate alkylallenes only some qualitative remarks with respect to equation (27) are possible for the $^1B_1$ state. For the (*S*)-1,3-dialkylallenes RHC=C=CHR (Table 7) equation (27) is reduced to (28) choosing $\lambda'(H) = 0$.

$$R(^1B_1) = \epsilon'[\lambda'(R)]^2 \tag{28}$$

TABLE 9. Rotatory strengths of the $^1B_1$ CD bands of (*S*)-1,3-dialkylallenes RCH=C=CHR and their relation to substituent constants

Compound	R	$R(^1B_1)^a$ (cgs)	$\lambda'(R)^b$	F'
36	Me	-6.31×10^{-40}	2.51×10^{-20}	−0.14
89	Et	-6.17×10^{-40}	2.48×10^{-20}	−0.13
88	*t*-Bu	-8.64×10^{-40}	2.94×10^{-20}	−0.19

[a] Obtained for the optically pure compounds (Table 7) and $R_{0i} = 0.23 \times 10^{-38}\sqrt{\pi}\Delta\epsilon_{0i}\Delta_{0i}/\lambda_{0i}$ with $\Delta_{0i} = 15$ nm and $\lambda_{0i} = 220$ nm.
[b] $\lambda'(R) = +(|R(^1B_1)|)^{1/2}$.

In Table 9 the rotatory strengths for the (*S*)-dialkylallenes 36, 88 and 89 are summarized. From these data it is clear that $\epsilon' = -1$. In agreement with the λ values for the calculation of the molar rotation of allenes the λ' parameters are chosen to be positive $[\lambda'(R) = +(|R(^1B_1)|)^{1/2}]$. Then it is seen from Table 9 (column four and five) that the $\lambda'(R)$ parameters parallel the Dewar–Grisdale field parameters F'[74]. Therefore, the substituent effect on the $^1B_1$ circular dichroism of alkylallenes seems to be governed by polar effects, which is consistent with the observations for the substituent effects on the molar rotation.

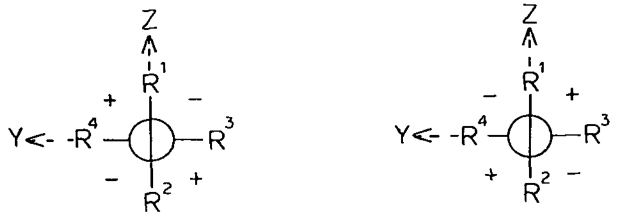
For the prediction of absolute configurations of allenic hydrocarbons from CD data sector rules have been proposed, which relate the sign of the lowest-energy $^1A_2(^1A'')$ CD band to the position of the substituents[70]. In their simplest form the symmetry rules for the two lowest-energy CD bands of allenic hydrocarbons turn out to be *YZ* quadrant rules (Figure 15). For instance, if the static Coulombic field of a substituent mixes the magnetic dipole allowed $^1A_1 \rightarrow {}^1A_2$ $[^1A' \rightarrow {}^1A''(\pi,\bar{\pi}^*)]$ transition with an *x*-polarized electric dipole allowed excitation $[^1A_1 \rightarrow {}^1B_2$ for allenic D_{2d} systems, $^1A' \rightarrow {}^1A'(\pi,\pi^*)$ for allenylic C_s systems] to produce optical activity, the field has a pseudoscalar component with *YZ* symmetry. If the perturbing field arises from positive charges (e.g. incompletely screened nuclei of substituent atoms) the quadrant rules have the signs depicted in Figure 15.

The simple *YZ* quadrant rule is in general consistent with the experimental CD data for chiral allenes (Table 7) and the theoretical CD data (Table 8).

Treatment of the circular dichroism of alkylallenes on the basis of a 'dynamic coupling' of the magnetic transition moment of the lowest-energy $^1A_1 \rightarrow {}^1A_2$ transition with the transient electric dipole induced in the substituent leads to a 'bifurcated-quadrant rule'[70], which is also in agreement with the CD data.

Dynamic coupling theory to second order, which relates the optical activity of (*S*)-1,3-dimethylallene (36) to the coupling of the two induced dipoles in the methyl substituents, predicts positive rotatory strengths for the $^1A_2$ and $^1B_2$ excited states and negative ones for the $^1B_1$ and $^1A_1$ excited states[71]. With the exception of the not observable $^1A_2$ circular dichroism this is correct with respect to the band assignment for alkylallenes proposed in Section V.A. In this treatment optical activity arises from the anisotropic polarizabilities of the methyl groups. The major component of the induced dipole in the $=C-CH_3$ bond lies along the $C_{sp^2}-C_{sp^3}$ bond direction.

The sign of the rotatory strength of the $^1B_2$ electric dipole allowed band in 36 may be predicted by the particular phase relationships between the induced dipoles in the two $C_{sp^2}-C_{sp^3}$ bonds due to Coulombic interactions with the $^1A_1 \rightarrow {}^1B_2$



$^1A_2[^1A''(\pi,\bar{\pi}^*)]$ $^1B_1[^1A''(\bar{\pi},\pi^*)]$

FIGURE 15. *YZ* quadrant rules for chiral allenes connecting the position of a substituent with the sign of the $^1A_2$ $[^1A''(\pi,\bar{\pi}^*)]$ CD band (near 40,000 cm^{-1}) and the $^1B_1$ $[^1A''(\pi,\bar{\pi}^*)]$ CD band (near 45,000 cm^{-1}).

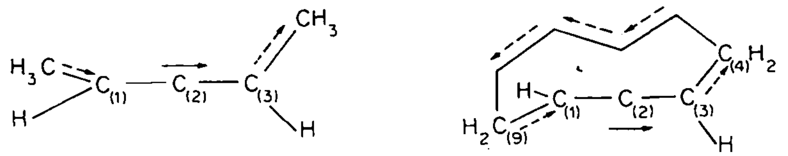


FIGURE 16. The phase relationship between the electric dipole moment of the $^1A_1 \rightarrow {}^1B_2$ transition (full arrow) and the induced moments along the C—C bonds in (*S*)-(+)-1,3-dimethylallene and (*R*)-(+)-1,2-cyclononadiene. Reproduced with permission from P. Crabbé, E. Velarde, H. W. Anderson, S. D. Clark, W. R. Moore, A. F. Drake and S. F. Mason, *J. Chem. Soc., Chem. Commun.*, 1261 (1971).

transition dipole (Figure 16)[70]. In a similar way the positive rotatory strength of the $^1B_2$ band in (*R*)-(+)-1,2-cyclonononadiene (**8**) has been explained[70] separating the overall effect into an allene-type axial chirality effect and a (coupled) alkyl chain conformational chirality effect (Figure 16). The induced dipoles along $C_{(3)}$—$C_{(4)}$ and $C_{(1)}$—$C_{(9)}$ couple to give a negative $^1B_2$ rotatory strength, as in (*R*)-1,3-dimethylallene. On the other hand, the dipole along $C_{(5)}$—$C_{(6)}$—$C_{(7)}$—$C_{(8)}$ couples with the $^1B_2$ transition dipole to generate a substantially larger positive rotatory strength[70]. The same result emerges for conformations other than the one in Figure 16. The circular dichroism of the $^1A_1 \rightarrow {}^1B_2$ transition in alkylallenes near 185 nm has by far the greatest rotatory strength and therefore, according to equation (6) (Section II), it makes the major contribution to the optical rotation at the sodium D line, especially as the low-energy $^1A_2$ circular dichroism near 245 nm is extremely weak in most cases. For instance, the optical rotatory dispersion of optically pure (*S*)-(+)-4-methylhexa-1,2-diene (**10**) (Table 7) may be described by equation (29) with λ_{0i} = 200 nm[21].

$$[\phi]_\lambda = \frac{18.66 \times 10^6}{\lambda^2 - \lambda_{0i}^2} \quad \text{for } \mathbf{10} \tag{29}$$

C. Allene Carboxylic Acids and Allenic Ketones

The primary aspect of circular dichroism of alkylallene carboxylic acids and allenic ketones has been concerned with the investigation of the excited states of

TABLE 10. U.v. absorption and circular dichroism characteristics of (*S*)-(+)-2-ethylpenta-2,3-dienoic acid (**56**) (in ethanol)[a,c]

	U.v.			CD		
State (transition)[b]	λ (nm)	ε (l mol^{-1} cm^{-1})	$D \times 10^{38}$	Δε (l mol^{-1} cm^{-1})	$R \times 10^{40}$	$g \times 10^4$
$^1A''(\bar{\pi},\pi^* + n,\pi^*)$	272	80	5.9	−0.0087	−0.014	−0.92
$^1A''(n,\pi^* - \bar{\pi},\pi^*)$	257	170	11.1	+0.018	+0.026	+0.94
$^1A''(\pi,\bar{\pi}^*)$	246	130	9.1	+0.078	+0.15	+6.6
$^1A'(\pi,\pi^*)$	216	8600	1040	+1.0	+2.9	+1.1

[a] From the resolution of the spectra into Gaussian bands[15].

[b] Cf. Reference 15 for details of the band assignments.

[c] Taken from W. Runge, W. Kosbahn and J. Winkler, *Ber. Bunsenges. Phys. Chem.*, 79, 381 (1975) and reproduced by permission of Verlag Chemie, GmbH, Weinheim.

these molecular systems[15]. The interpretation of the excited states is achieved using correlations with the excited states of allene carboxylic acid $H_2C{=}C{=}CHCOOH$ (**96**) and acetylallene (**6**), which represent the prototypical chromophores for the molecules under consideration. In Figure 17 the u.v. and CD spectra of some alkylallene carboxylic acids are displayed[15]. The weak shoulders in the u.v. spectra at 40,000 cm^{-1} correspond to two, or probably three, CD bands. Resolution of the u.v. and CD spectra of (*S*)-(+)-2-ethylpenta-2,3-dienoic acid (**56**) into three symmetrical Gaussian bands supported the assumption that the low-energy parts of the electronic spectra of alkylallene carboxylic acids result from three weak electronic transitions which correlate with $^1A''$ excited states in **96**[15]. U.v. absorption and CD

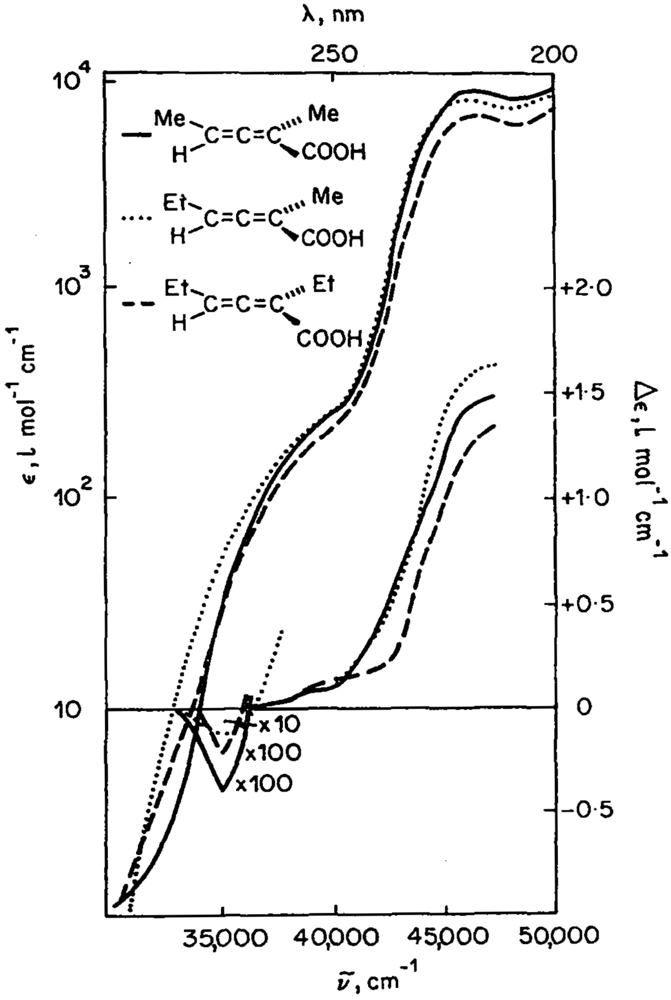


FIGURE 17. U.v. and CD spectra of alkylallene carboxylic acids (in ethanol). Taken from W. Runge, W. Kosbahn and J. Winkler, *Ber. Bunsenges. Phys. Chem.*, 79, 381 (1975), and reproduced by permission of Verlag Chemie, GmbH, Weinheim.

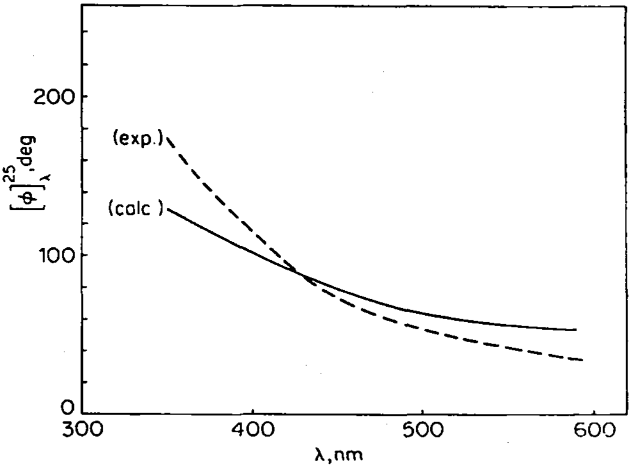


FIGURE 18. Experimental and calculated (equation 6) optical rotation of (*S*)-(+)-2-ethylpenta-2,3-dienoic acid in the transparent region (in ethanol).

characteristics as well as band assignments for 56 are given in Table 10. It can be seen that the circular dichroism of the bands associated with $\pi,\bar{\pi}^*$ and $\bar{\pi},\pi^*$ (and n,π^*) excitations are very weak, as has also been observed for alkylallenes. This example demonstrates the power of circular dichroism to resolve overlapping electronic bands. Furthermore, the combined use of u.v. and CD spectroscopy facilitates the band assignments considerably, taking the *g*-factor (equation 11) into consideration. Table 10 shows that with respect to the magnitude of the *g*-factors $\sigma\rightarrow\pi^*$ ($\bar{\pi}\rightarrow\pi^*$ and $n\rightarrow\pi^*$) and $\pi\rightarrow\sigma^*(\pi\rightarrow\bar{\pi}^*)$ transitions are well differentiated. The circular dichroism of the π,π^* band near 216 nm is the only intense CD band of alkylallene carboxylic acids with an energy less than 50,000 cm^{-1}. It may be used to establish the absolute configurations of alkylallene carboxylic acids.

The π,π^* CD band is affected by α as well as by γ substituents, as can be seen from Figure 17. It determines essentially the optical rotatory dispersion in the transparent region according to the Rosenfeld equation (6). In Figure 18 the experimental and calculated (equation 6) rotations of 56 are displayed if only the rotatory strength of the π,π^* CD band is taken into consideration.

TABLE 11. U.v. and CD characteristics of allenic ketones

Compound	State	λ (nm)	Δε (l mol^{-1} cm^{-1})	ε (l mol^{-1} cm^{-1})	Reference
9[a]	$^1A''(n,\pi^*)$	297	+0.55	242	28c
	$^1A''(\bar{\pi},\pi^*)$ $^1A''(\pi,\bar{\pi}^*)$	255	+5.45		
	$^1A'(\pi,\pi^*)$	229		2350	
22	$^1A''(\bar{\pi},\pi^*)$ $^1A''(\pi,\bar{\pi}^*)$	255	−3.43		29d
	$^1A'(\pi,\pi^*)$	229	+2.98	12000	
	$^1A'(n,\bar{\pi}^*)$	211	−1.83		

[a] Estimated optical purity 8%.

In Table 11 u.v. and CD characteristics of allenic ketones are summarized. In carbonyl compounds n → π^* transitions have much lower transition energies than in carboxylic acids. Therefore, in **9** the band at 297 nm should correspond to the n → π^* excitation.

The intense u.v. band near 230 nm is surely associated with the $^1A'(\pi,\pi^*)$ excited state in acetylallene (**6**), whereas analogy with the alkylallene carboxylic acids suggests that the bands at 255 nm should correspond to $\overline{\pi} \rightarrow \pi^*$ and $\pi \rightarrow \overline{\pi}^*$ excitations. Again, these examples demonstrate the power of circular dichroism to resolve electronic bands.

For instance, the electronic band near 210 nm in allenic ketones can only be detected by CD spectroscopy. Tentatively, it can be correlated with a n → $\overline{\pi}^*$

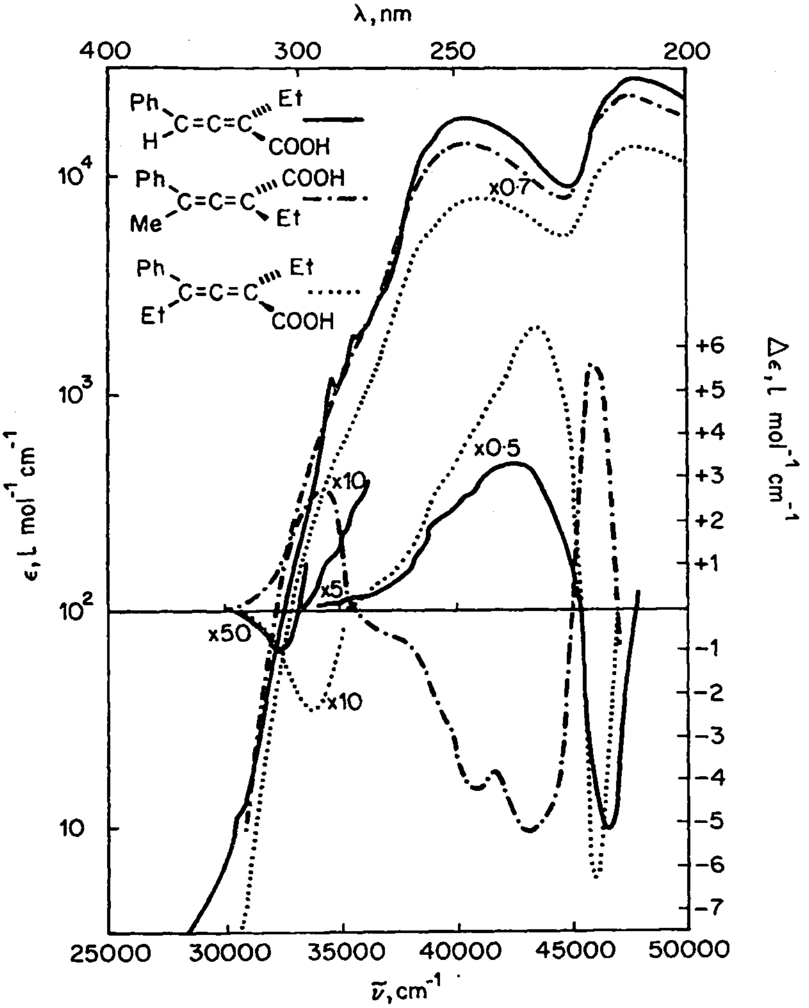


FIGURE 19. U.v. and CD spectra of 2-ethyl-4-phenylbuta-2,3-dienoic acids revealing the influence of a substituent in the γ-position (in ethanol). Taken from W. Runge and J. Winkler, *Ber. Bunsenges. Phys. Chem.*, 79, 610 (1975) and reproduced by permission of Verlag Chemie, GmbH, Weinheim.

transition in 6. Quantum-chemical CNDO/S calculations support this assignment; however, they predict a further excited state in this energy region[75].

D. Phenylallene Hydrocarbons and Phenylallene Carboxylic Acids

Phenylallene carboxylic acids represent molecular systems comprising two chromophoric subsystems, the phenylallene chromophore (Section III.A) and the allene carboxylic acid chromophore. Both are well accessible to experimental investigations and the study of the corresponding CD spectra offers an opportunity to deal with their optical activity in a more quantitative way.

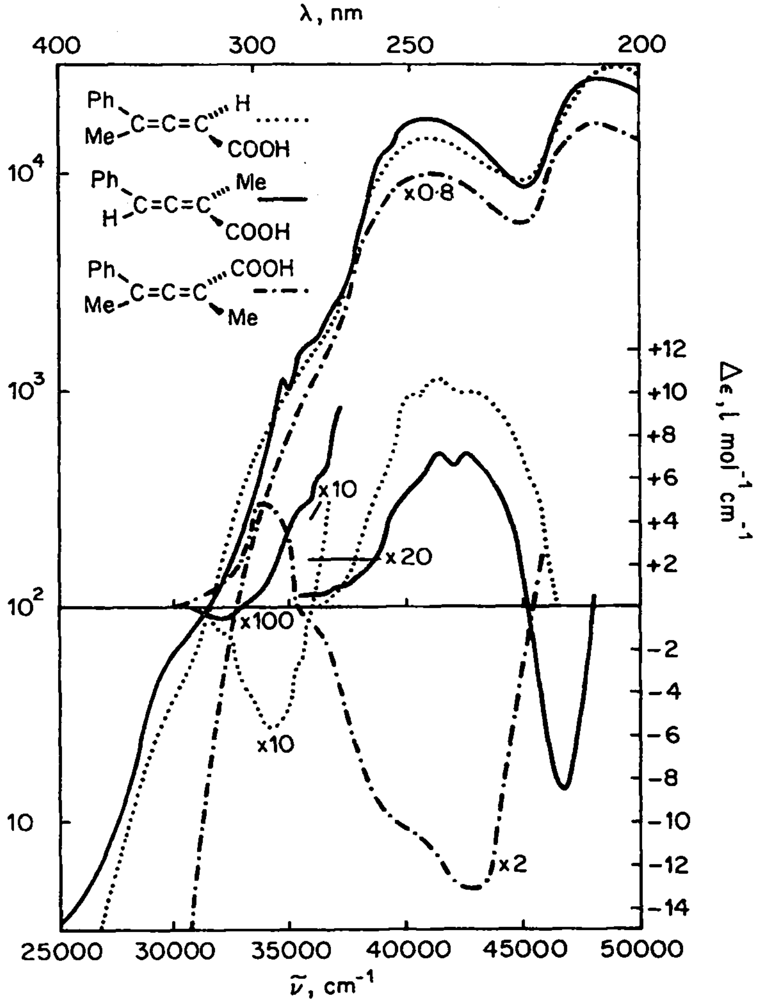


FIGURE 20. U.v. and CD spectra of methyl-substituted 4-phenylbuta-2,3-dienoic acids emphasizing the difference in spectral behaviour of constitutional isomers (in ethanol). Taken from W. Runge and J. Winkler, *Ber. Bunsenges. Phys. Chem.*, 79, 610 (1975) and reproduced by permission of Verlag Chemie, GmbH, Weinheim.

TABLE 12. U.v. and CD characteristics of phenylallene carboxylic acids (in ethanol)[a]

State	λ (nm)	$D \times 10^{38}$ (cgs)	$R \times 10^{40}$ (cgs)	$g \times 10^3$
		(39)		
$S_1(\bar{\pi},\pi^*)$	310	0.2	−0.2	−40
$S_2(\pi,\bar{\pi}^*)$	292	3	−1.0	−13
$S_3(B_{2u})$	282	18	+0.2	+0.45
$S_4(B_{1u})$	245	1000	+25	+1.0
$S_5(E_{2g(a)})$	235	70	+8	+4.5
$S_6(E_{1u(a)})$	221	150	+5	+1.3
$S_7(\pi,\bar{\pi}^*)$	211	1300		
$S_8(E_{1u(b)})$	205	1400		
		(45)		
$S_1(\bar{\pi},\pi^*)$	313	0.2	−0.011	−2.2
$S_2(\pi,\bar{\pi}^*)$	294	3	+0.3	+4.0
$S_3(B_{2u})$	282	18	+0.2	+0.45
$S_4(B_{1u})$	247	1200	+14	+0.47
$S_5(E_{2g(a)})$	235	80	+4	+2.0
$S_6(E_{1u(a)})$	221	160	+3	+0.75
$S_7(\bar{\pi},\bar{\pi}^*)$	216	1000	−8	−0.36
$S_8(E_{1u(b)})$	208	1400	>0	
		(46)		
$S_1(\bar{\pi},\pi^*)$	310	0.2	−0.029	−5.8
$S_2(\pi,\bar{\pi}^*)$	294	3	+0.4	+5.3
$S_3(B_{2u})$	282	18	+0.2	+0.45
$S_4(B_{1u})$	247	1200	+10	+0.33
$S_5(E_{2g(a)})$	233	80	+4	+2.0
$S_6(E_{1u(a)})$	221	160	+3	+0.75
$S_7(\bar{\pi},\bar{\pi}^*)$	217	1000	−11	−0.44
$S_8(E_{1u(b)})$	209	1400	>0	

[a] Taken from W. Runge and J. Winkler, *Ber. Bunsenges. Phys. Chem.*, **79**, 610 (1975) and reproduced by permission of Verlag Chemie, GmbH, Weinheim.

In Figures 19 and 20 the u.v. and CD spectra of some phenylallene carboxylic acids are displayed[16]. U.v. and CD characteristics, which result from approximate band resolutions[16], are summarized for some molecules in Table 12. The band assignments given in Table 12 are based upon correlations with the excited states in phenylallene, benzene or allene carboxylic acid[16,67]. The orbital system of the composite molecule correlating with the π system of phenylallene is denoted as π, whereas that of the allene carboxylic acid is denoted as $\bar{\pi}$ (see below).

Characteristically, the CD spectra of phenylallene carboxylic acids are much more structured than the u.v. spectra. One is able to identify eight electronic bands resulting from transitions with energies less than 50,000 cm^{-1} [16]. A band correlating with the n,π^* band in alkylallene carboxylic acids could not be detected.

There are several essential features of the CD spectra of phenylallene carboxylic acids. Firstly, the two lowest-energy CD bands are rather weak and sensitive to the ligand arrangement. In case of the molecules substituted only in the α-position (**45** and **46**) the corresponding bands are of opposite signs. These bands, which are also weak in the u.v. spectra, correlate with $^1A''(\pi,\bar{\pi}^*)$ and $^1A''(\bar{\pi},\pi^*)$ excited states in phenylallene[67]. Secondly, in the case of α-substituted phenylallene carboxylic acids there is a CD band near 47,000 cm^{-1} with an extreme small half-width. The particular form of this rather intense band results from overlap with the neighbouring CD bands of similar intensities but opposite signs. This band (S_7) is attributed to the electric dipole allowed π,π^* band of the carboxylic acid subsystem. Owing to the convention given above for the orbital system in phenylallene carboxylic acids this band has to be termed a $\bar{\pi},\bar{\pi}^*$ band[16].

From analogy with alkylallene carboxylic acids[15] the $\bar{\pi},\bar{\pi}^*$ band in phenylallene carboxylic acids is expected to shift to shorter wavelengths if no α substituent is present. Then overlap of the $S_7(\bar{\pi},\bar{\pi}^*)$ band and the $S_8(E_{1u(b)})$ CD bands of opposite signs results in a vanishing circular dichroism for $\bar{\nu} \geqslant 47{,}000$ cm^{-1} for 39.

The most remarkable feature of the CD spectra, however, is the fact that the u.v. band maxima (near 40,000 cm^{-1}) do not coincide with the CD band maxima (near 43,000 cm^{-1}). This non-correspondency is due to an additional electronic state, not observable in the u.v. absorption spectra, which should correspond to $^1E_{2g}$ in benzene[16].

With the rotatory strengths and the absorption positions given in Table 12 it is possible to calculate the optical rotatory dispersion of phenylallene carboxylic acids in the transparent region using equation (6). In Figure 21 experimental and calculated (equation 6) ORD curves are displayed[16]. It can be seen that the ORD curves may be reproduced to a large extent taking only the lowest-energy excited states into consideration (S_1–S_6 or S_1–S_7, respectively).

A more quantitative discussion of the origins of the optical activity of the electronic bands S_3–S_8 in phenylallene carboxylic acids is given in Reference 16. This treatment performed prototypically for phenylallene carboxylic acid (38) is based upon a distinct hierarchy of approximations. The starting point is the elec-

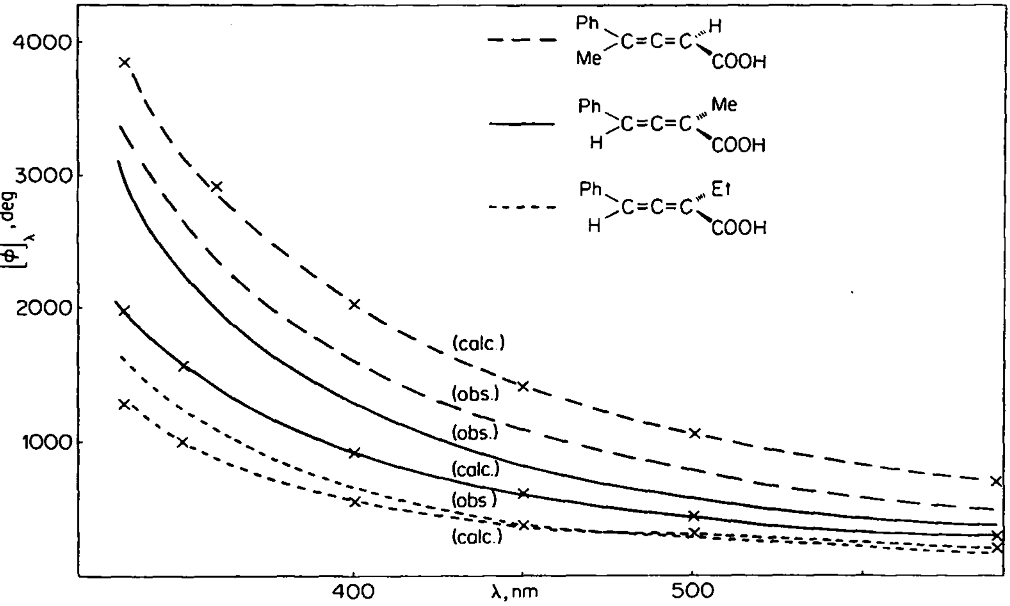


FIGURE 21. Observed and calculated (equation 6) rotatory dispersion of phenylallene carboxylic acids (in ethanol). Taken from W. Runge and J. Winkler, *Ber. Bunsenges. Phys. Chem.*, 79, 610 (1975) and reproduced by permission of Verlag Chemie, GmbH, Weinheim.

tronic structure of 38 and the kinds of electronic transitions in the chromophoric subsystems.

For a quantitative discussion of the circular dichroism one must decide (*a*) how to subdivide the whole molecule into subsystems, (*b*) what eigenfunctions are to be used in describing the unperturbed electronic states in the chromophoric subunits, and (*c*) what forces perturb these states. In general, for quantitative treatments of molecular properties of complex allenes it has turned out that the composite molecules should be related to two 1,1-disubstituted allenes[15-19]. Therefore, 38 is related to phenylallene $PhHC{=}C{=}CH_2$ (97) and allene carboxylic acid $H_2C{=}C{=}CHCOOH$ (96) (Figure 22).

The outermost (occupied and unoccupied) orbitals of phenylallene carboxylic acid, which are relevant for the electronic excitations with energies less than 50,000 cm^{-1} correlate with the corresponding π orbitals in phenylallene (97) (subsystem a) and allene carboxylic acid (96) (subsystem b), i.e. they correlate with orbitals which, with respect to their LCAO expansions, are only slightly changed in the CH_2 part relative to those of the molecules 96 and 97 taken as the subgroups.

Conventionally[16], in an LCAO expansion the π orbitals of phenylallene are composed of p_z atomic orbitals (AOs), the π orbitals of allene carboxylic acid of p_y AOs. In Figure 22 this correlation of the outermost orbitals of phenylallene carboxylic acid (38) based upon CNDO/S calculations[19,77] is displayed.

In zero order it is assumed that the orbital systems of the chromophoric subunits a and b do not interact, that there is no overlap and no electron exchange. Then corresponding orbitals in the composite system 38 are classified as π and $\bar{\pi}$. At this stage of approximation the π and $\bar{\pi}$ orbitals of 38 have nodal planes and may be

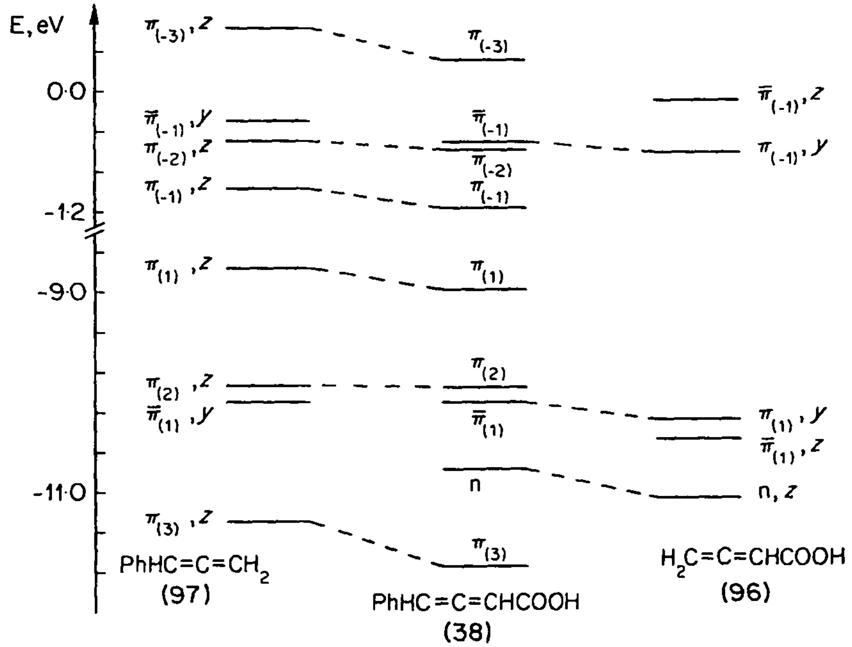


FIGURE 22. Correlation of the outermost orbitals of phenylallene carboxylic acid with the π orbitals of phenylallene and allene carboxylic acid, respectively.

treated as if the geometrical mirror planes of the subsystems were retained. However, 1,3-disubstituted allenes with different ligands are nonplanar and there is no plane of symmetry in the molecule. Symmetry arguments therefore lead to the expectation that the π and $\bar{\pi}$ electronic systems may no longer be treated separately, i.e. π and $\bar{\pi}$ orbitals are expected to mix. But, symmetry arguments do not allow any statement about the extent of the π–$\bar{\pi}$ mixing. According to quantum-theoretical perturbation theory to first order the extent of the mixing an orbital $|\sigma)$ with other orbitals $|\rho)$ depends upon the kind of perturbation operator v and the differences between the corresponding orbital energies ϵ_σ and ϵ_ρ respectively (equation 30), where $|\sigma)$ and $|\rho)$ denote the zero-order unperturbed orbitals and $|\sigma\rangle$ the perturbed orbitals σ to first order.

$$|\sigma\rangle = |\sigma) - \sum_{\rho\neq\sigma} \frac{(\rho|v|\sigma)}{\epsilon_\rho - \epsilon_\sigma}|\rho) \qquad (30)$$

Referring in particular to the π orbitals of the phenylallene subsystem it may be assumed that the perturbation of the relevant orbitals results from the electric field of the group moments $\mu(\mathrm{R})$ of the substituents in the γ position[62,76] (Figure 23). These group moments may be treated as point dipoles[62,76].

Then for an orbital π_i of the phenylallene subgroup the perturbation operator involves the interaction of the point dipole $\mu(\mathrm{R})$ with the orbital point charges. The potential v may be partitioned into two components v' and v'', v' being symmetric and v'' being antisymmetric with respect to the mirror plane xy of the unsubstituted phenylallene (Figure 23). Restricting ourselves for this more qualitative discussion of the π–$\bar{\pi}$ separability in phenylallenes to the orbital system given in Figure 22 an orbital $|\pi_i\rangle$ of the composite molecule **38** may be approximated by equation (31) to first order.

$$|\pi_i\rangle \approx |\pi_i) - \sum_{j\neq i} \frac{(\pi_j|v'|\pi_i)}{\epsilon_{\pi j} - \epsilon_{\pi i}}|\pi_j) - \sum_{k} \frac{(\bar{\pi}_k|v''|\pi_i)}{\epsilon_{\bar{\pi}k} - \epsilon_{\pi i}}|\bar{\pi}_k) \qquad (31)$$

In equation (31) the first sum mixes the orbital π_i with other π_j orbitals of the phenylallene subgroup, i.e. leads to a polarization. The second sum in (31) mixes π_i with the $\bar{\pi}_k$ orbitals of the allene carboxylic acid subunit. One is then in a position to discuss semiquantitatively a quantum-theoretical mechanism, which may induce optical activity in the electronic bands in phenylallenes. For simplicity we regard only one excited state, say S_4, and assume that in the unperturbed subunit S_4 is adequately described by a single excitation $(\pi_{(1)} \rightarrow \pi_{(-1)})$. In zero order we have, as in phenylallene (**97**) itself

$$(\pi_{(1)}|\mu|\pi_{(-1)}) \neq 0 \qquad (\pi_{(1)}|m|\pi_{(-1)}) = 0 \qquad (32)$$

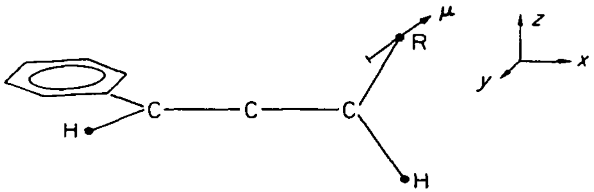


FIGURE 23. Perturbation of the π orbitals of phenylallene by a point dipole of the substituent in the γ position.

Therefore, the rotatory strength (equation 7) vanishes, as the excited state results from a strictly electric dipole allowed, magnetic dipole forbidden transition. Now the first-order perturbation term is used. If we restrict ourselves for simplicity to one term only of equation (31), e.g. the term mixing $\pi_{(-1)}$ and $\bar{\pi}_{(-1)}$, and use the zero-order form for $\pi_{(1)}$, we have for the magnetic dipole transition moment

$$
\begin{aligned}
(\pi_{(1)}|m|\pi_{(-1)}\rangle &= (\pi_{(1)}|m|\pi_{(-1)}) - \frac{(\bar{\pi}_{(-1)}|v''|\pi_{(1)})}{\epsilon_{\pi(-1)} - \epsilon_{\pi(1)}}(\pi_{(1)}|m|\bar{\pi}_{(-1)}) \\
&= - V''(\bar{\pi}_{(-1)}, \pi_{(1)})(\pi_{(1)}|m|\bar{\pi}_{(-1)}) \neq 0
\end{aligned}
\tag{33}
$$

Since V'' and also the magnetic transition moment are nonzero in first order a nonvanishing rotatory strength results.

A rough evaluation of the last sum in equation (31) shows that there should be a little mixing only of the π_i and $\bar{\pi}_k$ orbitals (all the terms V'' are small), i.e. in phenylallenes the π–$\bar{\pi}$ separability is largely retained. This is corroborated by CNDO/S calculations for 38[19,76] and may be seen from the LCAO expansions of the CNDO/S MOs. Consequently, to a good approximation the outermost π_i and $\bar{\pi}_k$ orbitals of phenylallene carboxylic acid (38) retain their nodal planes and the subsystems may be treated like groups with C_s symmetry.

Since the chromophoric subunits in 38 are nonplanar, a nonvanishing rotatory strength can already be produced with zero-order wave functions. Specifically, the above considerations show that the zero-order contribution should describe the relevant part of the particular chirality observation, as a mechanism involving π—$\bar{\pi}$ mixing is only of minor importance.

The excited states S_3–S_8 in phenylallene carboxylic acid result from electric dipole allowed transitions. Therefore, one may assume that the transitions in the two subunits produce, via electrostatic coupling, magnetic moments and thus give nonvanishing rotatory strengths. On the basis of the above 'independent systems' (IS) model, the optical activity of the excited states S_3–S_8 of 38 may be treated quantitatively by equation (34)[16].

$$
R_{0i} \approx -\frac{1}{\hbar c} \sum_{j \neq i} V_{0i^{a},0j^{b}} \frac{\tilde{\nu}_i \tilde{\nu}_j}{\tilde{\nu}_j^2 - \tilde{\nu}_i^2} (R_j - R_i) \cdot (\mu_{0j}{}^{b} \times \mu_{0i}{}^{a}) \tag{34}
$$

$(R_j - R_i) = R_{ji}$ is the distance between the two centres of gravity of the group a and b charge distributions for the transitions $0 \to i$ (in a; $i = 3, 4, 6, 8$) and $0 \to j$ (in b; $j = 7$). $\mu_{0j}{}^{b}$ and $\mu_{0i}{}^{a}$ are the electric transition moments of the corresponding electronic transitions with energies $\tilde{\nu}_j$ and $\tilde{\nu}_i$, respectively (in cm^{-1}). The Coulombic interaction potential $V_{0i^{a},0j^{b}}$ between the two nonoverlapping charge distributions on excitation is given by the dipole interaction formula (35).

For the calculation of the rotatory strength R_{0i} the directions of the transition dipole moments have been obtained from CNDO/S calculations for the subunits a and b (phenylallene and allenecarboxylic acid, respectively)[16]. The orientation of the various electric transition dipole moments are shown in Figure 24. Also the distances R_{ji} have been obtained from CNDO/S calculations. For the magnitudes of the transition moments, however, experimental values have been used[16].

$$
V_{0i^{a},0j^{b}} = \frac{1}{R_{ji}^3}\left[\mu_{0i}{}^{a} \cdot \mu_{0j}{}^{b} - 3\,\frac{(\mu_{0i}{}^{a} . R_{ji})(\mu_{0j}{}^{b} . R_{ji})}{R_{ji}^2}\right] . \tag{35}
$$

A comparison between the calculated and experimental rotatory strengths for phenylallene carboxylic acid (38) is given in Table 13. With the exception of

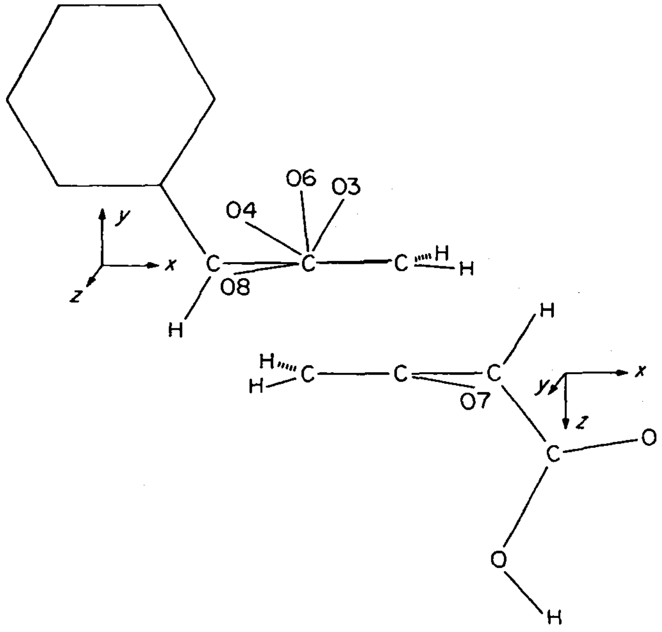


FIGURE 24. The direction of the electronic transition moments of electric dipole allowed transition in the subunits of phenylallene carboxylic acid. Taken from W. Runge and J. Winkler, *Ber. Bunsenges. Phys. Chem.*, 79, 610 (1975) and reproduced by permission of Verlag Chemie, GmbH, Weinheim.

$S_7(\pi,\pi)$ there is satisfactory agreement between calculated and observed rotatory strengths. Therefore, a 'coupled oscillator' mechanism[14] for electric transition moments is dominant for the Cotton effect of the intense electronic transitions in phenylallene carboxylic acids. If no other determination of the absolute configuration were available, the absolute configuration of phenylallene carboxylic acid (38) would have been correctly assigned.

TABLE 13. Experimental and calculated rotatory strengths of electric dipole allowed transitions of (*S*)-phenylallene carboxylic acid[a]

State	Calc. $R \times 10^{40}$ (cgs)	Exp. $R \times 10^{40}$ (cgs)
$S_3(B_{2u})$	+0.15	+0.15
$S_4(B_{1u})$	+32.5	+22
$S_6(E_{1u(a)})$	+3.7	+4
$S_7(\pi,\pi^*)$	−53.0	−9
$S_8(E_{1u(b)})$	+15.7	+9

[a] In Reference 16 the calculations have been performed for the *s-cis* conformation of 38. As the actual conformation is *s-trans* (cf. Chapter 2), the rotatory strengths have been recalculated with the *s-trans*-allene carboxylic acid.

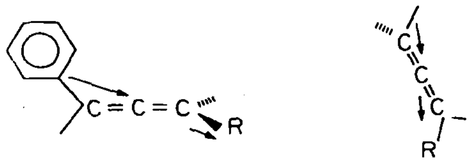


FIGURE 25. Out-of-phase coupling of the electric transition moments of the 40,000 cm^{-1} intense phenylallene electronic band and the electric transition moment of a further allenic subunit with the substituent R to give a positive Cotton effect.

The coupling of the 0 → 4 [$S_4(B_{1u})$] and 0 → 7 [$S_7(\bar{\pi},\bar{\pi}^*)$] transitions is especially useful for a conceptually simple description of the optical activity of the particular electronic bands and the qualitative deduction of absolute configurations of phenylallenes from the sign of the $S_4(B_{1u})$ band near 40,000 cm^{-1}. The out-of-phase coupling mode of these two transitions give the S_4 transition the overall form of a charge displacement through a right-handed helical path along and about the x axis (Figure 25). Thus, the $S_4(B_{1u})$ CD band should have a positive sign for the (*S*) configuration of phenylallenes.

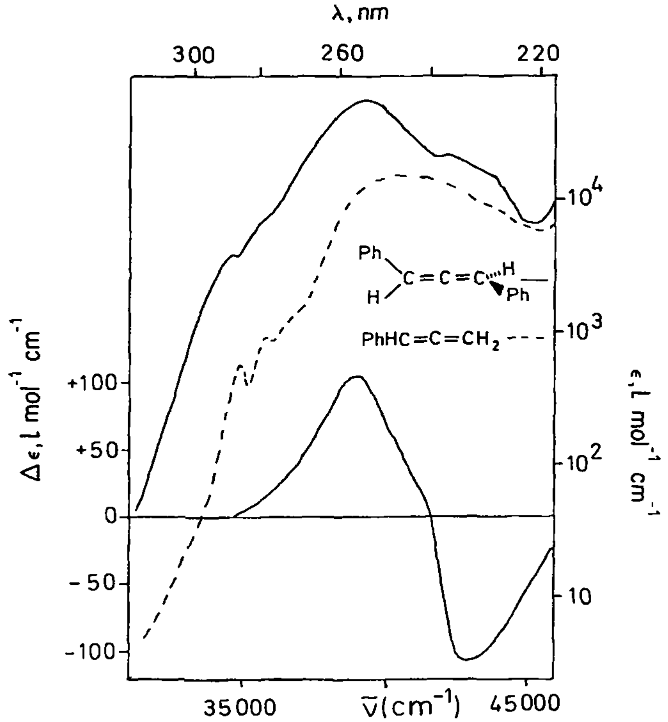


FIGURE 26. U.v. and CD spectra of (*S*)-(+)-1,3-diphenylallene and the u.v. spectrum of phenylallene. Reproduced with permission from S. F. Mason and G. W. Vane, *Tetrahedron Letters*, 1593 (1965).

TABLE 14. U.v. and CD characteristics of (*S*)-1,3-diphenylallene

State	U.v.[a]			CD[c]			
	λ (nm)	ϵ ($l\ mol^{-1}\ cm^{-1}$)	$D \times 10^{38}$ (cgs)[b]	λ (nm)	$\Delta\epsilon$ ($l\ mol^{-1}\ cm^{-1}$)	$R \times 10^{40}$ (cgs)[b]	$g \times 10^3$
^1B	255	52,000	4980	255	+200[d]	+480	+3.9
^1A	237	20,500	2120	233	−200	−516	−9.8

[a] From Reference 78.

[b] From $D = 0.92 \times 10^{-38}\sqrt{\pi}\,\epsilon(\Delta_{0i}/\lambda_{0i})$ (cgs) or $R = 0.23 \times 10^{-40}\sqrt{\pi}\Delta\epsilon(\Delta_{0i})$ (cgs), respectively with $\Delta_{0i} = 15$ nm.

[c] From Reference 77.

[d] Estimated value based upon an assumed optical purity of 50% for the compound studied in Reference 77.

This fact has been used to deduce the absolute configurations (*S*) for the dextrorotatory phenylallene carboxylic acids **41**–**45**[42,43]. Similarly, the positive circular dichroism ($\Delta\epsilon = +5.3$; $R \approx 16 \times 10^{-40}$ cgs) at 250 nm may be used to assign the (*S*) configuration to the phenylallene isocyanate **79**[56].

Starting from the dissection of 3-methyl-1-phenylallene (**1**) into phenylallene (**97**) and methylallene (**2**) subunits, the above arguments lead to the prediction of the (*S*) configuration if **1** exhibits a strong positive $S_4(B_{1u})$ CD band near 250 nm. Direct quantum-chemical CNDO/S calculations[72] are in disagreement with this prediction ($[R(S_4)] = -7.94$)[72b]. Furthermore, the optical activity of the electronic bands S_1–S_6[67] of **1** would give (*S*)-**1** a negative rotation at 589 nm if the CNDO/S results are used. However, according to the λ formula (15) this is unlikely, i.e. (*S*)-**1** should be dextrorotatory.

The discussion of the circular dichroism of (*S*)-1,3-diphenylallene (**37**)[77] (Figure 26) requires a reconsideration of the 'independent systems' model for the treatment of the circular dichroism of phenylallenes. In this case the formal subdivision of the molecule results in two identical phenylallene chromophoric subunits. Therefore, the 'coupled oscillator' mechanism reduces to the 'exciton case'[14]. However, this is only of minor importance for the discussion of the optical activity of electronic bands of **37**. The crucial point is that **37** has the symmetry of the pure rotation group C_2, which makes polar (μ) and axial (m) vectors indistinguishable from one another on the basis of symmetry, and, furthermore, also the distinction between π_i and $\bar{\pi}_k$ orbitals of the subunits a and b disappears. In **37** the distinction of the two chromophoric subunits and the π–$\bar{\pi}$ separability breaks down. In **37** the chromophore comprises the whole 1,3-diphenylallene molecule. The (outermost) orbitals ψ of **37** may be represented by symmetry-adapted linear combinations of the (only slightly modified) π_i orbitals of phenylallene (**97**) to give orbitals of irreproducible representation a or b.

$$\psi_{(i)}^{+} = (1/2)^{1/2}\left(\pi_{(i)}^{z} + \pi_{(i)}^{y}\right) \tag{36a}$$

$$\psi_{(i)}^{-} = (1/2)^{1/2}\left(\pi_{(i)}^{z} - \pi_{(i)}^{y}\right) \tag{36b}$$

(In the particular case of **37** the $\bar{\pi}_k$ orbitals of the subunit b are identical with the π_i orbitals of phenylallene expanded in p_y AOs.) For the 1,3-diphenylallene chromophore belonging to a pure rotation group all allowed transitions should in principle be associated with nonorthogonal electric and magnetic transition moments. Therefore, one may expect *g*-factors of the order $g \approx 10^{-3}$–10^{-4} (Section II), i.e. one order of magnitude larger than those of phenylallene carboxylic acid (**38**). U.v. and CD characteristics of (*S*)-1,3-diphenylallene (**37**)[77,78] are given in Table 14. There it is seen that the CD characteristics of **37**, indeed, are larger than those of phenylallene carboxylic acid (Table 13) by about one order of magnitude. A coupled oscillator (exciton) mechanism can only account for 10–20% of the observed effects in **37**. This shows that an assignment of the absolute configuration (*S*) to (+)-**37** on the basis of an exciton model of two weakly interacting subunits, as has been done by Mason and Vane[77], is not *a priori* justified. However, Hug and Wagnière[79] have later shown that a direct LCAO MO treatment of the optical activity of chromophoric systems of symmetry C_2, i.e. strongly interacting subunits giving an extended inherently chiral 'superchromophore', tend to show a similar pattern for the corresponding part of the spectrum as the exciton model.

Corresponding arguments apply for the discussion of the circular dichroism of the 1,3-diphenylpentatetraene **33**[80].

VI. ACKNOWLEDGEMENT

This work was supported by the 'Deutsche Forschungsgemeinschaft'.

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$[\phi]_{578}$ + 165°, $[\phi]_{546}$ + 188°, $[\phi]_{436}$ + 374° in isooctane; CD $\Delta\epsilon(\lambda) = -2.3 \times 10^{-2}$ (350 nm), + 5.3 (250 nm).

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The Chemistry of Ketenes, Allenes and Related Compounds
Edited by Saul Patai

CHAPTER **4**

The thermodynamics of allenes, ketenes and related compounds

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I. INTRODUCTION

Since the 1964 edition of *The Chemistry of Alkenes* there has been considerable progress in the chemistry of the cumulenes. This progress has not been matched by a concomitant interest on the part of thermochemists. The earlier edition was able to treat the thermodynamic properties in less than one printed page. More data are available now and some useful results have appeared from semiempirical quantum-mechanical calculations. The data base, still sparse, is sufficient to permit meaningful estimates to be made for the thermochemistry of compounds for which no data exist. As is usual, third-law entropies are rarer than are enthalpies of formation. The only such values that have appeared in recent years are data for the isomeric pentadienes reported by Messerly, Todd and Guthrie[1]. The thermochemical data, that is experiments from which $\Delta H_f{}^0$s may be calculated, have been reviewed and tabulated in three compilations. The first of these by Stull, Westrum and Sinke[2] also includes a review of the entropies available in 1969 and presents calculated free energies of formation. The second, by Cox and Pilcher[3], deals only with thermochemical data but is useful in including a variety of bond energy schemes which can be expanded to include the cumulenes as more information becomes available. The most recent review, by Pedley and Rylance[4] in 1977, is unique in being the first extensive set of tables that have been made self-consistent by computer fit.

Although true thermodynamic stability is judged by the free energy of formation, ΔG_f^0, the entropy data needed for its calculation are most often missing. Much useful information on relative stabilities among structurally similar systems can be gained from a consideration of enthalpies alone since the unknown entropies are often nearly identical for isomeric compounds. For example, we can state with a confidence of ca ±2 kcal mol^{-1} that 1,5-hexadiene is more stable than the allenic 1,2-hexadiene by 8 kcal mol^{-1}. Neither entropy is known, but $\Delta S \simeq 0$ by comparison with other isomeric systems[2] and the enthalpies of hydrogenation of allenes are 8 kcal more exothermic than those for systems containing two isolated double bonds. Such semiquantitative arguments are sufficient in most cases to judge whether or not an equilibrium between species might occur or which of several possible products will be the exclusive result of a planned experiment. If it is necessary for the reader to make more critical judgements, methods of entropy estimation are discussed by Stull, Westrum and Sinke[2] and by Janz[5].

Enthalpies of formation are becoming available from quantum-mechanical computation. The results are not sufficiently refined for the ΔH_f^0s to be of comparable quality to those obtained from thermochemical experiments. They can, however, be useful in judging trends and are all that we have available for some species – particularly reaction intermediates. Even such information as this is exceedingly sparse for allenic systems. Dewar and his coworkers have attacked the problem and further references can be found in a paper by Dewar and Kohn[6] containing results for simple allenes.

Our emphasis will be on the systems for which 'hard' data exist. We do this in the belief that precise information on a few systems is more useful in estimating unknown reaction parameters than is data of unknown precision for a large number of materials.

The relative energetic stabilities of multiply unsaturated compounds can be judged by comparing their enthalpies of hydrogenation with those for the simple alkenes. More negative enthalpies of hydrogenation can be interpreted as reflecting a structurally destabilizing effect, whereas more positive enthalpies of hydrogenation are indicative of relative stabilization. Table 1 presents such enthalpies of hydrogenation derived from the data tabulated by Pedley and Rylance[4].

For the hydrogenation reaction,

$$\text{1-Alkene(g)} \rightarrow \text{Alkane(g)},$$

we have $\langle \Delta H \rangle = -30.0 \pm 0.2$ kcal $(\mathrm{mol\ H_2})^{-1}$ for the average enthalpy. This value can be used as a 'standard' for judging the existence of stabilizing or destabilizing effects in multiple unsaturated compounds. For the dienes with isolated double bonds, 1,4-pentadiene and 1,5-hexadiene, the average enthalpy of hydrogenation is also -30.0 kcal $(\mathrm{mol\ H_2})^{-1}$, a value that can be interpreted to show a lack of interaction between the two double bonds. The less negative value, $\langle \Delta H \rangle = -27.2 \pm 0.8$ kcal $(\mathrm{mol\ H_2})^{-1}$, found as the average for the 1,3-dienes, indicates the stabilizing effect present in these compounds. The origin of this stabilization has been discussed by Mortimer[7] among others. For the alkynes we have $\langle \Delta H \rangle = -33.8 \pm 1.3$ kcal $(\mathrm{mol\ H_2})^{-1}$, indicating that the concentration of electron density into one bond has a considerable destabilizing effect relative to the alkenes.

TABLE 1. Enthalpies of hydrogenation

Compound	$\langle \Delta_{\text{hyd}} \rangle$ [kcal (mol H_2)$^{-1}$]
Propene	–29.8
1-Butene	–30.1
1-Pentene	–29.8
1-Hexene	–30.0
1-Heptene	–29.9
1-Octene	–30.4
1-Decene	–30.2
1,4-Pentadiene	–30.1
1,5-Hexadiene	–30.0
1,3-Butadiene	–28.3
2-Methyl-1,3-butadiene	–26.5
2,2-Dimethyl-1,3-butadiene	–26.7
1,3-Pentadiene	–27.2
Propyne	–34.8
1-Butyne	–34.9
1,5-Hexadiyne	–32.9
1,7-Octadiyne	–32.4
Allene	–35.3
1,2-Butadiene	–34.5
1,2-Pentadiene	–34.3
2,3-Pentadiene	–33.4
3-Methyl-1,2-Butadiene	–32.9

The enthalpies of hydrogenation of the allenes average at $\langle \Delta H \rangle = -34.1 \pm 0.9$ kcal (mol H_2)$^{-1}$ – a value almost identical to that for the alkynes. We conclude that the structural feature represented by a pair of adjacent double bonds destabilizes the molecule by some 8 kcal relative to the isolation of the double bonds. The interpretation of this destabilization in terms of electron interactions has been considered by theoreticians[6]. From the gross thermochemical point of view it can be expected that the allenes would resemble the alkynes in their reactions more than they would other alkadienes. We can summarize the data of Table 1 for the allenes, by writing

$$2\,H_2 + n,n + 1\text{-Alkadiene(g)} = \text{Alkane (g)},\ \langle \Delta H \rangle = -68 \text{ kcal}.$$

In the following paragraphs we shall review the thermochemical data for the few allenes for which such data are available.

II. ALLENES

The thermochemical data leading to the enthalpy of formation of *1,2-propadiene(allene)* are the hydrogenation data of Kistiakowsky and coworkers[8], and the results for the isomerization,

$$\text{Propyne(g)} = \text{Allene(g)},$$

as studied by Cordes and Gunzler[9]. These data have been reviewed on numerous occasions, most recently by Pedley and Rylance[4]. This last value differs only slightly from that selected by Cox and Pilcher[3] and we adopt it as $\Delta H_f^0 = 45.6 \pm 0.3$ kcal mol^{-1}.

Stull, Westrum and Sinke had reviewed[2] the earlier data that led to an entropy for allene. No new data have appeared since their 1969 compilation and we adopt their $S^0(298\ K) = 58.30$ cal mol^{-1} K^{-1}. It should be noted that this value has its origin in the summary of API Project 44[10].

For the reaction leading to the formation of allene from the elements,

$$3\,C(c) + 2\,H_2\,(g) = C_3H_4\,(g),$$

we calculate $\Delta G_f^0 = 48.02 \pm 0.5$ kcal mol^{-1}. For the gas-phase isomerization,

$$\text{Propyne(g)} = \text{Allene(g)},$$

$\Delta G^0 = 1.3 \pm 0.7$ kcal, equivalent to an equilibrium constant, $K_{298} \simeq 0.1$.

Allene, a gas at room temperature, melts at 136.9 K and boils at 238.6 K.

The enthalpy of formation of gaseous *1,2-butadiene* ($T_m = 137.0$ K, $T_b = 284.0$ K) is based on the flame calorimetry experiments of Prosen, Maron and Rossini[11]. Pedley and Rylance[4] conclude that $\Delta H_f^0 = 38.8 \pm 0.1$ kcal mol^{-1}. This value agrees well with that selected by Stull, Westrum and Sinke[2]. The latter authors report an entropy, $S^0 = 70.03$ cal mol^{-1} K^{-1}, based on their review of the available information. These values lead to

$$4\,C(c) + 3\,H_2\,(g) = C_4H_6\,(g),\ \Delta G_f^0 = 47.47 \pm 0.3\ \text{kcal mol}^{-1}.$$

A comparison with the free energy of formation of 1-butyne calculated by a similar selection of data ($\Delta G_f^0 = 48.30$ kcal mol^{-1}) indicates that in this case the diene is the more stable of the two isomers. 1,2-Butadiene is, however, considerably less stable than is 1,3-butadiene for which $\Delta G_f^0 = 36.0$ kcal mol^{-1} in the vapour phase.

For *1,2-pentadiene* we have available the data of Fraser and Prosen[12] for the enthalpy of combustion by flame calorimetry. From these results values for ΔH_f^0 have been recalculated by Cox and Pilcher[3], Stull, Westrum and Sinke[2], and, most recently, by Pedley and Rylance[4]. This last value, $\Delta H_f^0 = 33.6 \pm 0.2$ kcal mol^{-1}, identical to that of Cox and Pilcher and only slightly more negative than that of Stull, Westrum and Sinke, is adopted.

Messerly, Todd and Guthrie[1] have determined the heat capacity of 1,2-pentadiene ($T_m = 135.9$ K, $T_b = 318.0$ K) between 12 and 320 K. Their entropy for the saturated liquid at 298 K is $S^0 = 58.55$ cal mol^{-1} K^{-1}. The pertinent vaporization data can be obtained from the temperature-dependent vapour pressures reported by Osborn and Douslin[13], and when combined with the entropy of the liquid lead to $S^0(298\ K) = 80.02$ cal mol^{-1} K^{-1} for gaseous 1,2-pentadiene. This value is preferable to the one provided by Rossini and collaborators[10] in an earlier compilation.

For the standard free energy of the compound,

$$5\,C(c) + 4\,H_2\,(g) = H_2C{=}C{=}CHCH_2CH_3\,(g),$$

$\Delta G_f^0 = 49.04 \pm 0.2$ kcal mol^{-1}. The data needed for a comparison with the stability of 1-pentyne are lacking. Data available[1,4] for *cis-* and *trans-*1,3-pentadiene and for 1,4-pentadiene show that each of these compounds is more stable than the corresponding 1,2-diene.

Good[14] has determined the enthalpy of combustion of the liquid *3-methyl-1,2-butadiene*. Pedley and Rylance[4] have incorporated his data into their compilation as $\Delta H_f^0 = 24.2 \pm 1.0$ kcal mol^{-1}. Messerly, Todd and Guthrie[1] have determined the heat capacities of the saturated condensed phases ($T_m = 159.5$ K, $T_b = 314.0$ K) between 12 and 320 K. They present S^0(298 K) = 55.40 cal mol^{-1} K^{-1}, which we use to calculate $\Delta G_f{}^0 = 46.94 \pm 1.2$ kcal mol^{-1} for $H_2C{=}C{=}C(CH_3)_2$ (l).

We use the vapour pressure measurements of Osborn and Douslin[13] to estimate an enthalpy of vaporization of 6.7 kcal mol^{-1}, leading to $\Delta H_f{}^0 = 30.9 \pm 1.5$ kcal mol^{-1} for 3-methyl-1,2-butadiene(g). From these same data Messerly, Todd, and Guthrie[1] have calculated the entropy of the vapour as 76.77 cal mol^{-1} K^{-1}. This value is 0.4 cal mol^{-1} K^{-1} more positive than that selected by Stull, Westrum and Sinke[2] from the earlier API Project 44 results[10].

The computation of the free energy of formation,

$$5\,C(c) + 4\,H_2(g) = H_2C{=}C{=}(CH_3)_2(g),$$

$\Delta G_f{}^0 = 47.3 \pm 1.7$ kcal mol^{-1} K^{-1} is straightforward and indicates that the branched 3-methyl-1,2-butadiene is more stable than is its nonbranched isomer, 1,2-pentadiene.

Fraser and Prosen[12] have determined the enthalpy of combustion of *2,3-pentadiene*. Their results have been included in the tabulations of Cox and Pilcher[3], Stull, Westrum and Sinke[2], and Pedley and Rylance[4]. The first and last agree on a value for $\Delta H_f{}^0$ that is slightly more negative than that chosen by Stull, Westrum and Sinke. We choose the value of Pedley and Rylance, $\Delta H_f{}^0 = 31.8 \pm 0.2$ kcal mol^{-1}, primarily for its consistency with other values that have been selected.

The third-law entropy based on heat capacity measurements[1] between 12 and 320 K has been reported as 56.72 cal mol^{-1} K^{-1} for the liquid at 298 K. Messerly, Todd and Guthrie[1] have calculated an entropy of vaporization from the vapour pressures of Osborn and Douslin[13] and report S^0(298 K) = 78.66 cal mol^{-1} K^{-1} for $CH_3CH{=}C{=}CHCH_3$(g). We feel this value to be preferable to that reported by Stull, Westrum and Sinke[2] from their evaluation of earlier work.

For the formation of 2,3-pentadiene from the elements,

$$5\,C(c) + 4\,H_2(g) = CH_3CH{=}C{=}CHCH_3\ .g)$$

$\Delta G_f{}^0 = 47.63 \pm 0.3$ kcal mol^{-1}. Comparing this value to that for the 1,2-isomer shows that the 2,3-configuration of double bonds is the more stable. Any process that could produce both isomers should have a predominance of the 2,3-pentadiene by a factor of ca 10.

The vapour pressure data of Osborn and Douslin permit an estimate for the enthalpy of vaporization, 7.0 kcal mol^{-1}, from which we calculate $\Delta H_f{}^0 = 24.8 \pm 0.4$ kcal mol^{-1} for the liquid. This value and the third-law entropy cited earlier lead to $\Delta G_f{}^0 = 47.1 \pm 0.5$ kcal mol^{-1} for 2,3-pentadiene(l). The compound is a liquid at room temperature with $T_m = 147.5$ K and $T_b = 321.4$ K.

Although these are the only allenes for which actual thermochemical data exist, they are sufficient to permit the estimation of enthalpies of formation of other

TABLE 2

	Carbon centre	ΔH_f^0(g) (kcal mol^{-1})
I	$\{(C_d)-(C_d)(H)_2\}$	6.22
II	$\{(C_d)-(C_d)(C)(H)\}$	8.65
III	$\{(C)-(C_d)(H)_3\}, \{(C)-(C)(H)_3\}$	−10.12
IV	$\{(C)-(C_d)(C)(H)_2\}$	−4.92
V	$\{(C_d)-(C_d)(C)_2\}$	9.75
VI	$\{(C_d)-(C_d)_2\}$	

compounds containing the $\rangle C{=}C{=}C\langle$ moiety. Perhaps the simplest route to such estimations is the evaluation of a group contribution for the =C= carbon that is compatible with generalized group parameter schemes. We shall determine such a parameter using the values derived by Cox and Pilcher[3]. The enthalpies of formation of the gas-phase allenes will be constructed using six parameters. Five of these are listed by Cox and Pilcher and the last, $\{(C_d)-(C_d)_2\}$, will be found by difference. The types of carbon centres that are found in these molecules are shown in Table 2.

Allene: $2\,I + VI = 45.6$

1,2-Butadiene: $I + II + III + VI = 38.8$

1,2-Pentadiene: $I + II + III + IV + VI = 33.6$

3-Methyl-1,2-butadiene: $I + 2\,III + V + VI = 30.9$

2,3-Pentadiene: $2\,II + 2\,III + VI = 31.8$

Summing over the five compounds, we have

$$5\,I + 4\,II + 6\,III + IV + V + 5\,VI = 180.7,$$

leading to $\Delta H_f{}^0(g) = 34.18\ \text{kcal mol}^{-1}$ for the group contribution assignable to $\{(C_d)-(C_d)_2\}$. The precision of this value can be judged by comparing the observed and calculated enthalpies of formation for the allenes (Table 3) for which data have been presented previously.

The good agreement between the calculated and observed values permits some confidence in enthalpies of formation that can be estimated from the derived parameter. Such estimations will probably be best in acyclic compounds or in cyclic compounds where the three carbon linear array does not introduce additional strain. Ring strain in such cyclic allenes has been the subject of a recent review[15], although no thermochemical data are available for some of the interesting compounds considered.

There is no assurance that the 34.18 kcal mol^{-1} contribution for the =C= carbon is applicable for molecules containing a consecutive series of such entities. Such molecules have been subjected to considerable theoretical study, particularly from the point of view of torsional strain about the sequence of double bonds. The most useful results seem to be those of Dewar and Kohn[6] who have refined their MINDO/2 calculations to produce both rotational barriers (V_0) and enthalpies of formation. Their results include those in Table 4.

The validity of their calculations rests on the agreement between the calculated and experimental rotational barriers[6] [V_0(exp.) = 30 and 20 kcal mol^{-1} for butatriene and hexapentaene, respectively] and the enthalpy of formation of allene.

TABLE 3

Compound	ΔH_f^0(obs.) (kcal mol^{-1})	ΔH_f^0(calc.) (kcal mol^{-1})
Allene	45.6 ± 0.3	46.6
1,2-Butadiene	38.8 ± 0.1	38.9
1,2-Pentadiene	33.6 ± 0.2	34.0
3-Methyl-1,2-butadiene	30.9 ± 1.5	29.9
2,3-Pentadiene	31.8 ± 0.2	31.2

TABLE 4

Compound	ΔH_f^0(kcal mol^{-1})	V_0(kcal mol^{-1})
Allene	41.57	36.73
Butatriene	73.34	31.60
Pentatetraene	103.02	24.84
Hexapentaene	134.01	22.05

The calculated value for the enthalpy of formation is some 5 kcal mol^{-1} too negative. Using our new group parameter we calculate 81, 115 and 149 kcal mol^{-1} for the enthalpies of formation of butatriene, pentatetraene and hexapentaene respectively. Each of these values is increasingly more positive than the result of the MINDO/2 calculation. Thermochemical data for at least one of these compounds would be extremely desirable to affirm either calculation.

Spectral data have been reported for 1,2,4,5-butatetraene[16] and for 1,2,4-pentatriene[17]. For the latter compound the data are sufficiently complete to allow a calculation of the vapour-phase entropy as 74.01 cal mol^{-1} K^{-1}. Since this molecule has the third double bond isolated from the allenic moiety, we feel more confidence in our estimate of $\Delta H_f{}^0 = 64$ kcal mol^{-1} and $\Delta G_f{}^0 = 72$ kcal mol^{-1} for $H_2C{=}C{=}CHCH{=}CH_2(g)$. Enthalpies of formation are available for the isomeric *cis*- and *trans*-3-pentene-1-ynes as liquids[4]. With reasonable estimates for the enthalpy of vaporization (6 kcal mol^{-1}) and entropy (77 cal mol^{-1} K^{-1}), we conclude that the three C_5H_6 species have comparable stabilities.

We close our discussion of the thermochemistry of the allenic systems by emphasizing, once again, the similarities between the allenes and alkynes. A process capable of forming an alkyne, such as the dehydrohalogenation of 1,2-dibromopropane,

$$CH_3CHBrCH_2Br(G) = CH_3C{\equiv}CH(g) + 2HBr(g),$$

will form the corresponding allene as well:

$$CH_3CHBrCH_2Br(g) = H_2C{=}C{=}CH_2(g) + 2\ HBr(g).$$

The free energy changes and equilibrium constants for both of the above processes can be computed from data presented by Stull, Westrum and Sinke[2]. The indications are that the methylacetylene will be the predominant product and that the yield of allene might increase with decreasing temperature.

The labile nature of the $>C{=}C{=}C<$ structure can also be seen in attempts to consider the thermochemistry of polymerization. All possible reactions that would relieve the excess energy stored in the adjacent double bonds are likely to occur. There are no thermochemical data available, but we can hypothesize the dimerization of allene to 1,3-cyclohexadiene as a possible first step.

$$2\ H_2C{=}C{=}CH_2(g) = C_6H_2(g)$$

The entropy change for this dimerization is very unfavourable, probably in the range of −45 to −55 cal mol^{-1} K^{-1}. The enthalpy change, $\Delta H = -66$ kcal mol^{-1}, is, however, sufficiently exothermic to more than compensate for the unfavourable entropy.

The similarity to the alkynes and polymerization has been observed. Saussey, and coworkers[18] have studied the adsorption of 1- and 2-butyne and 1,2-butadiene

TABLE 5. Thermodynamic properties of allenes

Compound	ΔH_f^0 (kcal mol^{-1})	S^0 (cal mol^{-1} K^{-1})	ΔG_f^0 (kcal mol^{-1})
Allene(g)	45.6	58.30	48.0
1,2-Butadiene(g)	38.8	70.03	47.5
1,2-Pentadiene(l)	26.8	58.55	48.4
1,2-Pentadiene(g)	33.6	80.02	49.0
3-Methyl-1,2-butadiene(l)	24.2	55.40	46.9
3-Methyl-1,2-butadiene(g)	30.9	76.77	47.3
2,3-Pentadiene(l)	24.8	56.72	47.1
2,3-Pentadiene(g)	31.8	78.66	47.6
1,2,4-Pentatriene(g)	(64)[a]	74.01	72.0
Butatriene(g)	(77)[a]		
Pentatetraene(g)	(110)[a]		
Hexapentaene	(140)[a]		

[a] Estimated values.

on Al_2O_3. For all three materials they observed the identical absorbed species by i.r. spectroscopy. They also observed eventual polymerization. Brandsma and Verkruijsse[19] have reported on an allene to alkyne rearrangement in solution.

Our data for the allenes are summarized in Table 5.

III. KETENES

Older literature values[2,3] for the enthalpy of formation of ketene were based on the results of Rice and Greenberg[20] for the reaction

$$CH_2CO(g) + Na^+OH^-(aq.) = CH_3CO_2{}^-Na^+(aq.),$$

and for the reaction of ketene with a number of alcohols, leading to $\Delta H_f{}^0 = -14.78$ kcal mol^{-1}. The reaction with aqueous NaOH has been reinvestigated by Nuttall, Laufer and Kilday[21]. Their result, $\Delta H_f{}^0 = -11.4 \pm 0.4$ kcal mol^{-1}, was shown to be in accordance with observed photodissociation at 3690 Å.

Blake and Speis[22] have studied the kinetics and equilibrium in the system

$$CH_3COSH(g) + CH_2CO(g) = (CH_3CO)_2S(g),$$

and Blake, Davies and Speis[23] have reported similar results for the reaction

$$CH_3CO_2H(g) + CH_2CO(g) = (CH_3CO)_2O(g).$$

Auxiliary data for the sulphur-containing compounds are lacking, but the reaction involving acetic acid and acetic anhydride can be used to provide an independent value of $\Delta H_f{}^0$ for ketene. From their equilibrium constants, measured between 171 and 289°C, Blake, Davies and Speis report a reaction enthalpy of $\Delta H = -20.9$ kcal mol^{-1}. We take the mean reaction temperature to be 500 K and write

$$\Delta H_{298} = \Delta H_{500} - 0.6 \text{ (kcal mol}^{-1}\text{)}$$

using the heat-content data compiled by Stull, Westrum and Sinke[2] for the gaseous species. Pedley and Rylance[4] have tabulated enthalpies of formation for acetic acid ($\Delta H_f{}^0 = -103.3$ kcal mol^{-1}) and acetic anhydride ($\Delta H_f{}^0 = -135.9$ kcal mol^{-1}) which we use to calculate $\Delta H_f{}^0 = -10.8$ kcal mol^{-1} for ketene. This value is in excellent accord with the most recent experiments involving the reaction of ketene with aqueous NaOH and we adopt the Nuttall, Laufer and Kilday[21] value for the enthapy of formation of ketene.

Stull, Westrum and Sinke[2] recalculated the entropy of $CH_2CO(g)$ ($T_m = 122$ K, $T_b = 217$ K) from spectroscopic data[24,25] and report $S^0(298\ K) = 57.79$ cal mol^{-1} K^{-1}. Blake, Davies and Speis[23] also report $\Delta S^0 = -32.3$ cal mol^{-1} K^{-1} for the formation of acetic anhydride from ketene and acetic acid at ca 500 K. We use the heat capacities calculated by Stull, Westrum and Sinke[2] to compute

$$\Delta S_{298}{}^0 = \Delta S_{500}{}^0 - 1.58\ (\text{cal mol}^{-1}\ \text{K}^{-1}).$$

This result and the entropies[2] of acetic acid ($S^0 = 67.52$ cal mol^{-1} K^{-1}) and of acetic anhydride ($S^0 = 93.20$ cal mol^{-1} K^{-1}) lead to $S^0 = 57.8$ cal mol^{-1} K^{-1} for ketene. We adopt this value and calculate the free energy of formation for $CH_2CO(g)$:

$$2\ C(c) + H_2(g) + \tfrac{1}{2}\ O_2(g) = CH_2CO(g),\ \Delta G_f{}^0 = -11.2 \pm 0.4\ \text{kcal mol}^{-1}.$$

If we use this value to calculate the free energy of the reaction whereby ketene is formed in the 'cracking' of acetone,

$$(CH_3)_2CO(g) = CH_4(g) + CH_2CO(g),$$

we find that $\Delta G^0(298\ K) = +13.2$ kcal mol^{-1}, a value that makes the reaction improbable. At higher temperatures the reaction becomes more favourable, largely due to the positive ΔS, and the use of heat capacities for the gaseous species[2] leads to $\Delta G^0 = -9.7$ kcal mol^{-1} at ca 700°C.

There are no thermochemical data for the substituted ketenes, but we can estimate enthalpies of formation for some of the simpler species in the following manner, by considering reactions involving simple ketones where the carbon atom of interest has the same sp^2 hybridization as does the methylenic ketene carbon. Enthalpies for the redistribution of substituents on simple ketones and aldehydes are small. Examples using the data of Pedley and Rylance[4] include:

$$H_2C{=}O(g) + Me_2C{=}O(g) = 2MeHC{=}O(g),\ \Delta H^0 = 1.4\ \text{kcal mol}^{-1}$$

$$Me_2C{=}O(g) + Ph_2C{=}O(g) = 2MePhC{=}O,\ \Delta H^0 = 3.6\ \text{kcal mol}^{-1}$$

$$H_2C{=}O(g) + Ph_2C{=}O(g) = 2PhHC{=}O(g),\ \Delta H^0 = 5.8\ \text{kcal mol}^{-1}$$

As a first approximation we can take $\Delta H^0 = 0$ for redistribution reactions that involve ketene and one of the simple aldehydes or ketones. For example the reaction between ketene and benzophenone can be used to generate diphenylketene:

$$H_2C{=}C{=}O(g) + Ph_2C{=}O(g) = H_2C{=}O(g) + Ph_2C{=}C{=}O(g)$$

If we assume $\Delta H = 0$ for this reaction and use the known enthalpies of formation[4]

TABLE 6. Thermodynamic properties of ketenes

Compound	ΔH_f^0 (kcal mol^{-1})	S^0 (cal mol^{-1} K^{-1})	ΔG_f^0 (kcal mol^{-1})
Ketene(g)	−11.4	57.8	−11.2
Methylketene(g)	(−25)[a]	(68)[a]	(−18)
Dimethylketene(g)	(−37)[a]	(75)[a]	(−23)
Phenylketene(g)	(+6)[a]		
Diphenylketene(g)	(+29)[a]		

[a] Estimated values.

of benzophenone (ΔH_f^0 = +14.10 kcal mol^{-1}) and formaldehyde (ΔH_f^0 = −25.98 kcal mol^{-1}) we compute ΔH_f^0 = +29 kcal mol^{-1} for $Ph_2C{=}C{=}O(g)$. Other enthalpies of formation estimated in a similar fashion are listed in Table 6. There are no heat capacity data available from which to calculate third-law entropies for the substituted ketenes. Some spectral data are now becoming available[26,27] but they are still too incomplete to allow entropy calculations. If it is necessary to compute free energies of formation of substituted ketenes for equilibrium constant evaluations it is suggested that the required entropies are estimated as being some 5 cal mol^{-1} K^{-1} greater than those for the corresponding ketone or aldehyde.

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The Chemistry of Ketenes, Allenes and Related Compounds
Edited by Saul Patai

CHAPTER 5

Detection, determination and identification of allenes and ketenes

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I. INTRODUCTION

The analytical chemistry of allenes and ketenes has not been extensively reviewed. This chapter brings together information on methods for both classes of compounds. Since most of the reported work has focused on the parent molecules, allene (propadiene) and ketene, much of the discussion will centre on these compounds and some of the simple derivatives. Neither mass spectral or chiroptical properties of allenes and ketenes will be discussed in this chapter since full chapters have been devoted to each of these subjects. Methods employing techniques such as Raman spectroscopy and microwave spectroscopy have not been included in this discussion. This exclusion is based on the need for highly specialized equipment which is generally not available in most chemical laboratories.

Also, since the parent compounds, allene and ketene, are gaseous under ambient laboratory conditions, instrumental techniques are emphasized over wet chemical methods. This emphasis is also reflected in the recent literature relating to this subject.

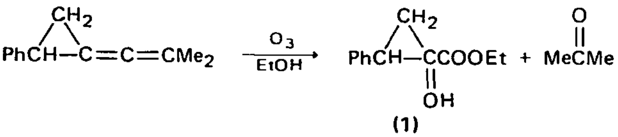
II. CHEMICAL METHODS

A. Allenes

Few chemical methods are available for allenes. Lebedew[1] observed that when allenes are heated and oxidized, they dimerize to form cyclobutanes. Upon oxidation of the cyclobutanes, succinic acids are formed which can be used as a means of identifying the parent allene. With this method, allene reacted at 500°C for a few seconds gives a yield satisfactory for identification[2]. 2-Methyl-2,3-butadiene (dimethylallene) requires reaction at 150°C for several days[1]. Allenes react with tetranitromethane to form yellow-orange products[3]. Allene, dimethylallene and *t*-butylallene (4,4-dimethyl-1,2-pentadiene) give yellow colours while phenylallene gives an orange colour.

1,2-Butadiene (methylallene) adds bromine across one double bond only. This reaction has been used to determine (by titration) the amount of 1,2-butadiene in a mixture with *n*-butane[4]. Upon catalytic hydrogenation, 1,2-butadiene quantitatively adds two moles of hydrogen per mole of hydrocarbon[4]. Allenes have been characterized by hydrogenation to the corresponding propane[5].

Allenes undergo oxidation to produce carbonyl compounds and carbon dioxide. Identification of the resultant carbonyl compounds can be used as proof of the structure of the parent allene[6]. While several agents can be used for this oxidation, e.g. potassium permanganate in acetone or pyridine and chromic acid in acetic acid, ozone is preferred since it does not oxidize any aldehyde products to the corresponding carboxylic acids. Allenes that contain a cyclopropyl ring structure are oxidized to a ketone and a hydroxy ester (1)[7]. Subsequent treatment of the

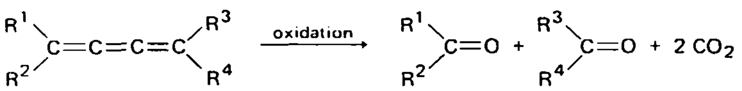


(1)

(1)

$$1 \xrightarrow[\text{2. HCl}]{\text{1. NaOMe}} PhCH_2CH_2COCOOH \qquad (2)$$

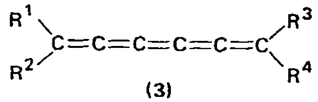
hydroxy ester with sodium methoxide and hydrochloric acid yields the corresponding α-keto carboxylic acid (equation 2). Butatrienes (2) undergo similar



(3)

(2)

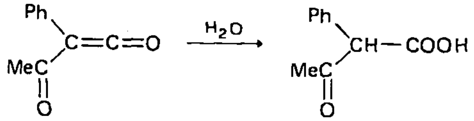
forced oxidation to yield the carbonyl compounds and two molecules of carbon dioxide (equation 3)[8]. Hexapentaenes (3) also undergo forced oxidation to produce the corresponding carbonyl compounds and four molecules of carbon dioxide[9].



(3)

B. Ketenes

Ketene has been determined by a number of chemical methods based on its relatively high reactivity. Ketenes react rapidly with water to form the corresponding carboxylic acid (equation 4)[10]. This property has been utilized to quantitate

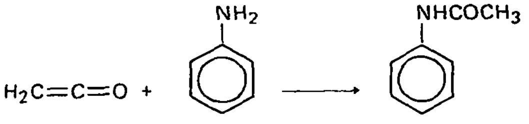


(4)

ketene in several methods. Rice and coworkers[11], trapped ketene in water and titrated the resultant acetic acid with standard base to determine the amount of ketene in the system. In a study of the thermal decomposition of cyclobutanone[12], ketene was trapped in water and determined by titration of the acetic acid formed. Ketene in gaseous mixtures has also been determined by passing the effluent from a chamber through a standard solution of sodium hydroxide (equation 5)[13]. The amount of ketene trapped was determined by titration of the residual sodium hydroxide.

$$H_2C{=}C{=}O + NaOH \longrightarrow CH_3COO^- Na^+ + H_2O \qquad (5)$$

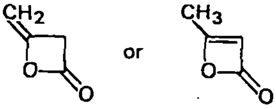
The formation of acetanilide from ketene (equation 6) has also been employed to determine the ketene present in a gaseous mixture[14]. The effluent from a



(6)

chamber used to expose rats to ketene gas was passed through an aqueous aniline solution saturated with acetanilide. As ketene reacts with aniline, the acetanilide formed precipitates from solution. The resultant acetanilide precipitate was collected, dried and weighed to determine the average chamber ketene concentration. (The aniline derivatives of ketenes can also be used for identification of the parent ketene[11].) Ozata and coworkers[15] utilized this reaction to identify ketene in mixtures of acetic acid and fuming sulphuric acid. In this experiment, acetic acid and fuming sulphuric acid were heated to 80°C. The vapour produced was passed into aniline by means of nitrogen as a carrier gas under reduced pressure. Acetanilide was then identified in the aniline solution by gas–liquid chromatography. After ruling out the possibility of an anhydride intermediate, the formation of acetanilide was taken as evidence for ketene formation. Attempts to identify the corresponding ketene from isobutyric acid and sulphuric acid were unsuccessful.

Ketene and diketene (4) have been analysed after reaction with resorcinol[16]. The vapour of ketene and diketene in air was absorbed in one millilitre of sulphuric acid



(4)

(80%) and 0.1 ml of 1% resorcinol was added. The concentration of the ketenes was determined by visual comparison of luminescence intensity (ultraviolet light excitation) of the resulting solution to standard solutions. The sensitivity of this method is 0.02 μg/ml total ketene and diketene. If the sample is first reacted with water to produce acetic acid from ketene, only the diketene content is measured.

Ketene reacts readily with hydroxylamine to form acethydroxamic acid (equation 7)[17]. This reaction has been employed by Diggle and Gage[18] for the

$$H_2C{=}C{=}O + NH_2OH \longrightarrow CH_3CONHOH \qquad (7)$$

determination of ketene in air. The ketene is trapped in alkaline hydroxylamine reagent in which the ketene reacts to form acethydroxamic acid. Upon complexation with ferric iron the hydroxamic acid gives an intense reddish-blue colour. Mendenhall[19] used the same methodology for the determination of ketene in air mixtures. The colour was measured at 540 nm in a 10 cm light path with a linear calibration curve up to 2 p.p.m. Ethyl acetate was used as the standard since it produces the same hydroxamic acid as ketene.

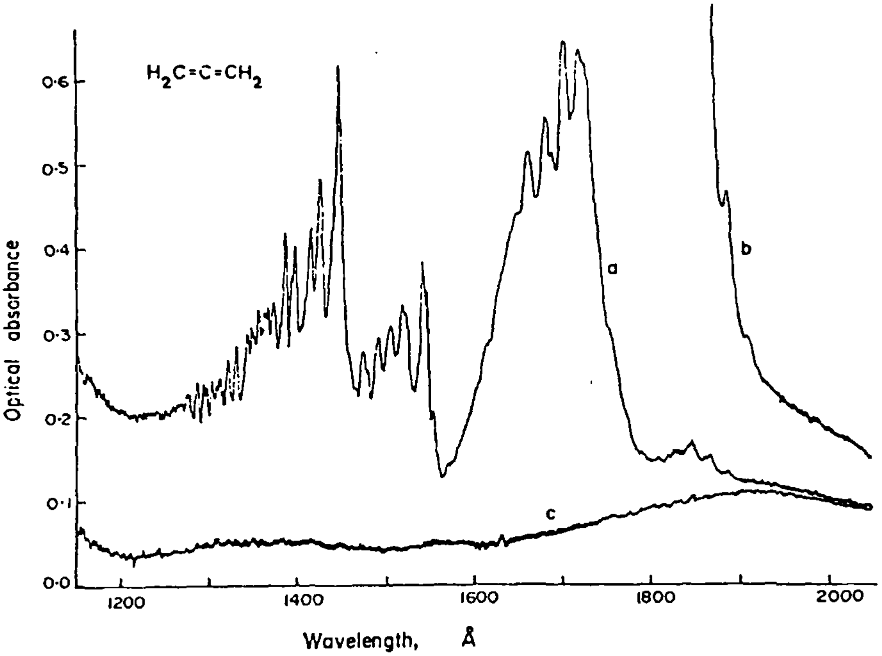


FIGURE 1. The vacuum ultraviolet absorption spectra of allene at room temperature. (a) Pressure = 95 microns; (b) pressure = 2100 microns; (c) blank. Taken from A. A. Iverson and B. R. Russell, *Spectrochim. Acta*, 28A, 447 (1972), and reproduced by permission of Pergamon Press.

III. PHYSICAL METHODS

A. Ultraviolet–visible Spectroscopy

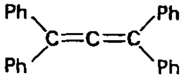
1. Allenes

Allene presents essentially no absorption of light above 200 nm. This is not unexpected since there is very little (if any) conjugation across the allene system. This lack of conjugation is a result of the orbitals of the π electrons of the two double bonds lying in planes perpendicular to each other. In fact, the allene bond acts as an insulator between conjugated systems.

The vacuum ultraviolet spectrum of allene is shown in Figure 1[20]. Prominent absorption bands appear in the region of 1650–1750 Å with considerable fine structure at 1390–1550 Å. None of these bands are accessible with conventional spectrophotometers. Hence, absorptiometric measurement in the ultraviolet region is not practical for simple allenes. Suttcliffe[21] had earlier determined an absorption maximum of 1710 Å in the vacuum ultraviolet for allene.

Vacuum ultraviolet spectra of 1,1-dimethylallene and tetramethylallene give absorption maxima as summarized in Table 1.

The lack of conjugation across the double bond of allene is illustrated by the spectrum of tetraphenylallene (5). This compound exhibits a wavelength of maximum absorbance at 267 nm ($\epsilon = 12,000$). 1,1-Diphenylethylene (6) has a maximum at 250 nm ($\epsilon = 11,000$) and *trans,trans*-diphenyl-1,3-butadiene (7) has a maximum at 328 nm ($\epsilon = 56,000$)[23]. The spectrum of 5 more closely resembles that of 6 than 7 in which the phenyl rings are conjugated. In 95% ethanol, 1,3-diphenylallene exhibits a strong absorption band at 255 nm ($\epsilon = 52,000$)[5] which is quite similar to the maximum of 6.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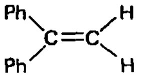
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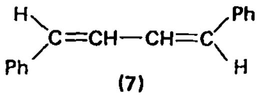

(7)

However, each double bond of the allene portion will conjugate with systems attached directly to it. For example, the vinyl allenol (8) shows a maximum at 229 nm ($\epsilon = 24,700$) in 95% ethanol[24]. The dehydro product (9) analogous to 8

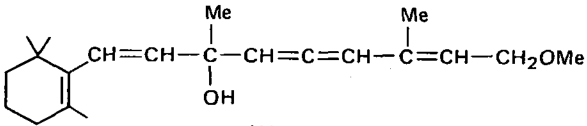
TABLE 1. Prominent absorption bands in vacuum ultraviolet for 1,1-dimethylallene and tetramethylallene[a]

1,1-Dimethylallene		Tetramethylallene	
λ_{max}(nm)	ϵ[b]	λ_{max}(nm)	ϵ
198.3	1,350	216.0	1,350
172.7	25,500	195.5	12,450
170.2	24,400	190.6	9,400
158.4	19,700	169.1	29,000
155.8	18,900	*c*	
145.7	11,500		

[a] Data from Reference 22.

[b] Molar absorptivity (litres/mole^{-1} cm^{-1}).

[c] Seven bands between 152 and 161 nm with ϵ from 12,500 to 28,300.



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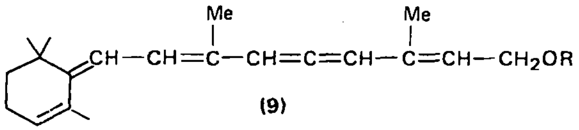


(9)

shows the peak at 229 nm ($\epsilon = 19{,}200$) and an additional peak at 317.5 nm ($\epsilon = 49{,}400$). The additional peak appearing at 317.5 nm is a result of the four double bond conjugated system involving the six-membered ring.

$$HC\equiv C-C\equiv C-CH=C=CH-CH=CHCH=CHCH_2CO_2H$$

(10)

The antibiotic mycomycin (10) has been shown to be (−)-3,5,7,8-*n*-trideca-tetraene-10,12-diynoic acid[25]. In this molecule, the lack of conjugation across the double bond can be demonstrated by comparison of its ultraviolet absorption patterns with some model compounds as shown in Table 2. The Δ^7-allenic double bond in conjugation with the 3,5-diene and the Δ^8-allenic double bond in conjugation with the 10,12-diyne should constitute two isolated chromophores each containing three conjugated double bonds, i.e. a triene and an enediyne. In Table 2, the longest wavelength maxima of mycomycin and known triene and enediyne compounds are shown to be in good agreement.

The substitution of Br,I or cyano groups in simple allenes causes a shift of absorption maxima to slightly higher wavelengths, e.g. $H_2C=C=CH-CN$, $\lambda_{max} = 211$ nm[26].

Butatrienes and hexapentaenes display considerably more ultraviolet and visible absorption spectra than simple allenes. In these compounds, alternate double bonds can act as conjugated systems giving rise to absorption maxima at higher wavelengths.

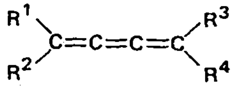
Butatriene generally exhibit two absorption maxima, one in the region of 245–350 nm and another in the region of 400–500 nm. Some representative examples

TABLE 2. Correlation of light absorption characteristics of mycomycin and model compounds[a]

Compound	Longest wavelength maxima (nm)		
Mycomycin (10)	256[b]	267	281
$PrC\equiv C-C\equiv C-CH=CHCH_2OH$	252	266.5	282.5
$MeCH=CH-C\equiv C-C\equiv CH$	251	264	280
$Me(CH_2)_2(CH=CH)_3(CH_2)_7COOH$	257	267	278
$H_2C=CH-CH=CH-CH=CH_2$	248	258	268

[a] Data from Reference 25.
[b] Shoulder.

TABLE 3. Spectral characteristics of some butatrienes



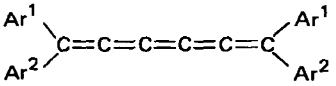
R^1	R^2	R^3	R^4	λ_{max}(nm)		Reference
PhCH=CH	H	PhCH=CH	H	400	430	*a*
Ph	Me_3C	Ph	Me_3C	245	323	*b*
Ph	*m*-BrC_6H_4	Ph	*m*-BrC_6H_4	275	427	*c*
Ph	*p*-ClC_6H_4	Ph	*p*-ClC_6H_4	282	430	*c*
Ph	*p*-$NO_2C_6H_4$	Ph	*p*-$NO_2C_6H_4$	273	466	*c*
Ph	Ph	Ph	*p*-BrC_6H_4	–	424	*d*
Ph	Ph	Ph	*p*-$NO_2C_6H_4$	274	453	*c*
Ph	Ph	Ph	Ph	318	420	*c*

[a] R. Kuhn and H. Krauch, *Chem. Ber.*, 88, 309 (1955).
[b] F. Bohlmann and K. Kieslich, *Chem. Ber.*, 88, 1211 (1955).
[c] J. Godineau, P. Cadiot and A. Willemart, *Compt. Rend.*, 246, 2499 (1958).
[d] W. Chodkiewicz, P. Cadiot and A. Willemart, *Compt. Rend.*, 240, 1554 (1955).

of butatriene spectra are given in Table 3. A more comprehensive listing of absorption maxima for butatrienes is presented in Reference 27.

Hexapentaenes often exhibit three absorption maxima between 370 and 550 nm. Some representative absorption maxima are shown in Tables 4 and 5. The maximum appearing at the highest wavelength was characteristically the most intense[9].

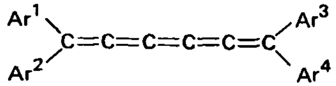
TABLE 4. Absorption maxima of some symmetrical hexapentaenes[a]



Ar^1	Ar^2	λ_{max}(nm)		
Ph	Ph	370	440	448
p-BrC_6H_4	Ph	365	435	495
p-BrC_6H_4	*p*-BrC_6H_4	370	425–430	507
p-$CH_3OC_6H_4$	*p*-$CH_3OC_6H_4$	380	422	517
β-$C_{10}H_7$[b]	Ph	370	435	510
β-$C_{10}H_7$	*p*-$CH_3OC_6H_4$	377	430	525
α-C_4H_3S[c]	Ph	385	435	525
α-C_4H_3O[d]	Ph	380	425–430	525
p-$NO_2C_6H_4$	*p*-$CH_3OC_6H_4$	363	435	555

[a] Data from Reference 9.
[b] β-Naphthyl-.
[c] α-Thienyl-.
[d] α-Furyl-.

TABLE 5. Absorption maxima of some non-symmetrical hexapentaenes[a]



Ar^1	Ar^2	Ar^3	Ar^4	λ_{max}(nm)		
Ph	Ph	β-$C_{10}H_7$	Ph	370	435	500
Ph	Ph	p-$CH_3OC_6H_4$	p-$CH_3OC_6H_4$	375	425	503
p-$NO_2C_6H_4$	Ph	β-$C_{10}H_7$[b]	p-$CH_3OC_6H_4$	–	425	529
Ph	Ph	p-$NO_2C_6H_4$	Ph	355	445	512
β-$C_{10}H_7$	p-$CH_3OC_6H_4$	p-$CH_3OC_6H_4$	p-$CH_3OC_6H_4$	373	424	522
Ph	Ph	Biphenylene		368	445	515

[a] Data from Reference 9.
[b] β-Naphthyl-.

2. *Ketenes*

Simple ketenes absorb light in the ultraviolet regions and some absorb in the low visible wavelengths. This is evident by the colour of some of these compounds, e.g. diphenylketene is orange[28].

In the vapour phase, ketene has absorption maxima at 224 and 324 nm[29]. The maxima for 1,1-di(trifluoromethyl)ketene are shifted to slightly lower wavelengths, 194 and 315 nm. These bands are tentatively assigned to n—π* transitions.

1,1-Diphenylketene gives absorption maxima at 350 and 405 nm. This bathochromic (or red) shift suggests that the phenyl rings in this system are in conjugation[29].

Little use of these absorption properties has been made in the development of quantitative methods. One study[30] used measurement of absorption at 320 nm to determine ketene in the gaseous mixture produced by acetone pyrolysis. In this method, Beer's Law is obeyed from 5—40% (v/v) of ketene in the mixture.

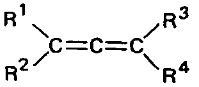
B. Infrared Spectroscopy

1. *Allenes*

The asymmetric stretching absorption band for the allene portion (C=C=C) is very useful for identifying and detecting the allene functional group. This absorption band appears around 1950 cm^{-1} in most allenes. Wotiz and Celmer[31] studied this absorption in a variety of substituted allenes. The results of this study are shown in Table 6. From these data, it is obvious that allenes which contain a carboxy, an amido or an ester group attached directly to the allenic bond give a doublet when the allene is in the terminal position and a singlet when the allenic group is within the chain.

In a more elaborate study, Wotiz[32] examined the infrared spectra of 58 allenic compounds. The findings are consistent with the previous study and present an extension of the previous generalizations. It was found that the asymmetric stretching frequency at 1950 cm^{-1} appears as a doublet when the allene group is terminal and is substituted by electron-withdrawing groups, e.g. carboxy, ester, amido, acyl chloride, carbonyl, trifluoromethyl and cyano functional groups. The intensity of

TABLE 6. Asymmetric stretching frequencies for some substituted allenes[a]



R^1	R^2	R^3	R^4	1930 cm^{-1}	1940 cm^{-1}	1950 cm^{-1}
Bu	H	H	H	–[b]	++	–
H	CO_2H	H	H	+	–	+
Pr	CO_2H	H	H	+	–	+
Bu	CO_2H	H	H	+	–	+
Pe	CO_2H	H	H	+	–	+
Bu	CO_2H	H	Me	–	++	–
Bu	CO_2H	Me	Me	–	++	–
Bu	CO_2Me	H	H	+	–	+
Pr	$CONH_2$	H	H	+	–	+
Bu	$CONH_2$	H	H	+	–	+
Bu	CH_2OH	H	H	–	++	–

[a] Data from Reference 31.
[b] – Peak missing, + strong peak present, ++ very strong peak present.

the absorption band increases with increasing substitution of electronically similar groups. The band appearing at 850 cm^{-1} is characteristic of the terminal methylene group ($H_2C=$) of the allene and its absence is good evidence for the absence of a terminal allene group[32]. (This band has a weak overtone at 1700 cm^{-1} of low intensity.)

Symmetrically substituted allenes, e.g. tetramethylallene, do not exhibit the characteristic absorptions at 1900–2000 cm^{-1}. Tetrafluorallene has a strong absorption band at 2065 cm^{-1} (4.87 microns)[33].

A comparison of the characteristic absorption bands of allene, and the di- and tetra-deuterated derivatives is presented in Table 7[34]. The substitution of deuterium for hydrogen results in a slight shift to lower wavelengths of the asymmetric stretch of the allenic backbone.

Substitution of fluorine atoms for hydrogen in allene shifts the asymmetric stretch to longer wavelengths in the following manner: monofluoroallene[35], 1970 cm^{-1}; 1,3-difluoroallene[35], 1980 cm^{-1}; trifluoroallene[35], 2040 cm^{-1}; tetrafluoroallene[33], 2065 cm^{-1}. 1,1-Difluoroallene[36] shows this absorption peak at 2020 cm^{-1}.

Cyclic allenes display absorption peaks at 1950 cm^{-1} and in the region of 850 cm^{-1} as shown in Table 8[37]. These compounds, although cyclic, show the absorption band characteristic of a terminal allene group[32].

TABLE 7. Infrared absorption bands of allene and its deuterated derivatives[a]

Vibrational mode	$H_2C=C=CH_2$	$HC=C=CD_2$	$D_2C=C=CD_2$
C—H stretching	3005 cm^{-1}	2226	2230
C=C=C stretching	1957	1941	1921
CH_2 bending	1398	1416	1034

[a] Data from Reference 34.

TABLE 8. Infrared absorption bands of cyclic allenes[a]

Compound	Asymmetric stretch	Methylene stretch
1,2-Cyclononadiene	1950 cm^{-1}	850 cm^{-1}
1,2-Cyclodecadiene	1950	869
1,2-Cyclotridecadiene	1950	870

[a] Data from Reference 37.

A number of allenes and their corresponding asymmetric stretching bands are summarized in Table 9.

A complete infrared spectrum of allene from 2–15 microns (5000–666 cm^{-1}) is available in the literature[40].

Seyfried and Hastings utilized the absorption band of 1,2-butadiene at 1960 cm^{-1} to measure this compound in the presence of 1,3-butadiene[41]. Wotiz[39] performed a semiquantitative estimate of 1,2-heptadiene at 1950 cm^{-1} in the presence of 1-heptyne and 2-heptyne.

2. *Ketenes*

The infrared spectrum of ketene shows several characteristic absorption bands. Drayton and Thompson[42] observed very strong bands near 1120 cm^{-1} (1109, 1122 and 1135 cm^{-1}) and near 2150 cm^{-1} (2140, 2150 and 2160 cm^{-1}). These bands were assigned to symmetric stretching modes of the ketene backbone (C=C=O). Strong bands at 1375 cm^{-1} and 1400 cm^{-1} were assigned to the methylene group deformation mode. Additional bands at 3045 cm^{-1} and 3070 cm^{-1} were assigned to the symmetric C–H stretch. Barnes and collaborators[43] assigned the band appearing at 2150 cm^{-1} to the symmetric stretching of ketene but did not elaborate on the exact atoms involved in this mode.

TABLE 9. Asymmetric stretching absorption bands for some allenes

Compound	Absorption band (cm^{-1})	Reference
$H_2C{=}C{=}Et_2$	1959	38
$MeCH{=}C{=}CMe_2$	1970	38
$MeCH{=}C{=}C(Me)Bu$-*t*	1961	38
t-$BuCH{=}C{=}CMe_2$	1968	38
$PhCH{=}C{=}CMe_2$	1960	38
$BuCH{=}C{=}CH_2$	1950	39
$PhCH{=}C{=}CHPh$	1947	5
$H_2C{=}C{=}CHSiBu_3$	1937	26
$H_2C{=}C{=}CHGe(Alk)_3$	1935	26
$BrCH{=}C{=}CHCH_2OR^a$	1962	26
$BrCH{=}C{=}CHCH_2COOMe$	1960	26
$BrCH{=}C{=}CHCH_2GeBr_2Cl$	1957	26

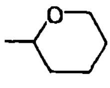
[a] R = H, Me, 

TABLE 10. Infrared absorption bands of ketene, ketene-d$_1$ and ketene-d$_2$[a]

Band	Mode	CH_2CO	CHDCO	CD_2CO
1	C—H Stretch	3069 cm^{-1}	2268 cm^{-1}	3115 cm^{-1}
2	C=O Stretch	2151	2121	2150
3	CH_2 Deformation	1388	1228	1293
4	C=C Stretch	1120	890	1022
5	C—H Stretch	3166	2375	2297
6	CH_2 Rocking	978	798	815
7	–	588	530	–
8	–	788	712	–
9	–	528	450	515

[a] Data from Reference 44.

Arendale and Fletcher[44] examined the infrared spectra of ketene, ketene-d$_1$ and ketene-d$_2$. Principal components of the spectra along with band assignments are given in Table 10.

The symmetric stretching (C=O) band of diphenylketene[29] has been reported at 2105 cm^{-1}. The same workers report a value of 2195 cm^{-1} for di(trifluoromethyl)-ketene.

The principal infrared absorption bands for some silyl derivatives of ketene are summarized in Table 11[45].

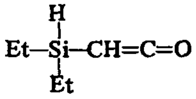
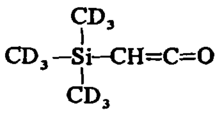
A compound that resembles both a ketene and an allene, carbon suboxide (11)[46] has a very strong absorption band at 2285 cm^{-1} and additional strong bands at 3750, 3087, 1575 and 549 cm^{-1}.

O=C=C=C=O

(11)

Coomber and coworkers[47] detected ethylketene at 2132 cm^{-1} in a study of the vapour-phase photolysis of *trans*-crotonaldehyde.

TABLE 11. Principal infrared absorption bands for silyl derivatives of ketene[a]

Compound	C=O stretch	C=C stretch	CH stretch
 $Et-\overset{H}{\underset{Et}{Si}}-CH=C=O$	1275 cm^{-1}	2115 cm^{-1}	3039 cm^{-1}
 $CD_3-\overset{CD_3}{\underset{CD_3}{Si}}-CH=C=O$	1281	2122	3048
$Cl_3Si-CH=C=O$	1296	2165	3067
$(Me_3Si)_2C=C=O$	1295	2085	–
$(Me_3Si)HC=C=O$	1270	2112	3038

[a] Data from Reference 45.

TABLE 12. Chemical-shift data for halogen-substituted allenes $H_2C{=}C{=}CHX$[a]

Substituent	$=CH_2(\delta)$[b]	$=CHX(\delta)$	$J_{HH'}$
I	0.57	−0.59	6.3 ± 0.1
Br	0.21	−0.81	6.1 ± 0.1
Cl	−0.01	−0.72	6.1 ± 0.1

[a] Data from Reference 51.
[b] Parts per million; water, reference standard.

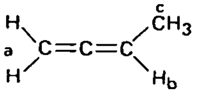
C. Nuclear Magnetic Resonance Spectroscopy

1. *Proton nuclear magnetic resonance spectroscopy (^{1}H-n.m.r.)*

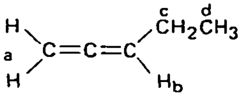
a. Allenes. Proton magnetic resonance spectroscopy is useful for establishing the presence of an allene as well as providing information on the structure of substituents on the allene molecule. Simple allene gives a signal at 4.55 p.p.m. (δ) relative to TMS (tetramethylsilane)[38]. The coupling constant (through 4 bonds) for allene is 7.0 c/s (cycles/second). This represents an example of fairly long-range coupling between protons. The signal for the allenic protons has been reported as 4.55 p.p.m. by another group[48]. The allenic protons for 1,1-dimethylallene appear at 4.44 p.p.m. (δ)[49] and at 4.42 p.p.m. for 1,1-dimethylallene-d$_1$[49]. Using water as the reference standard, another group[50] reported a value of 0.49 p.p.m. (δ) for the allenic protons. These authors also reported a coupling constant of 7.0 ± 0.1 c/s.

The substitution of a halogen atom into allene causes an upfield shift of both the allenic proton on the terminal carbon bearing the substituent and also on the other

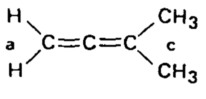
TABLE 13. Chemical-shift data for proton magnetic resonance spectra of simple allenes[a]



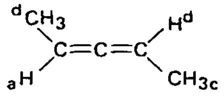
(I)



(II)



(III)

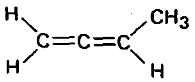
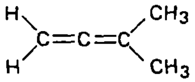
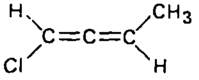
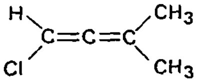


(IV)

Compound	Chemical shift, δ (p.p.m.)[b] a	b	c	d	J_{HH}(cycles) (4-bond)	J_{H,CH_3} (5-bond)
I (1,2-Butadiene)	4.49	4.94	1.58	–	6.67	3.47
II (1,2-Pentadiene)	4.54	5.03	1.95	0.99	–	–
III (3-Methyl-1,2-butadiene)	4.40	–	1.62	–	–	3.15
IV (2,3-Pentadiene)	4.89	–	1.56	–	6.35	3.20

[a] Data from Reference 52.
[b] TMS, reference standard.

TABLE 14. Five-bond coupling constants (J_{H,CH_3}) for 1,2-butadienes

Compound	J_{H,CH_3} (c/s)	Reference
	3.47	52
	3.03	53
	2.40	52
	2.14	52

terminal carbon as shown in Table 12. The coupling constants ($J_{HH'}$) are also slightly decreased by halogen substitution[51].

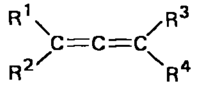
The chemical-shift values of the allenic protons are toward slightly higher field than normally observed for ethylenic protons. This suggests that the π orbitals about the sp-hybridized central atom give a long-range anisotropic contribution to proton shielding[51].

Other useful information as to the nature of substituents on the allene molecule can be obtained from ^{1}H-n.m.r. spectra. The spectral data for some simple derivatives of allene are given in Table 13[52]. The allenic protons of all four compounds appear between 4.40 and 5.03 p.p.m. (δ). However, the protons attached to the terminal carbon that is substituted with a methyl or ethyl group appear at slightly downfield positions. Methyl and methylene protons appear at upfield positions as expected. The four-bond coupling constants (J_{HH}) for 1,2-butadiene and 2,3-pentadiene (6.67 and 6.35 c/s, respectively) are quite similar to that for allene. The coupling constants for five-bond coupling (J_{H,CH_3}) range from 3.15 to 3.47 c/s. The substitution of one proton in the allene molecule by a chloride, bromide, iodide, methyl or ethyl group causes a decrease in the four-bond coupling constant (J_{HH}) by 0.9, 0.7, 0.7, 0.33 and 0.23 c/s, respectively. Furthermore, the effect of substitution on coupling constants is additive. This is illustrated very well with 1-chloro-1,2-butadiene which has a four-bond coupling constant (J_{HH}) of 5.80 c/s which is 1.20 c/s lower than that of allene as would be predicted. Further evidence for this effect is given in Table 14 which lists some five-bond coupling constants (J_{H,CH_3}).

Additional chemical-shift data[38] are presented in Table 15. Note that the substitution of a phenyl ring for an allenic proton results in a significant downfield shift for the remaining allenic proton.

The allenic protons for cyclic allenes appear slightly downfield from the signals produced by acyclic allenes[37]. The signals for the allenic protons of 1,2 cyclononadiene, 1,2-cyclodecadiene and 1,2-cyclotridecadiene appear at 5.17, 4.90 and 4.93

TABLE 15. Chemical-shift data for substituted allenes[a]



Compound	Chemical shift, δ (p.p.m.)[b]			
	$H_{(1)}$[c]	$H_{(2)}$	$H_{(3)}$	$H_{(4)}$
$H_2C{=}C{=}CH_2$	4.55	–	–	–
$H_2C{=}C{=}CHMe$	4.55	–	1.61	4.93
$H_2C{=}C{=}CMe_2$	4.43	–	1.65	–
$H_2C{=}C{=}CMeEt$	4.55	–	–	–
$H_2C{=}C{=}CEt_2$	4.66	–	1.92	1.03
$MeCH{=}C{=}CMe_2$	4.80	1.57	1.63	–
$MeCH{=}C{=}CMeBu$-*t*	4.92	1.57	1.67	1.05
t-$BuCH{=}C{=}CMe_2$	4.86	0.99	1.65	–
$PhCH{=}C{=}CMe_2$	5.93	7.17	1.78	–

[a] Data from Reference 38.

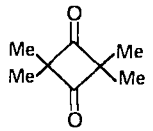
[b] TMS reference standard in CCl_4.

[c] The terminal allenic proton in all cases.

p.p.m. (δ), respectively. The allylic proton signals appear at 2.10, 1.91 and 1.95 p.p.m. (δ) respectively.

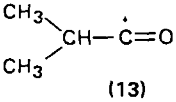
b. Ketenes. Relatively little information is available for the proton magnetic resonance spectra of ketenes. Since there are only two protons on the simplest ketene (CH_2CO), substitution on the ketene often removes these and hence any characteristic spectra of the ketenic protons. Consequently, the ^{1}H-n.m.r. spectrum of a disubstituted ketene would arise only from the substituents. A chemical-shift value of 2.47 p.p.m. (δ) has been reported for neat ketene[48]. This value shifts to 2.20 p.p.m. in a 9% solution of tetramethylsilane (TMS). The monodeuterated derivative of ketene has a chemical shift of 2.17 p.p.m. (δ) in 9% TMS. Chemical-shift values for 1-diethylsilylketene, 1-trideuteromethylsilylketene and 1-trichlorosilylketene have been reported as 8.35, 8.30 and 7.16 p.p.m. (τ) respectively[45] with hexamethyldisilazane (HMDS) as the reference standard ($\tau = 10.0$ p.p.m.).

In a study of ketene formation from carboxylic acids in fuming sulphuric acid, Ozata and coworkers[15] observed the following signals in a product mixture formed from the reaction of isobutyric acid: 1.92 p.p.m. (doublet, $J = 7.1$ c/s, 6H); 4.20 p.p.m. (septet, $J = 7.1$ c/s, 1H); 1.67 p.p.m. (singlet, ~1H); 1.80 p.p.m. (singlet, ~1H); 3.90 p.p.m. (singlet, ~1H). The observed weak singlets at 1.67 and 1.80 p.p.m. (δ) suggest the presence of the dimer of dimethyl ketene, 2,2,4,4-tetramethyl-1,3-cyclobutanedione (12). The suggested presence of this compound was further confirmed by the ^{1}H-n.m.r. signals of an authentic sample of the dimer:



(12)

1.68 and 1.83 p.p.m. (δ). An authentic sample of dimethylketene in fuming sulphuric acid gave a sharp singlet at 3.90 p.p.m. (δ). The presence of this same signal in the reaction mixture suggests that dimethyl ketene is formed in this reaction. The authors postulated that the doublet at 1.92 p.p.m. and the septet at 4.2 p.p.m. could be accounted for by structure (13). In this case, the α-proton would produce the septet and the β-protons would produce the doublet.

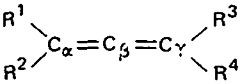


(13)

2. *Carbon-13 nuclear magnetic resonance spectroscopy*

a. Allenes. Carbon-13 nuclear magnetic resonance spectroscopy (^{13}C-n.m.r.) produces some very useful information with regard to the structure of allenes. Allenes, as a class, are unique because of the extremely low-field chemical shift of the central atom. This is shown in Table 16 for a variety of allenes[54]. The substituents (alkyl) cause a movement in the upfield direction for the chemical shift of the central atom. A methyl group causes an upfield shift of 3.3 p.p.m., an ethyl group 4.8 p.p.m. and an *S*-alkyl group 7 p.p.m. The C_α and C_γ (also referred to as

TABLE 16. ^{13}C-n.m.r. chemical-shift values for allene and substituted allenes[a]



Substituents				Chemical shifts		
R^1	R^2	R^3	R^4	C_α[b]	C_β	C_γ
H	H	H	H	74.8	213.5	74.8
Me	H	H	H	84.4	210.4	74.1
H	H	Me	Me	72.1	207.3	93.4
Me	Me	Me	Me	92.6	200.2	92.6
Et	H	H	H	91.7	208.9	75.3
SMe	H	H	H	90.0	206.1	81.3
OMe	H	H	H	123.1	202.0	90.3
OEt	H	H	H	121.7	202.3	89.4
Ph	H	H	H	94.5	210.3	78.7
Br	H	H	H	72.7	207.6	83.8
COOH	H	H	H	88.1	217.7	80.0
CN	H	H	H	80.5	218.7	67.2
CH_2SMe	H	H	H	88.6	210.5	76.1
H	H	Me	SMe	80.1	203.6	99.9
H	H	*i*-Pr	SEt	80.8	201.9	110.0
Ph	Ph	Ph	Ph	113.6	209.5	113.6

[a] Data from Reference 54.

[b] Shift values in Reference 54 are reported using carbon disulphide as the reference standard. The values reported in this table have been calculated on the basis of TMS as the reference standard. A value of 193.7 p.p.m. was used for the calculations[55].

TABLE 17. ^{13}C-n.m.r. chemical-shift values for cyclic allenes[a]

	Chemical shifts[b]		
Compound	C_α	C_β	C_γ
Cyclonona-1,2-diene	92.7	206.5	92.7
Cyclonona-1,2,6-triene	90.5	206.7	90.5
Cyclodeca-1,2.6,7-tetraene	90.2	208.3	90.2
Cyclotrideca-1,2-diene	91.8	205.2	91.8
Cyclohexadeca-1,2,9,10-tetraene	90.6	205.7	90.6

[a] Data from Reference 57.

[b] Chemical shifts in p.p.m. relative to TMS. See footnote *b* of Table 16 for method of calculation.

$C_{(1)}$ and $C_{(3)}$ carbons appear about 30 p.p.m. upfield relative to the corresponding chemical shifts for ethylene carbons.

Similiar results were noted by Crandall and Sojka[56]. In nonfunctionalized allenes, the sp carbons (C_β) appear at a lower field than CS_2 (– 20 to – 5 p.p.m.) whereas the sp^2 carbons (C_α and C_γ) appear at slightly higher fields (90–120 p.p.m. relative to CS_2) than normal olefinic or aromatic carbons. A modest upfield displacement of the chemical shift of the central atom occurs upon alkyl substitution. An additive value of 3 p.p.m. per methyl group was observed.

Similar results were observed with cyclic allenes[57] as shown in Table 17. The chemical-shift values for the $C_{(1)}$ and $C_{(3)}$ carbons are the same since these are symmetrical molecules.

Cumulenes exhibit similar patterns[58] but the chemical shift of the $C_{(2)}$ atom (central carbon in allene) gives a signal at higher field than allene as shown in Table 18.

The effect of fluorine substitution on the ^{13}C-n.m.r. spectrum of allene is shown in Table 19[35]. The chemical shifts of the terminal carbons are shifted downfield by fluorine substitution while the shift of the central carbon resonance is in an upfield direction. The magnitudes of these shifts are greater than those observed with alkyl substitution of methyl allenes[54]. Furthermore, no apparent additivity effect is present with fluorine substitution.

TABLE 18. ^{13}C-n.m.r. chemical-shift values for allene and cumulenes[a]

	Chemical shifts[b]		
Compound	$C_{(1)}$	$C_{(2)}$	$C_{(3)}$
$H_2C=C=CH_2$	73.6	212.5	–
$Ph_2C=C=CPh_2$	112.5	208.3	–
$H_2C=C=C=CH_2$	118.0	171.1	–
$Ph_2C=C=C=CPh_2$	122.7	152.0	–
$Ph_2C=C=C=C=CPh_2$	117.8	181.6	119.3
$Ph_2C=C=C=C=C=CPh_2$	125.7	149.4	127.3

[a] Data from Reference 58.

[b] Chemical shifts in p.p.m. relative to TMS.

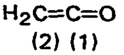
TABLE 19. ^{13}C-n.m.r. chemical-shift values for allene and fluoroallenes[a]

Compound	Chemical shifts[b]		
	C_α	C_β	C_γ
$H_2C{=}C{=}CH_2$	74.8	213.5	74.8
$HFC{=}C{=}CH_2$	129.8	200.2	93.9
$HFC{=}C{=}CFH$	132.2	176.5	132.2
$F_2C{=}C{=}CH_2$	156.2	181.4	104.8
$F_2C{=}C{=}CFH$	145.8	149.8	133.8
$F_2C{=}C{=}CF_2$	140.6	118.1	140.8

[a] Data from Reference 35.
[b] Chemical shifts in p.p.m. relative to TMS.

Coupling constants (J_{CC}) for allene have been reported[59] as 98.7 ± 0.3 c/s for J_{12} and 20.2 ± 0.2 c/s for J_{13}. The coupling constant for ^{13}C and proton in allene (J_{CH}) has been reported as 127 c/s[49].

b. Ketenes. The ^{13}C-n.m.r. spectra of ketenes present some very interesting data.

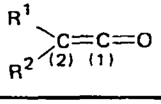


$$\underset{(2)}{H_2C}{=}\underset{(1)}{C}{=}O$$

(14)

Carbon 1 of ketene (14) produces a signal at a very low field, 194 p.p.m. relative to TMS[60]. This is considerably lower than the signals for the terminal carbons of ethylene (122.8 p.p.m.) and allene (74 p.p.m.) and indicates that this carbon is extensively deshielded. On the other hand, the terminal carbon of ketene, $C_{(2)}$, gives a signal at 2.5 p.p.m. (relative to TMS). This is an extremely high-field position and represents one of the most shielded carbon atoms observed with ^{13}C-n.m.r. In a subsequent study, Firl and Runge[61] examined the ^{13}C-n.m.r. spectra of addi-

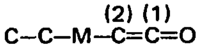
TABLE 20. ^{13}C-n.m.r. chemical-shift values for simple ketenes[a]



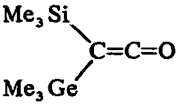
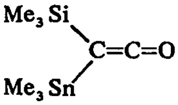
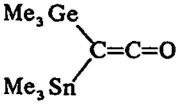
R¹	R²	Chemical shifts[b]	
		$C_{(1)}$	$C_{(2)}$
H	H	194.0	2.5
H	Me	200.0	10.9
H	Et	200.0	18.6
Me	Et	206.0	26.9
Me	Ph	205.6	33.8
Et	Ph	205.6	42.1
Ph	Ph	201.3	47.0

[a] Data from Reference 61.
[b] Chemical shifts (δ) in p.p.m. relative to TMS.

TABLE 21. ^{13}C-n.m.r. chemical-shift values for germanium, tin and silyl derivatives of ketene[a]



$\overset{}{C}-\overset{(2)}{C}-M-\overset{(1)}{C}=C=O$

Compound	Chemical shifts[b] $C_{(1)}$	$C_{(2)}$
$Me_3SiCH=C=O$	179.2	−0.1
$Et_3SiCH=C=O$	179.2	−4.9
$(Me_3Si)_2C=C=O$	166.8	1.7
$Et_3GeCH=C=O$	179.4	−4.8
$(Me_3Ge)_2C=C=O$	167.0	0
$(Et_3Ge)_2C=C=O$	165.7	−8.5
$(Me_3Sn)_2C=C=O$	161.7	−13.9
$(Et_3Sn)_2C=C=O$	161.3	−20.5
	166.2	0.5
	164.4	−5.8
	164.6	−6.3
$Ph_2C=C=O$	201.2	47.6

[a] Data from Reference 62.

[b] Chemical shifts (δ) in p.p.m. relative to TMS.

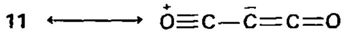
tional ketenes. The findings are similar in that the $C_{(1)}$ carbon appears at low field while the $C_{(2)}$ carbon appears at a much higher field. Their data are summarized in Table 20.

From this limited set of data, it appears that substituent effects on chemical-shift values are additive with methyl contributing 8.4 p.p.m., ethyl 16.1 p.p.m. and phenyl 23.0 p.p.m. Using these values, the calculated chemical shifts for the $C_{(2)}$ carbons (using ketene as the reference compound) are: methylketene, 10.9; ethylphenylketene, 41.6; diphenylketene, 48.5 p.p.m. Comparison of these values with the experimentally observed values in Table 20 suggests that these approximations are reasonable. The chemical-shift values for the $C_{(1)}$ carbon of the ketenes are relatively unaffected by substitution on the $C_{(2)}$ carbon and parallel the values for the central carbon of the corresponding allene. In both cases, the chemical shifts appear some 100 p.p.m. downfield from the corresponding alkenes.

The chemical-shift values[62] for germanium, tin and silicon derivatives of ketenes appear at even higher fields for the $C_{(2)}$ carbon and also at higher fields for the $C_{(1)}$

carbon as illustrated in Table 21. Downfield displacement of the chemical shifts for sp and sp^2 carbons increases with the substitution of Sn, Ge and Si groups in the order given.

Carbon suboxide (C_3O_2) (**11**) gives a signal for the $C_{(2)}$ (central atom) carbon at −14.6 p.p.m. relative to TMS. This is a very high-field position and indicates that the central atom is highly shielded[63]. The shift for the $C_{(1)}$ carbon also appears at a higher field position, 129.7 p.p.m., than ketene. The high-field position can be rationalized by a resonance structure of carbon suboxide (**15**). The high electron density at the $C_{(2)}$ carbon of **15** results in the high shielding.



$$\mathbf{11} \longleftrightarrow \overset{+}{O}\equiv C-\overset{-}{C}=C=O$$

(15)

D. Gas Chromatography

Gas chromatography is a very useful method for the identification and quantitation of both allenes and ketenes. The retention times of these compounds in a given chromatographic system can be used to establish the identity of an allene or ketene and the area of the peak on the chromatographic tracing can be used to determine the amount of compound present.

1. Allenes

Kovats' retention indices for allene have been determined for a number of stationary phases as shown in Table 22[65]. Since most allenes are quite low boiling, low column temperatures are utilized in the chromatographic analysis of these compounds. Hively[66] studied the gas chromatographic properties of a variety of hydrocarbons. Summarized in Table 23 are the relative retention times (with respect to methylal) for some allenes on five stationary phases. The column materials were prepared by mixing 40 g of the liquid phase (stationary phase) to 100 g of Columpak and then rolling this mixture overnight to insure even coating. The boiling points of the allenes studied are: allene, −34.5°C; 1,2-butadiene, 10.85°C; 3-methyl-1,2-butadiene, 40°C; 1,2-pentadiene, 44.86°C; 2,3-pentadiene,

TABLE 22. Kovats' retention indices[a] for allene[b]

Liquid phase	Column temperature (°C)	Retention index
Squalane (27%)[c]	28	317
Silicone fluid (20%)	50	333
Diethylhexyl sebacate (20%)	50	359
Diisodecyl phthalate (20%)	50	367
Dimethylformamide (20%)	20	425
Dimethylsulpholane (15%)	20	459
Propylene carbonate (15%)	20	496
Formamide (25%)	20	551

[a] For a discussion of these indices see Reference 64.
[b] Data from Reference 65.
[c] Weight per cent of liquid phase on solid support.

TABLE 23. Relative retention times[a] for simple allenes[b]

	Column A[c]		Column B	Column C			Column D			Column E
Compound	25°C	37°C	25°C	25°C	37°C	45°C	25°C	37°C	45°C	25°C
Allene	0.072	–	0.078	0.099	–	–	0.121	–	–	0.045
1,2-Butadiene	0.210	0.236	0.275	0.360	0.402	0.440	0.48	0.437	0.423	0.102
3-Methyl-1,2-butadiene	0.415	–	–	0.92	–	0.96	1.32	1.10	0.97	0.159
1,2-Pentadiene	0.51	0.54	0.80	1.12	1.11	1.13	1.58	1.29	1.14	0.196
2,3-Pentadiene	0.52	0.53	0.86	1.17	1.16	–	1.69	1.36	1.17	0.202

[a] Methylal used as reference: relative retention time = 1.000.

[b] Data from Reference 66.

[c] All columns contained 40% (w/w) liquid phase on Columnpak; Column A: dimethylsulpholane, 2.5 m; Column B: tritolyl phosphate, 2,5 m; Column C: di-*n*-decyl phthalate, 2.5 m; Column D: mineral oil, 2.5 m; Column E: 2,2′-oxydipropionitrile, 2.5 m.

48.27°C. Examination of Table 23 shows that these allenes are eluted in order of their boiling points for all five stationary phases.

Crespi[67] used a column of magnesium silicate (1–2 m in length) to separate allene from butanes. This column material used here separates compounds on the basis of differential absorption to the surface of the magnesium silicate particles. Another group[68] separated allene from propylene and propyne on a column of 32% paraffin oil on Celite 503 at 0°C. A thermal conductivity detector with helium carrier gas was used in this study. Capillary columns packed with graphited carbon black impregnated with about 0.4% (w/w) with squalane have been used to separate allene and 1,2-butadiene from other hydrocarbons in the C_1–C_4 range[69]. Using 2 m columns at 30°C, these workers determined the relative retention volumes (with respect to *n*-pentane) of allene (0.020) and 1,2-butadiene (0.125).

Gas chromatography has been used by many workers to quantitate allene in gaseous mixtures. In a study of the hydrocarbons in methane, Zocchi[70] preconcentrated allene at –83°C by trapping it on carbowax 20M coated on alumina (40–60 mesh). The allene was then released from the trap by heating to 45°C. On a column of the same material, allene gave a retention time of about 15.5 minutes. Using flame-ionization detection allene was measured down to the parts per billion range in methane gas. Using a 10% dimethylsulpholane column (10 m x 0.125 in) at 25°C, Rohrschneider and Jaeschke[71] determined a concentration of 3 parts per million (p.p.m.) of allene in propylene. Allene in propene has been determined using a stationary phase consisting of 30% silver nitrate in ethylene glycol[72]. At 25°C, allene gives a retention time of about seven minutes in a 2 m column (4.5 mm I.D.). Using thermal conductivity detection these workers were able to measure allene down to 5 p.p.m.

In a study of the impurities in propylene obtained from petroleum cracking, Herranz[73] was able to detect allene to 10 p.p.m. For this analysis, the stationary phase used was β,β′-oxydipropionitrile on Chromosorb.

Allene has been determined as an impurity in vinyl chloride using a column of tricresyl phosphate on Chromosorb P[74]. Allene gave relative retention times of 0.48 (at 35°C) and 0.52 (at 50°C) with respect to vinyl chloride. Less than 0.2 p.p.m. of allene was found in commercial vinyl chloride. Allene has also been determined as an impurity in butadiene[75]. In this study, columns of 20% dibutyl maleate on 60/80 mesh Chromosorb P-NAW (25 ft x 1/8 in) and 10% bis(2-methoxyethoxy)ethyl ether on 60/80 mesh Chromosorb P-NAW (15 ft x 1/8 in) were connected in series. At 25°C, allene gave a retention time of about seven minutes in this system. A concentration of allene of 0.56% (w/w) was found in the gas phase effluent from a naphtha feedstock. Allene has also been analysed in 1,3-butadiene using a Vulcan G stationary phase modified with 4.8% picric acid[76]. In this study, allene had a retention time of 6.5 min at 46°C. A concentration of 70 p.p.m. allene was found in 1,3-butadiene.

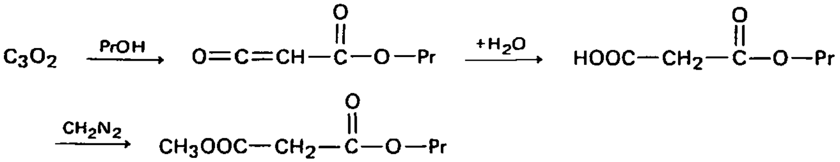
2. *Ketenes*

Ketene has been analysed in the pyrolysate of diketene and of acetic acid using a 1.5 m column of Poropak R, a polymeric solid material[77]. These same workers achieved a good separation of ketene and allene from other gaseous components of a mixture (air, CO, methane, ethane and ethylene) using a column of 20% dioctyl phthalate on Microsorb W. In a study of the photolysis of cyclobutane, a ketene peak was observed using a Porapak Q column[78]. However, the recovery of authentic samples of ketene was not quantitative on this column. Laufer[79] was able to separate ketene (retention time 1.8 min) on a 30/60 mesh Haloport F column (2.5 m x 0.25 in) at −35°C with a helium flow rate of 75 ml/min. However, methylketene was not quantitatively recovered from the column. At −78°C, ketene had a retention time of 2 min while methylketene was retained on the column.

Polushkin and Kolesov[80] examined several liquid phases (dinonyl phthalate, trichloroethyl phosphate, PPhMS-4 (a silicone), squalane, tricresyl phosphate and dibutyl phthalate) for the separation of ketene from acetone. PPhMS-4 was the best stationary phase, producing a good separation from acetone and a short retention time (less than 2 min) for ketene. Applying this column to the analysis of ketene produced by thermal degradation of acetone, an error of 2.3% was obtained at a concentration of 12% w/w (ketene in acetone).

A different approach to the analysis of ketene in the gas phase was taken by Breuer and collaborators[81]. These workers reacted ketene with an excess of anhydrous methanol to yield methyl acetate in a quantitative fashion. Since this reaction was carried out in the gas phase, the possibility of ketene dimerization was greatly reduced. Using flame ionization detection and a dimethylsulpholane column at room temperature, nanomole quantities of methyl acetate (and hence ketene) could be detected.

Carbon suboxide (C_3O_2) has been analysed via ketene formation and gas chromatography[82]. In this method carbon suboxide is converted to a propyl ester and then to a diester by the action of diazomethane as shown in equation (8). Pyrolysis of the diester yields ketene which is analysed directly by gas chromatography. Carbon suboxide has also been analysed by gas chromatography on an apiezon N column[83].



$$C_3O_2 \xrightarrow{PrOH} O{=}C{=}CH{-}\overset{\overset{O}{\|}}{C}{-}O{-}Pr \xrightarrow{+H_2O} HOOC{-}CH_2{-}\overset{\overset{O}{\|}}{C}{-}O{-}Pr \xrightarrow{CH_2N_2} CH_3OOC{-}CH_2{-}\overset{\overset{O}{\|}}{C}{-}O{-}Pr \qquad (8)$$

E. Miscellaneous Methods

The polarographic half-wave potential for allene has been reported as −2.29 V (vs saturated calomel electrode)[84]. This very large reduction potential makes it impractical to analyse allene by polarography in most solvents.

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The Chemistry of Ketenes, Allenes and Related Compounds
Edited by Saul Patai

CHAPTER **6**

The generation of neutral and ionized allenes, cumulenes and heterocumulenes by electron impact

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I. INTRODUCTION

In the past a vast number of papers have been published dealing with the influence of nearly all kinds of functional groups on the electron impact induced fragmentation of organic compounds. However, there are comparatively few studies of the mass spectra and fragmentation mechanisms of compounds with cumulated double bonds like allenes, cumulenes and heterocumulenes (e.g. ketenes).

Among these studies the number of contributions which investigate the fragmentation mechanisms and ion structures of ionized cumulenes and heterocumulenes is even smaller. New instrumental techniques like field ionization kinetics (FIK)[1], ion cyclotron resonance (ICR)[2], collisional activation (CA)[3] and chemical ionization (CI)[4] seem to be very well suited for mechanistic studies in mass spectrometry. Unfortunately the majority of publications are restricted to the reproduction of mass spectra and the more or less speculative assignment of ionic or neutral structures of cumulenes.

The reader should bear in mind that most of the fragmentation mechanisms cited in the following survey are not proved by special experimental techniques. This survey will show:

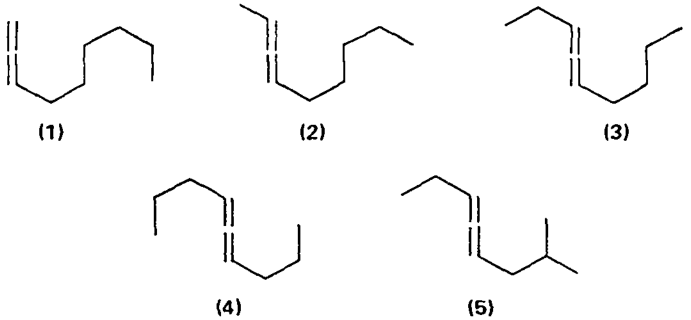
(1) the typical fragmentation pathways (including isomerization) of ionized cumulenes and heterocumulenes;
(2) the generation of ionized and neutral species containing cumulated double bonds.

We hope that this survey will stimulate mass spectrometrists to further mechanistic work and more detailed studies in this field of organic mass spectrometry.

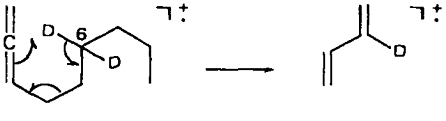
II. ELECTRON IMPACT INDUCED REACTIONS OF ALLENES AND HETEROCUMULENES

A. Allenes and Related Compounds

For many years the question as to whether ionized allenes and acetylenes isomerize to common ion structures[5] has been discussed. Recently this problem was reinvestigated by Djerassi and coworkers[6]. They prepared a variety of deuterium-labelled model compounds which were studied at different electron energies. The mass spectra of the compounds 1–5 (Scheme 1) differ so considerably at 70 and 12 eV that a complete isomerization of the molecular ions via H-shift may be excluded. This is true for those species with a lifetime of $<10^{-6}$ sec as well as the metastable ions (lifetime $\sim 10^{-5}$ sec). The main fragmentation reaction which is revealed by the analysis of the deuterated allenes, e.g. 6, is a hydrogen transfer to the central carbon atom of the allenic system (McLafferty rearrangement). The most favoured transition state for this rearrangement is a six-membered ring. Five- or seven-membered rings are of minor importance (Scheme 2). Whether the hydrogen transfer is a concerted or stepwise process cannot be decided yet. Allenes with



SCHEME 1.

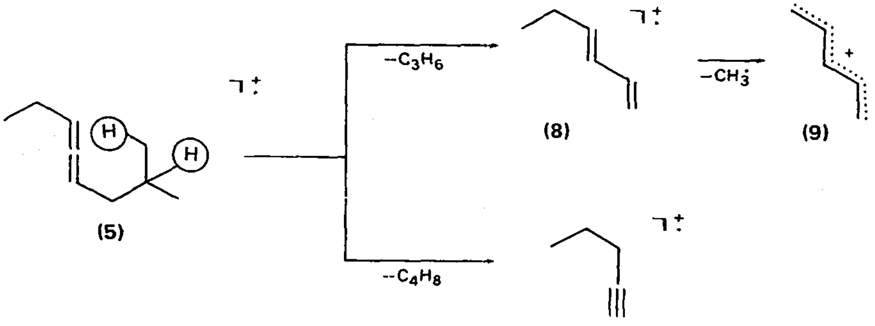


(6) (7)

SCHEME 2.

branched alkyl chains, e.g. 5, display a further type of hydrogen transfer. The hydrogen is transferred to the terminal carbon atom of the unsaturated π system.

Both rearrangements proceed preferably via a six-membered transition state. The main difference between these processes is the higher tendency for secondary decomposition of the first one: this process is preferred by a factor of 2 and is followed by intensive loss of methyl (allylic bond cleavage). The formal alkyne radical cation 10 does not show any further fragmentation (Scheme 3).

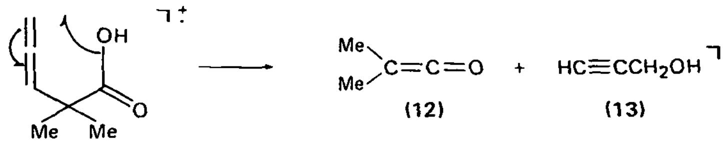


SCHEME 3.

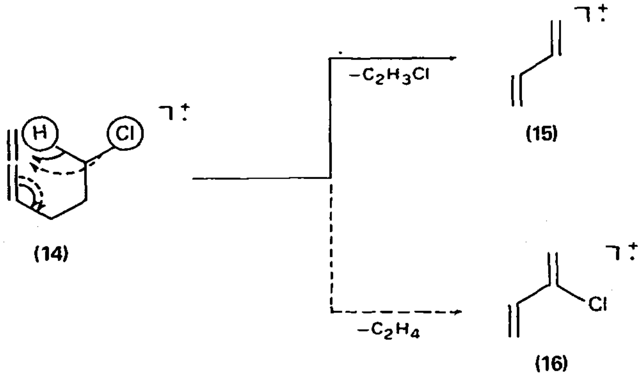
Loss of alkyl radicals from 1–5 seems to follow more complex mechanisms. The elimination of C_2H_5 from 5 involves more than 85% of $C_{(1)}$, $C_{(2)}$ and leads to a formal allenic cation. Loss of ethyl from 3 involves equal parts of $C_{(1)}$, $C_{(2)}$ and $C_{(8)}$, $C_{(9)}$. The elimination of methyl groups from 5 seems to be even more complex: 85% of these originate from the methyl groups of the isopropyl group whereas $C_{(1)}$ contributes only 15% of the methyl by allylic bond cleavage.

Allenic systems show a marked tendency to accept different atoms and parts of functional groups in intramolecular rearrangements which is demonstrated by the fragmentation of 11 and 14 (Scheme 4). The allene carboxylic acid 11 fragments via hydroxyl transfer and subsequent elimination of dimethylketene 12 to ionized propargyl alcohol (13) (100%)[7]. A further example is the transfer of either chlorine or of hydrogen, followed respectively by loss of ethylene or of C_2H_3Cl from the ω-chloro-substituted allene 14[8].

Allenes and cumulenes containing branched alkyl groups, e.g. isopropyl or *t*-butyl, give very abundant alkyl fragments (e.g. $C_4H_9^+$ or $C_3H_7^+$). Fragment ions

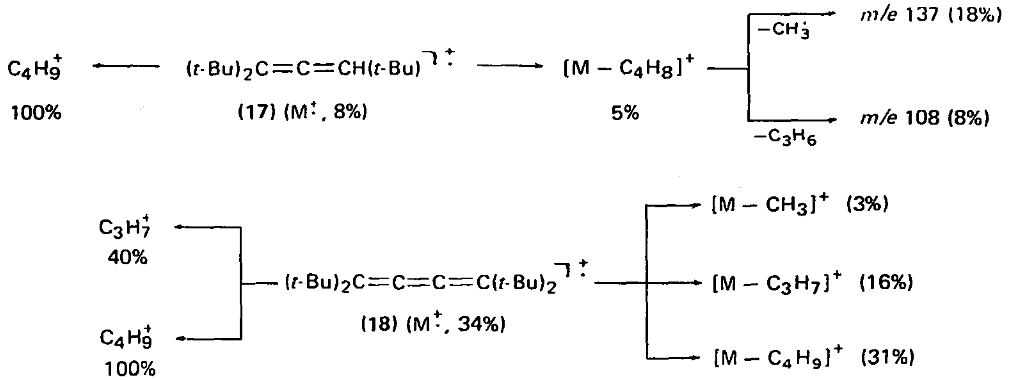


(11) (12) (13)



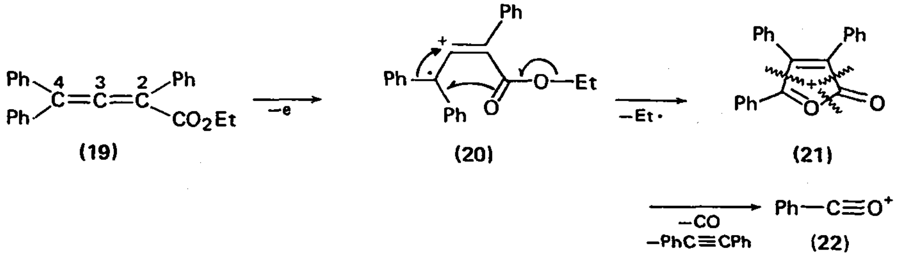
SCHEME 4.

which originate from the central allenic group are less intensive. Scheme 5 shows the most important decomposition pathways of the compounds 17[9] and 18[10] which are typical examples for this group (relative intensities are expressed in % base peak = 100%).



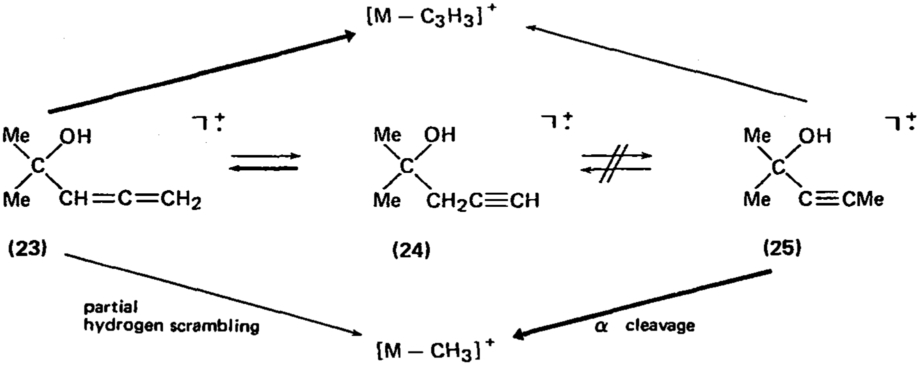
SCHEME 5.

Richter[12] found an interesting type of neighbouring-group participation in the mass spectra of allene carboxylic acid esters. Loss of alkyl from the ester function is normally not a favoured process[11]. In the case of allene carboxylic ethyl esters, however, loss of ethyl proceeds via rearrangement of **19** to **20** and **21**. A similar reaction is known from the proton-catalysed cyclization of free allene carboxylic acids in solution. The authors suggest that the primary ionization leads to a deformation of the linear structure of $C_{(2)}$, $C_{(3)}$, $C_{(4)}$. The ion **20** is thought to be the crucial intermediate of the radical-induced ethyl loss. A neighbouring-group effect resulting from vibrational deformations seems to be less probable because of the distance of $C_{(4)}$ and the carbonyl group of the ester. If the allene function is in conjugation to the ester group, e.g. β,γ-allene carboxylic acid esters, not elimination of alkyl is not observed. A variety of different decomposition processes which follow complex fragmentation mechanisms[13] predominate. It should be pointed out that the sequence **20** → **21** → **22** (Scheme 6) is an interesting example of an oxygen transfer (for further discussion of this topic see Reference 14).



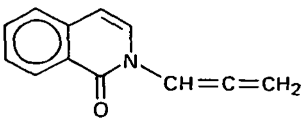
SCHEME 6.

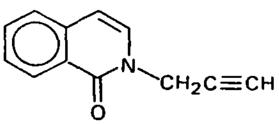
Bogentoft and coworkers[15] investigated the isomerization of the allenic and acetylenic alcohols 23–25 under electron impact (Scheme 7). Although 23 and 24 show nearly identical mass spectra the mass spectrum of 25 differs markedly which indicates that no isomerization has taken place. Intensive loss of $C_3H_3^\bullet$ (supposedly an allenic radical) is characteristic for 23 and other tertiary alcohols. This reaction is completely missing in the case of 25. A further difference between the mass spectra of 23, 24 on one hand and 25 on the other is the formation of the $(M - CH_3)^+$ ions. Whereas loss of methyl from 25 is a simple α cleavage, 23 undergoes partial hydrogen scrambling prior to decomposition[15c]. Whether hydrogen scrambling is accompanied by carbon scrambling is open to question.

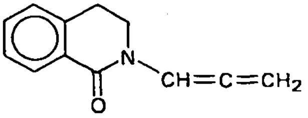


SCHEME 7.

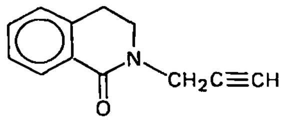
In general the isomerization of ionized allene to acetylene and vice versa within the mass spectrometric time-scale cannot be predicted *a priori*. This is supported by the mass spectra of 26–29[15b]. 26 and 27 show identical mass spectra [main sequence: $M^{+\cdot}$ (100%) → $[M - CO]^{+\cdot}$ (6%) → $[M - CO - HCN]^{+\cdot}$ (27%) → $[M - CO - 2HCN]^{+\cdot}$ (15%)]. However, 28 and 29 differ considerably. This indicates that the decomposing molecular ions do not isomerize to a common structure. Loss of


(26)


(27)



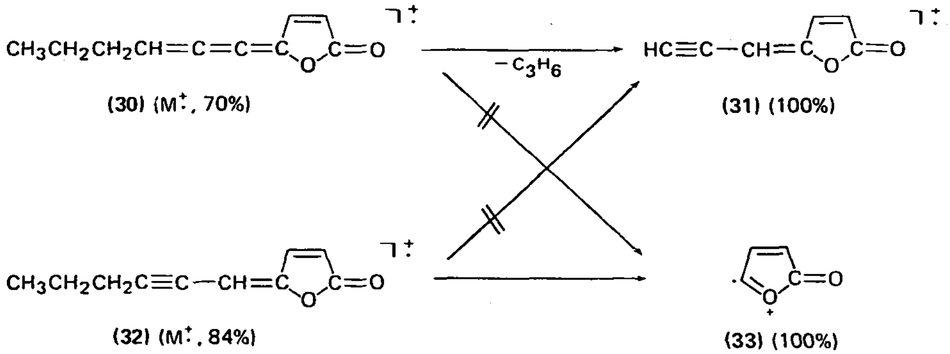
(28)



(29)

hydrogen yields the base peak in the spectrum of **29** whereas this fragment ion is of minor abundance (8%) in the mass spectrum of **28**.

Similar relations can be observed in the case of naturally occurring allenic and acetylenic compounds. **30** shows an elimination of C_3H_6 via a cyclic transition state (*m/e* 128: 100%) and gives **31**. This fragmentation is missing in the mass spectrum of the isomeric acetylenic ester which loses $C_3H_7^{\bullet}$ (*m/e* 119) instead. The base peak *m/e* 82 (ion **33**) results from a complex process (Scheme 8)[16].



SCHEME 8.

Extensive investigations by Bohlmann and coworkers[17] permit us to summarize the following rules of fragmentation:

(*a*) Allenes show a marked tendency to form even-numbered fragments. The presence of an ester function favours the isomerization of the allenic double bonds in the direction of the ester group. Direct reactions of the ester functions like α cleavage and McLafferty rearrangement are of minor importance.

(*b*) There is a high tendency for an isomerization of the triple-bond system to the allenic system which leads to the majority of significant fragments, especially at low electron energy.

(*c*) Conjugated systems tend to isomerize via six-membered transition states. Hydrogen as well as alkyl groups may be transferred.

Schemes 9–11 give some examples for these rules.

B. Heterocumulenes Containing One Heteroatom

The mass spectrum of ketene (**52**) as well as diketene (**53**) was discussed by Long and Friedman[18] as early as 1953*. **53** gives peaks at *m/e* 42 (100%, $M^{+\bullet}$), *m/e*

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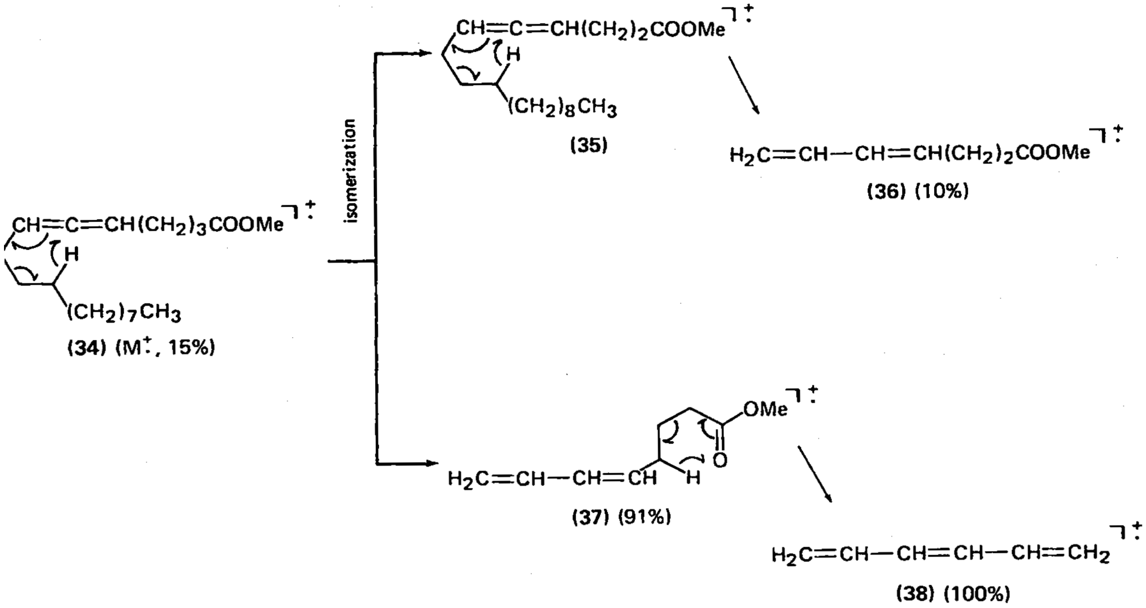
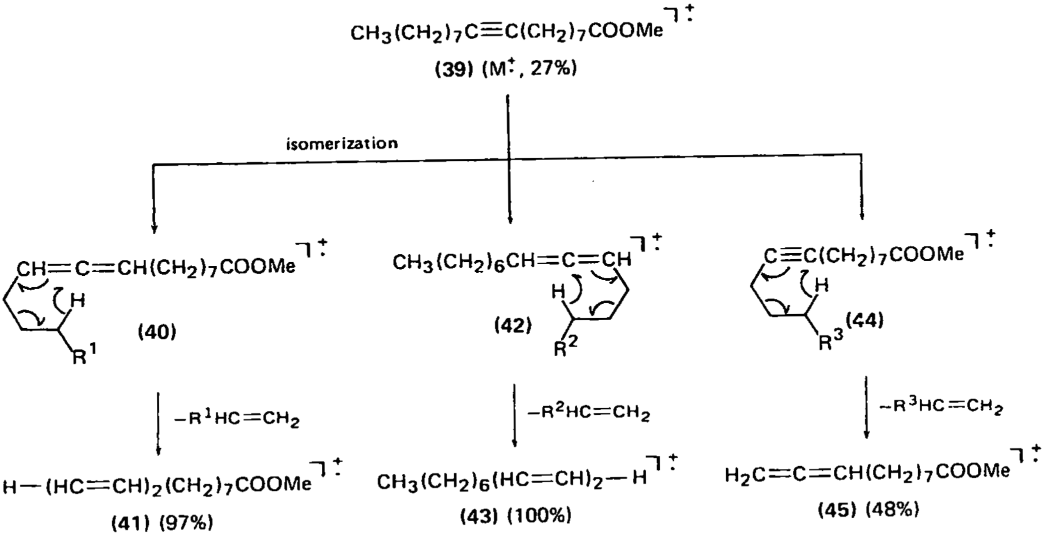
* For very recent results on the properties and reactions of gaseous ketene radical cations, see: J. Vogt, A. D. Williamson and J. L. Beauchamp, *J. Amer. Chem. Soc.*, 100, 3478 (1978).

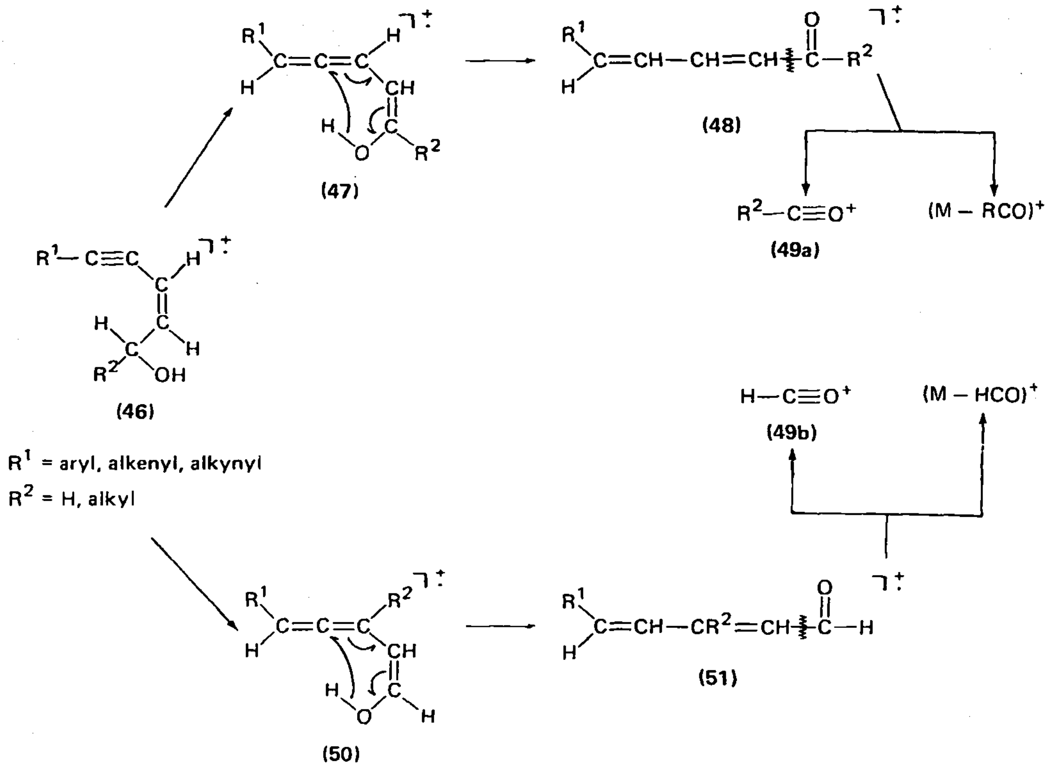
41 (21%), *m/e* 29 (6%), *m/e* 28 (15.2%), *m/e* 26 (2.1%), *m/e* 14 (71.5%), *m/e* 13 (10.2%) and *m/e* 12 (7.3%). No ion *m/e* 15 (CH_3^+) but an intensive ion *m/e* 14



SCHEME 9.



SCHEME 10.

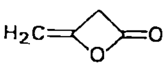


SCHEME 11.

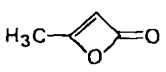
($CH_2^{+\cdot}$) was observed. The authors argued that this was an unequivocal indication for the structure 53 rather than for the alternative one 54. Although 53 is the correct structure the argumentation is not quite valid because thermic and electron impact induced isomerizations may precede the fragmentation. The fragment *m/e* 43 (CH_3CO^+, 11.7%), for example, indicates that an isomerization process has to precede the decomposition of the molecular ion.

$H_2C{=}C{=}O$

(52)

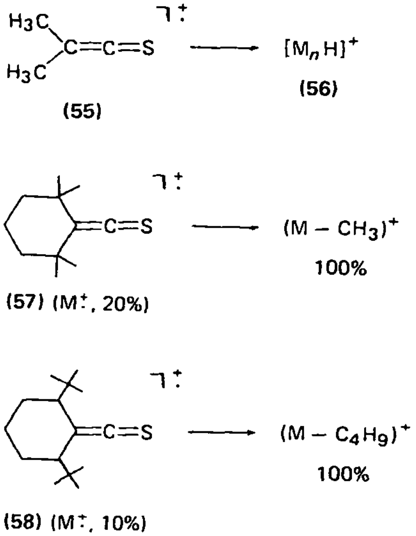


(53)



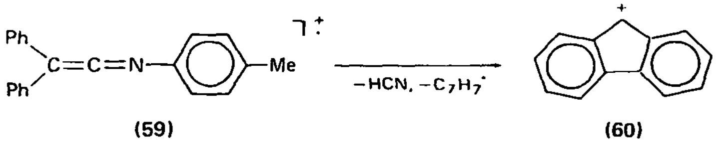
(54)

At low temperatures the mass spectrum of the thermally unstable dimethylthioketene (55) can be studied[19]. An intensive molecular ion which oligomerizes at higher temperatures can be observed at -20°C. The intensity ratio $M^{+\cdot}/(M_2H)^+$ drops from 5.0 to 0.08 if the temperature is raised to 45°C. Sterically hindered thioketenes, e.g. 57, 58[20], do not oligomerize. The mass spectra of these thioketenes give clear molecular ions. The base peak is normally loss of alkyl (Scheme 12).



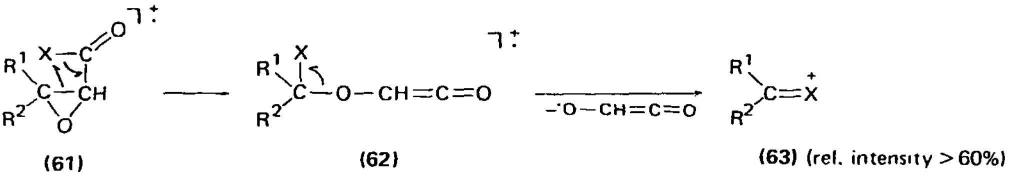
SCHEME 12.

Diphenylketene-*N*(*p*-toly)imine (59)[21] shows an intensive molecular ion and a fragment *m/e* 165 ($(C_{13}H_9)^+$), probably a fluorenyl cation (60). The mechanistic details have not yet been studied.



SCHEME 13.

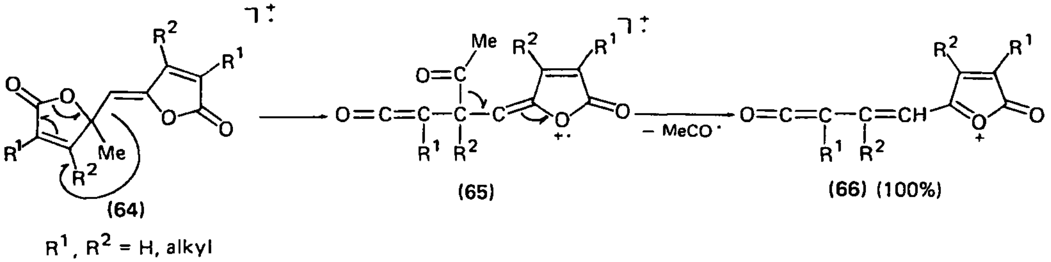
Ketene-like structures have been proposed as intermediates for a variety of fragment ions of electron impact induced decompositions. Schemes 14, 15 and 16 give examples for such processes (Scheme 14: glycidic esters and amides[22]; Scheme 15: α,β-unsaturated γ-dilactones[23]; Scheme 16: penicilline-G methyl ester[24]).



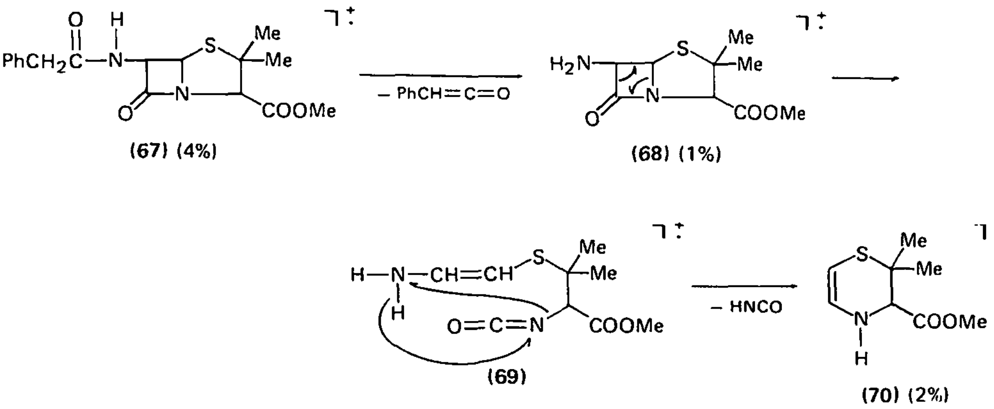
R1, R2 = Ph, H; cyclohexyl

X = *O*-alkyl; NH2

SCHEME 14.



SCHEME 15.



SCHEME 16.

C. Heterocumulenes Containing more than One Heteroatom

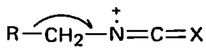
The enthalpy of formation ($\Delta H_f{}^0$) of neutral isocyanic acid was determined for the first time by accurate appearance potential measurements and determination of the kinetic energy release for the fragmentation process given in equation (1). Compernolle[25] calculated a $\Delta H^0_{f(HNCO)}$ of -25 ± 3 kcal/mol.

$$HNCO \rightarrow HNCO^{+\cdot} \rightarrow HC{\equiv}O^+ + N^\cdot \qquad (1)$$

The mass spectra of aromatic and aliphatic isocyanates and cyanates[26] have been thoroughly investigated. By ^{13}C-labelling it could be demonstrated[27] that loss of CO originates exclusively from the isocyanate group of phenyl isocyanate (71). The ion 73 is the main fragment (α cleavage) of isocyanates and isothiocyanates with an alkyl chain R < C_5 (72: X = O, S)[28,29].

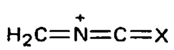
$Ph{-}N{=}C{=}O$

(71)



$R{-}CH_2{-}\overset{+}{N}{=}C{=}X$

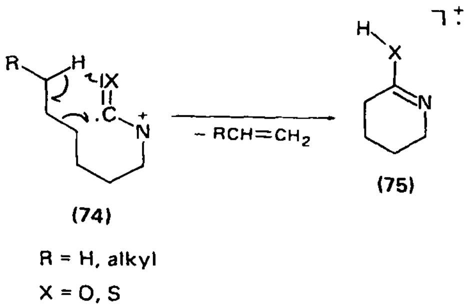
(72)



$H_2C{=}\overset{+}{N}{=}C{=}X$

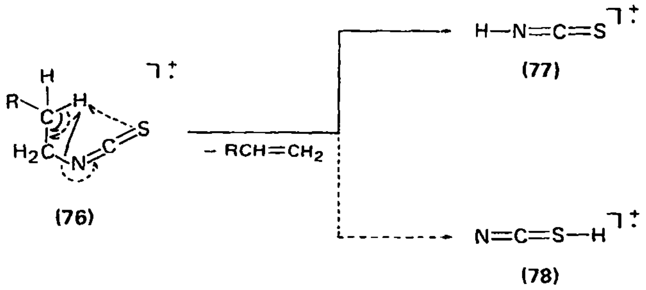
(73)

Isocyanates as well as isothiocyanates yield intensive peaks for the elimination of alkenes via bicyclic transition states. These ions have probably a cyclic structure[28,29] (Scheme 17).



SCHEME 17.

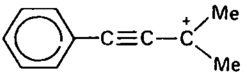
Besides these common fragmentation pathways of isocyanates and isothiocyanates the different positions of the sulphur give rise to the striking difference in the loss of XH• (X = O, S). The isothiocyanates (74) show a strong loss of SH•, whereas no hydroxyl elimination takes place in the case of the isocyanates. Isocyanates with a short side-chain (up to C_5) give an ion *m/e* 59 which is formed via a four- or six-membered ring (Scheme 18). Labelling experiments and appearance potential measurements[30] did not distinguish between these two alternative mechanisms. Probably a collisional activation[3] study could help to answer this question.



SCHEME 18.

III. GENERATION OF NEUTRALS CONTAINING CUMULATED DOUBLE BONDS BY ELECTRON IMPACT

As already indicated in Schemes 4, 7, 14 and 16 a variety of neutrals with cumulated double bonds are formed during the fragmentation of different kinds of compounds. The principal problem in discussing the structure of neutrals in mass spectrometry is the fact that neutrals cannot be detected directly. Only mass differences, label retentions, appearance potential measurements of the corresponding ions (!) etc. lead to tentative conclusions concerning the structures of neutrals. Therefore, no direct proof of a neutral structure is possible. A clear example for this problem is the study of the C_3H_4 elimination from the ions 79 and 80[31]. From thermochemical considerations the neutral cannot be eliminated as cyclopropene (81). However, no determination based on energetic measurements or extensive investigation of D- and ^{13}C-labelled analogues of 79 and 80 can be made between the allene 82 or propyne 83. All C-atoms of the C_5 side-chain of 79 are involved on a statistical equivalency in the formation of the neutral whereas the C-atoms of the isopropyl group of 80 are exclusively involved in the loss of C_3H_4. The deuterated analogues of 79 and 80 show further that a partial hydrogen exchange between the CH_3 group and the phenyl ring precedes the elimination of the neutral.



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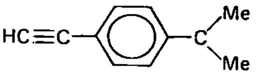


(80)

(81)

$H_2C{=}C{=}CH_2$

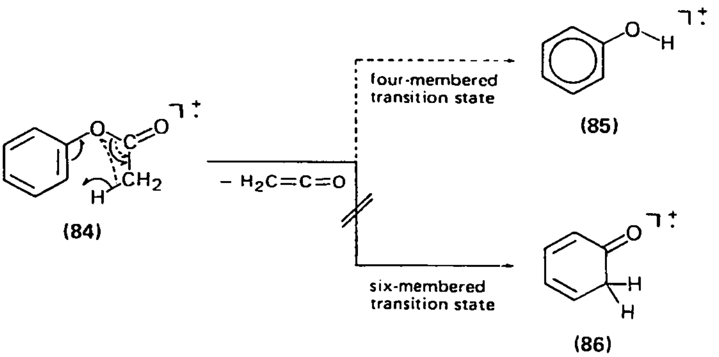
(82)

$CH_3C{\equiv}CH$

(83)

Whereas the mechanism of the elimination of C_3H_4 from 79 to 80 and the structure of the neutral leave some questions open, loss of ketene from a variety of precursors seems to be more or less clear[32]. There is no doubt that the neutral has the structure of ketene (52) and the mechanistic details of the elimination modes have been recently elucidated.

For instance the elimination of ketene* from ionized phenyl acetate (84) may occur via a four-membered or six-membered transition state leading to ionized phenol 85 or alternatively cyclohexadienone (86). Isotope and substituent effects[33] (especially '*ortho*' effects[34]) and a recent ICR study[35] clearly support the structure of the ion 85. No ion 86 is formed even as an intermediate (Scheme 19). Similarly ionized vinyl alcohol is formed only by elimination of ketene from vinyl acetate[33,36]. This reaction may be interpreted as a symmetry-allowed $[\pi_a{}^2+\sigma_s{}^2]$ cycloreversion.



SCHEME 19.

Unimolecular loss of ketene is observed from the molecular ions of 87, 88, 90 and 91, too. Ketene is generated directly from the β-keto ester 87[37] by a McLafferty rearrangement, whereas extensive rearrangements have to precede the C_2H_2O loss from 87—91. 88, for example, primarily rearranges to 89 in analogy to the

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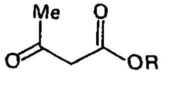
* Ketene elimination from *ortho*-substituted acetonitrides *anions* has been recently reported: J. A. Benbow, J. C. Wilson and J. H. Bowie, *Int. J. Mass Spectrom. Ion Phys.*, 26, 173 (1978).

photochemical behaviour of 88[38]. After some complex rearrangements ketene is eliminated. A relatively complex mechanism is responsible for the C_2H_2O loss from 90 and 91[39]. Investigation of labelled compounds and a FIK study give evidence that the C-atoms of the ketene come from the C_α and C_β of 90 and 91. From the short-living ($<10^{-10}$ sec) molecular ions of dihydrocinnamyl aldehyde, ketene is formed by specific hydrogen transfer from C_α to the phenyl ring. The longer-living species of 90 show an extensive hydrogen exchange between C_α and C_γ and the C_α and both *ortho* hydrogens. The ketene hydrogens originate nearly exclusively from C_α and C_β when the neutral is generated from cinnamyl alcohol. The contributions of the hydrogens of the OH group and the phenyl ring are of minor importance. In addition the situation is further complicated by a partial rearrangement 91 → 90. This is a process the proportion of which depends on the ionization energy. The elimination of *t*-butylketene from 92 probably proceeds via the intermediate 93[40] in a rearrangement reaction.



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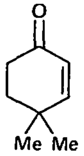
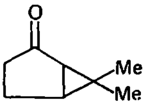
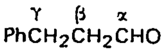


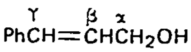
(88)



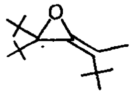
(89)


$\mathrm{Ph}\overset{\gamma}{\mathrm{CH_2}}\overset{\beta}{\mathrm{CH_2}}\overset{\alpha}{\mathrm{CHO}}$

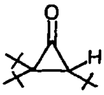
(90)


$\mathrm{Ph}\overset{\gamma}{\mathrm{CH}}{=}\overset{\beta}{\mathrm{CH}}\overset{\alpha}{\mathrm{CH_2}}\mathrm{OH}$

(91)

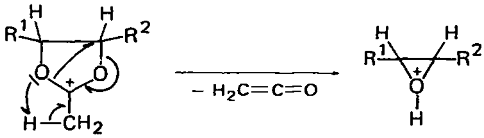


(92)



(93)

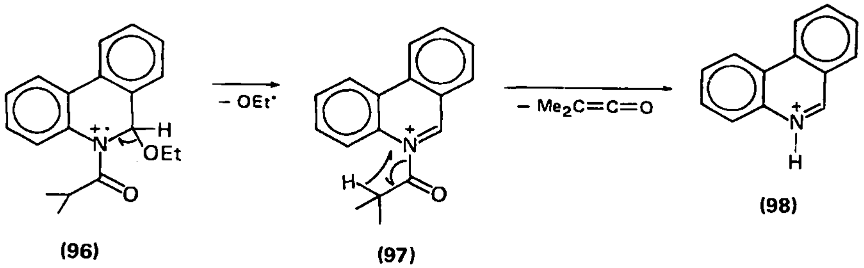
Schemes 20—23 give examples for the formation of ketene and substituted ketenes from a variety of fragment ions. The $(M - CH_3)^+$ ions of the acetonide 94 lose C_2H_2O, and form a protonated epoxide 95[41] (Scheme 20). The ion 98 is the base peak in the mass spectrum of the substituted 5,6-dihydrophenanthridine 96 which is generated by loss of dimethylketene from 97 (Scheme 21)[42]. A four-membered transition state according to Scheme 21 is involved in the elimination of acetylketene from *N*-aryl-substituted pyrrolidine ions[43], too. The mass spectra of α,ω-dicarboxylic acid dimethyl esters 99 demonstrate an interesting mechanistic phenomenon. Whereas the $(M - CH_2COOH_3)^+$ ions of 99 which do *not* fragment further within 10^{-5} sec have a cyclic structure 101a[44], the fragmenting ions form 101b by a OCH_3^- migration. Ketene is eliminated from 101b[45] (Scheme 22).



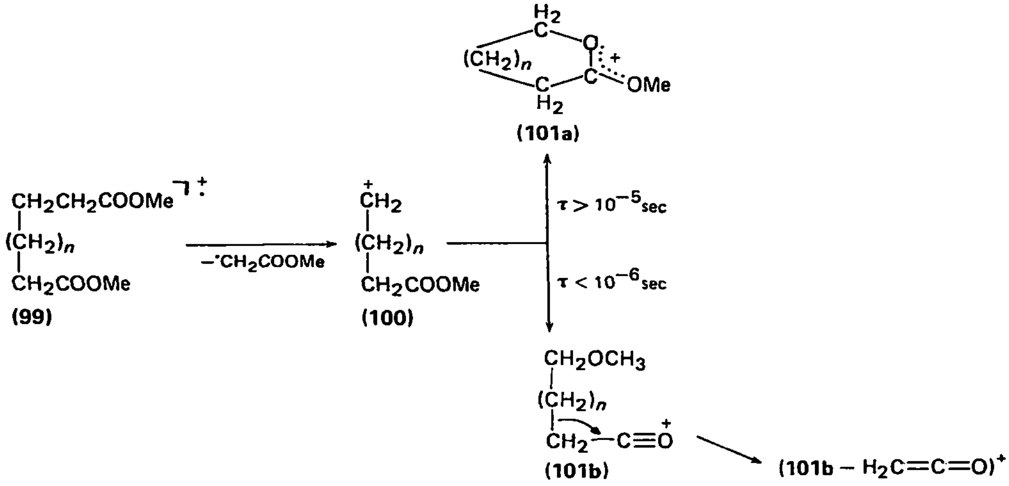
(94) (95)

SCHEME 20.

Multiple hydrogen rearrangements are involved in the loss of ketene from the $(M - H)^+$ ions of 102 which was investigated by D- and ^{13}C-labelling. The phenyl-



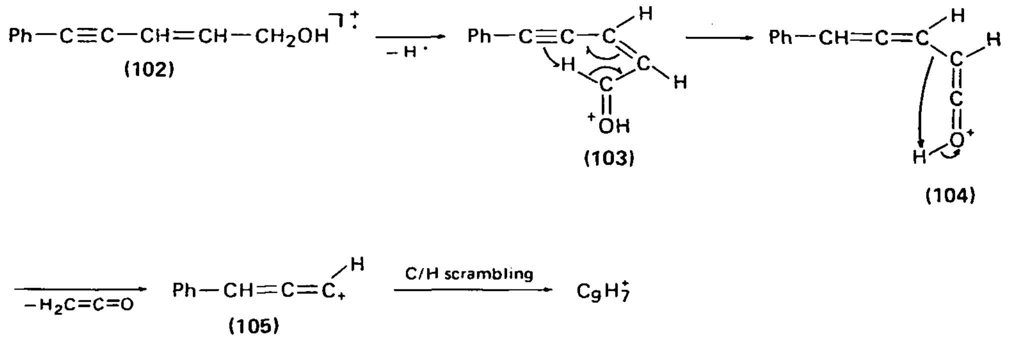
SCHEME 21.



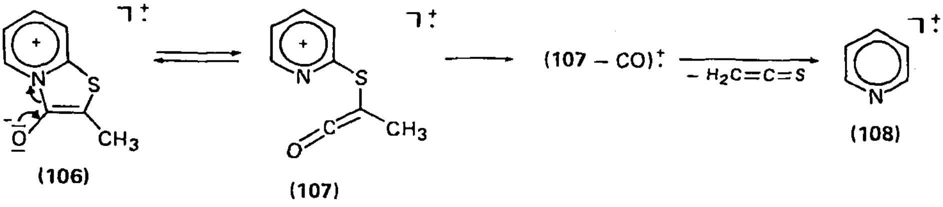
SCHEME 22.

substituted carbocation **105** has no stable structure; the species show extensive carbon and hydrogen scrambling processes[46] (Scheme 23).

An interesting example for the elimination of neutral heteroallenes is the loss of thioketene from the $(M - CO)^+$ fragment of thiazolo (3.2-α)pyridinium-3-oxide **106** which leads to ionized pyridine[47] (Scheme 24).

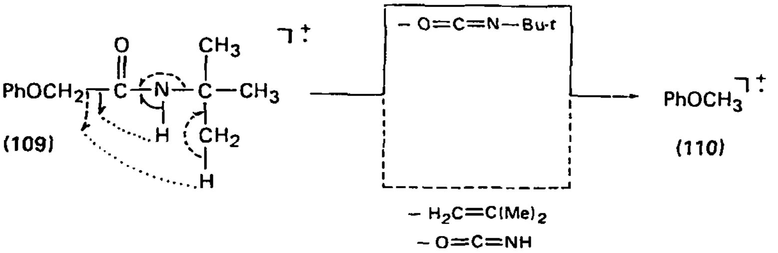


SCHEME 23.



SCHEME 24.

Thorough investigations of the derivatives of urea[48], semicarbazone[49] and thiosemicarbazone[50] revealed that the neutral X=C=Y (X = NH, CH_2; Y = O, S) is easily generated by electron impact. An unusual elimination of *t*-butyl isocyanate, respectively isocyanic acid and isobutylene from phenoxyacetamide (**109**) was investigated by Tomer[51] (Scheme 25). The formation of ionized anisole (**110**) takes place alternatively via a four-membered (40%) and a six-membered (60%) transition state. However, the ethyl derivative shows exclusively the transfer of a hydrogen from the NH function to the CH_2 group (> 90%, four-membered ring).



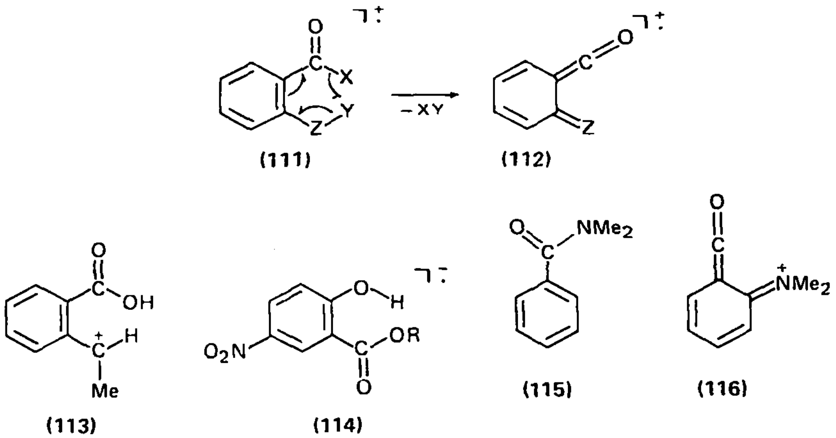
SCHEME 25.

IV. IONIZED ALLENES, KETENES AND HETEROCUMULENES

A. 'Ortho' Effects

Ions with ketene-like structures are formed from 1,2-disubstituted arenes by an interaction of the vicinial substituents. Generally hydrogen, oxygen or part of the substituent are transferred to the neighbouring function and a neutral X–Y (e.g. H_2O, ROH) is eliminated[34]. This reaction, which is not restricted to open-shell cations, is not necessarily a concerted one. Closed-shell cations, e.g. **113**[52], and open-shell anions (**114**)[53] may fragment via '*ortho*' effects[34] and yield ketene-like ions. The highly specific elimination of an *ortho*-hydrogen from **115** may be interpreted as an unusual '*ortho*' effect. The hydrogen elimination (vinylogous α cleavage) is accompanied by migration of the nitrogen-containing group and probably leads to **116**[54].

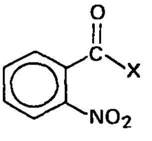
'*Ortho*' effects accompanied by an oxygen transfer[14,34] are very complex processes. In some cases parallels to related photochemical reactions have been found. The intensity of fragments from such mass spectrometric processes seems to depend mainly on the nature of the heteroatoms. Some of these oxygen transfers which lead to ions with cumulated double bonds should be briefly cited here.**117a**,**b**[14,55]



(111) (112) (113) (114) (115) (116)

SCHEME 26.

forms **118** (loss of X–O°: 14–21%), **120** (81%) is generated from **119**[14] whereas **121** gives **122** (30%) by consecutive loss of $CCl_3^{\bullet}$ and CO_2[56]. In addition **122** is formed by OH elimination of **123**[57]. It should be mentioned that OH elimination from *ortho*-nitrotoluene (**124**) gives a fragment which has supposedly the structure **125**[58].



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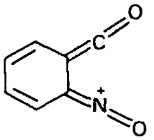
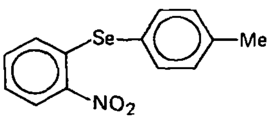
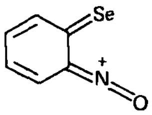


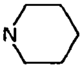
(118)

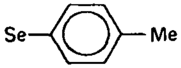


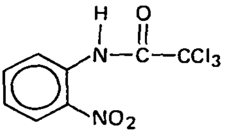
(119)



(120)

(a) X = 

(b) X = 



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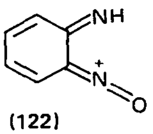
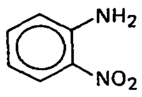
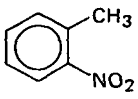


(122)



(123)



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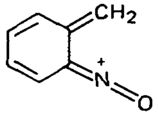
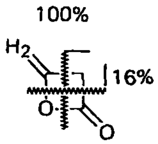


(125)

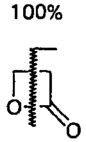
B. Cycloreversions

1. Four-membered ring systems

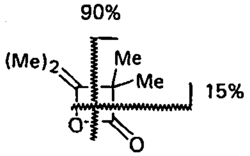
Diketene (53), as already mentioned in Section I.B, fragments to ionized ketene (52, 100%)[18]. The generation of ionized ketenes is observed from other β-lactones, too (e.g. 126[59] and 127[60]). Ionized allenes are the result of CO_2 elimination from 53 and 127.



(53)

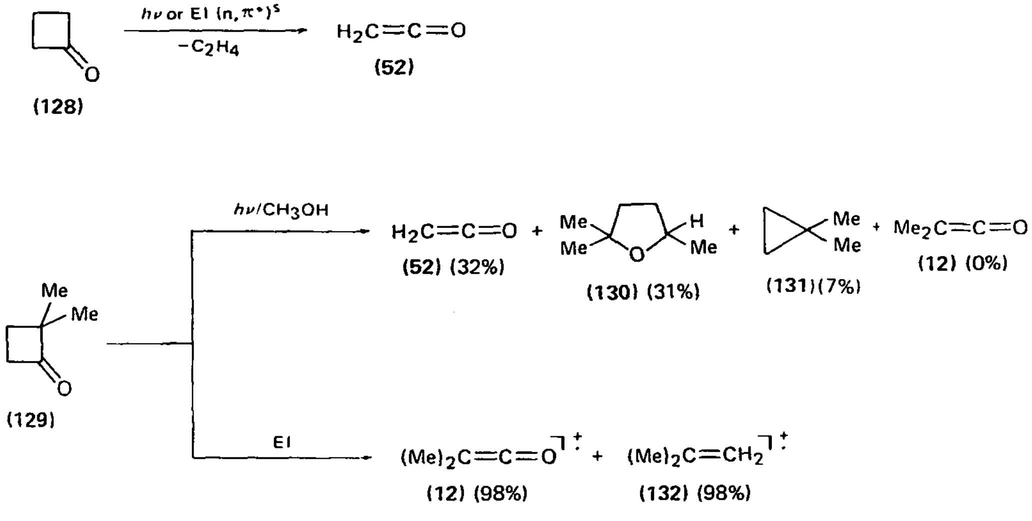


(126)



(127)

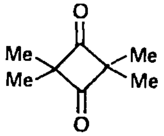
The parallels between electron impact induced and photochemical reactions of cyclobutanones have been thoroughly studied by several groups[61]. The formation of ketene from unsubstituted cyclobutanone (128) seems to proceed via a [n,π*] singlet state under photochemical and electron impact conditions. The higher alkylated cyclobutanones like 129, however, show different reaction products under electron impact and photochemistry. Electron impact yields ionized dimethylketene (12) and isobutylene (132). The photochemical reaction gives mainly ketene (Scheme 27).



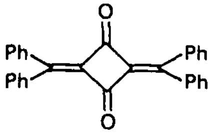
SCHEME 27.

Provided that the cycloreversion of 129 under electron impact proceeds via an α cleavage (like the photochemical reaction), one should expect that the distribution of reaction products will depend on the stability of the radical cations. If this were really true, ionized ketene (52) should be the main product. Since this is not the case for the mass spectrometric reaction the authors concluded that this reaction takes place via a concerted cycloreversion rather than a multistep process[61]. A concerted cycloreversion would mean a random deformation of all C—C bonds of the four-membered ring and the charge distribution of the products would be determined by the electronic reorganization of the transition state. Indeed, detailed investigations of Turro and coworkers[60] could show that the charge distribution of the products from di-, tri- and tetrasubstituted cyclobutanones corresponds in a first approximation to the ionization potentials of these species. Generally the fragments with the lowest ionization potential carries the positive charge.

Cyclobutane-1,3-diones like **133**[60] and **134**[62] have been studied, too. These yield dimethyl- and diphenyl-ketene respectively by a cycloreversion. In addition diphenylketene shows intensive signals for the loss of two molecules of CO (**135**, **136**).



(133)

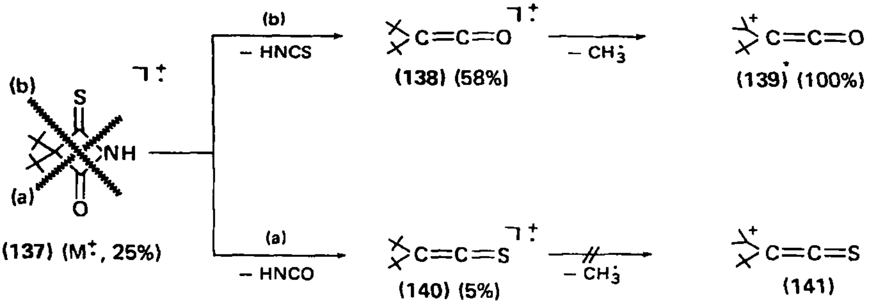


(134)

$\left[Me_2C{=}CMe_2\right]^{+\cdot}$ (135) (27%)

$\left[Ph_2C{=}C{=}C{=}CPh_2\right]^{+\cdot}$ (136) (15%)

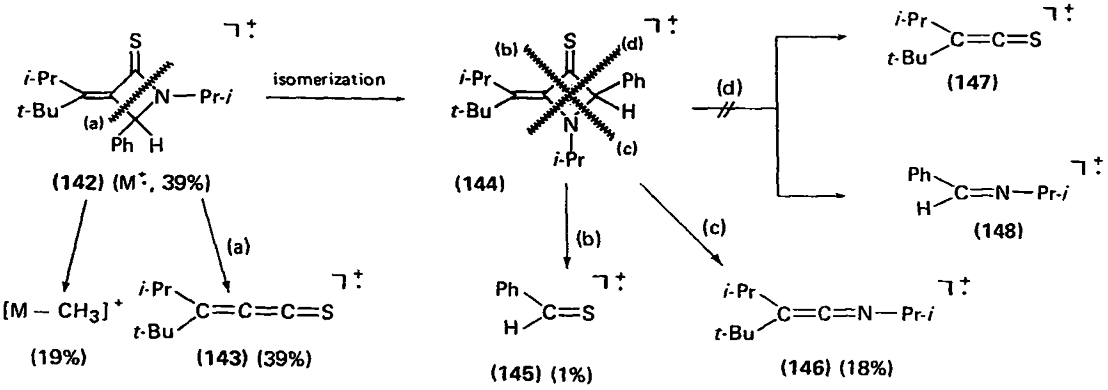
The main fragmentation of **137** is the elimination of HNCS which is followed by loss of methyl. The alternative process — loss of HNCO — is clearly less favoured[20] (Scheme 28).



SCHEME 28.

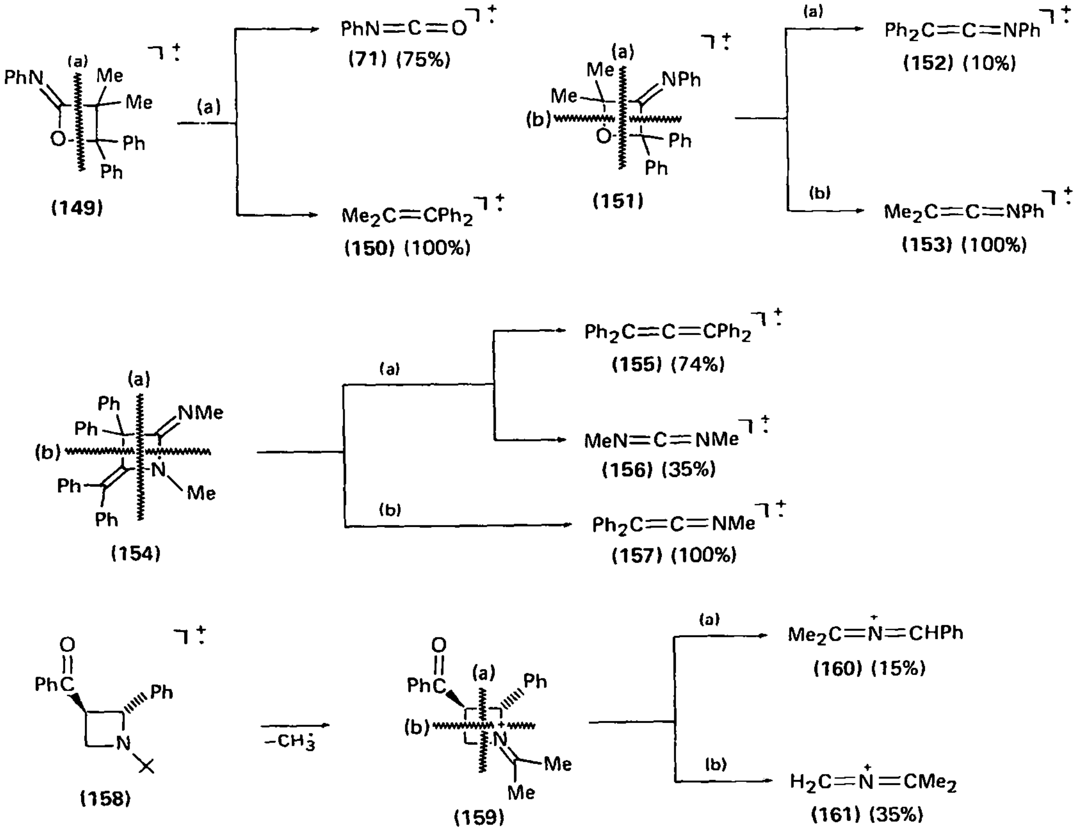
β-Thiolactams like **142** and their analogues[63] yield several fragments with cumulated double bonds under electron impact (Scheme 29). **142** forms **143** by cycloreversion. The formation of **145** and **146** results from a combination of isomerization and cycloreversion. No fragmentations of **144** following mode (d) could be observed.

Scheme 30 gives some further examples for cycloreversions of four-membered ring systems. The fragments **71** and **150** from **149** carry the positive charge. **149** does not show a sequence (b) which would formally correspond to an inversion of a thermic [2 + 2] cycloaddition. This type of reaction yields the base peak (**153**) in the spectrum of **151**. In addition **151** forms the ionized ketene imine **152**[64]. The iminoazetidine **154** gives ionized fragments for both fragmentation pathways. The most intensive ion **157** may be interpreted as [2 + 2] cycloreversion[65] (sequence b). The mass spectrum of the azetidine derivative **158**[66] shows that *fragment ions* may undergo cycloreversion, too. The ion **159** which is formed by loss of methyl from



SCHEME 29.

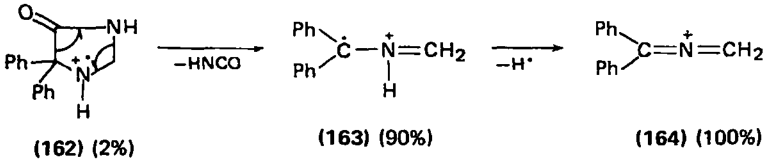
158 gives the intensive fragments **160** and **161**. This fragmentation may be interpreted as a cycloreversion. The fragments which contain the nitrogen carry the positive charge (Scheme 30).



SCHEME 30.

2. *Five-membered ring systems*

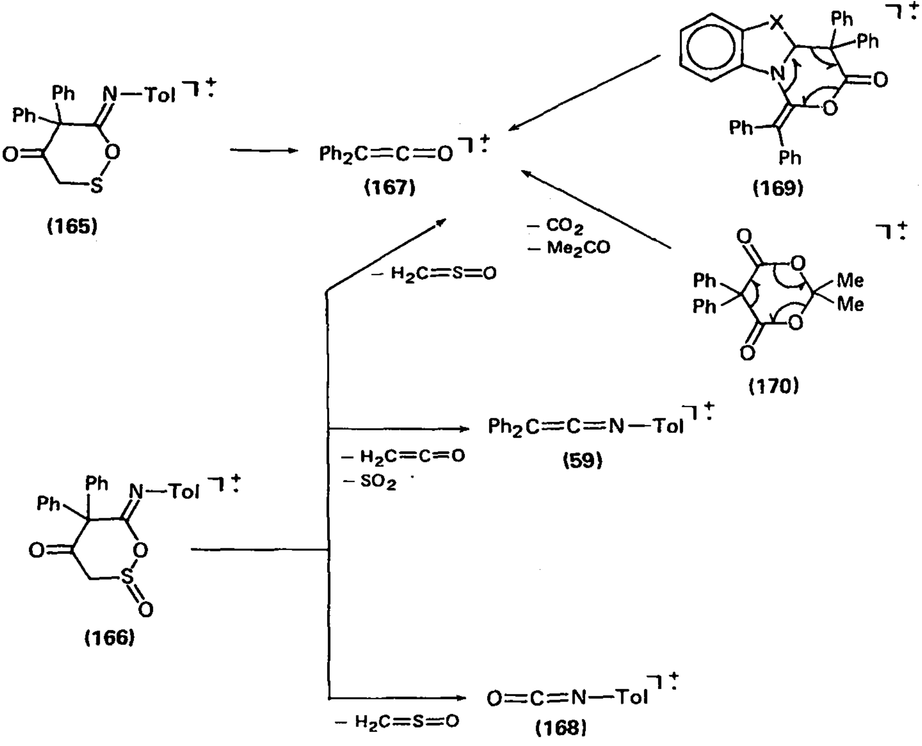
5,5-Diphenylimidazolidone-4 (**162**) decomposes under electron impact by loss of HNCO (**163**) followed by hydrogen abstraction which leads to the azaallene **164**[67] (Scheme 31).



SCHEME 31.

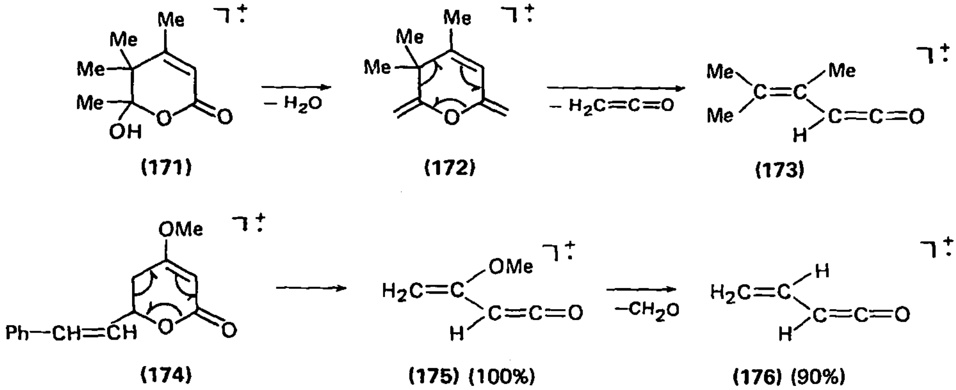
3. *Six-membered ring systems*

It is interesting to compare the electron impact induced cycloreversions of **165** and **166**[22]. Whereas **165** yields mainly **167**, the sulphoxide **166** shows a variety of reactions which lead to $H_2C{=}C{=}O$ and SO_2, and $H_2C{=}S{=}O$ (cycloreversion). **167** is generated by decomposition of **169**[68] and **170**[69], too.



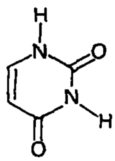
SCHEME 32.

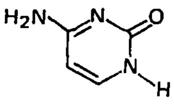
Six-membered rings already containing one double bond very often give a cyclic fragmentation (Retro-Diels–Alder, RDA) which leads to a variety of products with cumulated double bonds. Some examples of the numerous references should be cited here. The electron impact induced dehydration of the δ-lactol **171** to **172** is followed by ketene elimination to yield **173**[70]. RDA cleavage of **174** gives **175** which further loses CH_2O and forms ionized vinylketene (**176**)[71] (Scheme 33).

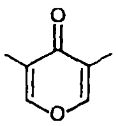


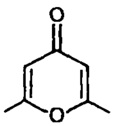
SCHEME 33.

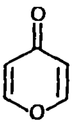
Uracil (**177**), cytosine (**178**), thymine (**179**) and 6-methyluracil (**180**) give completely different RDA fragmentation products enabling one to differentiate between these compounds[72]. Especially the isomers **179** and **180** (Scheme 34) may be easily distinguished by their mass spectra. Both ions lose HNCO. However, the reactivity of these two primary fragment ions is completely different: **181** loses H$^•$, but no methyl, whereas **184** loses methyl, but no H$^•$. The isomeric γ-pyrones **187** and **188**[73] show similar behaviour.

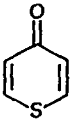

(177)


(178)


(187)

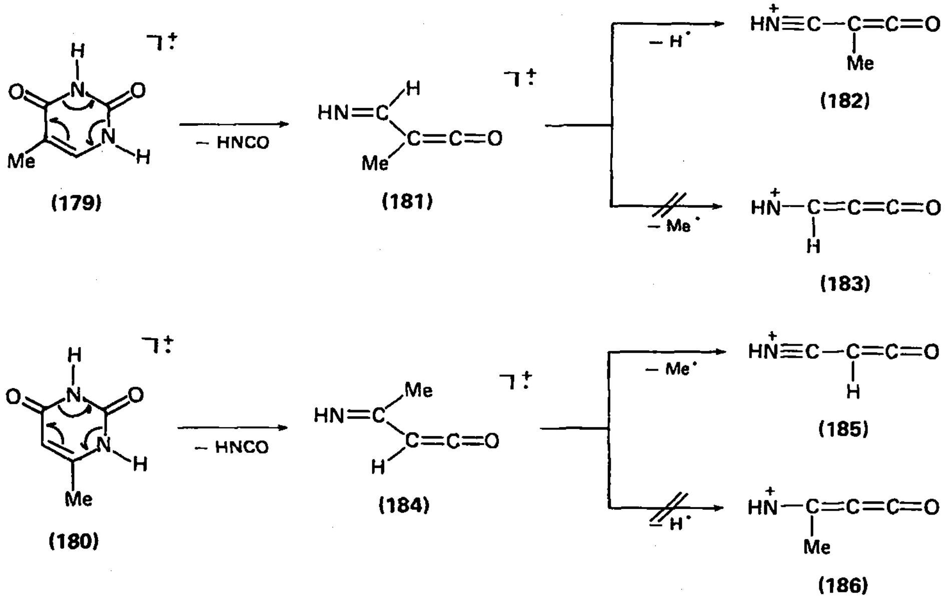

(188)


(189)


(190)

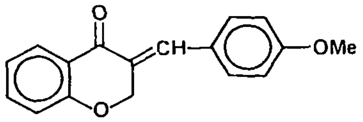

(191)

The mass spectra of **189**[73] and **190**[74] contain quite characteristic fragments. The abundance of these ions is probably caused by the stability of the ketene-like structures. It should be pointed out that **191** does not fragment via a RDA reaction[75].

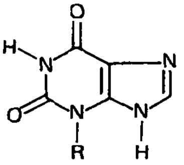


SCHEME 34.

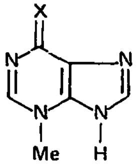
The bicyclic compounds **192**[76], **193** and **194**[77] show the formation of fragments with ketene structures as well. **197**, which is the base peak in the spectrum of **195**, may be explained by assuming that an isomerization (**195** → **196**) precedes the elimination of X–NSO (X = H,D)[78]. The mechanism of the RDA fragmentation of the sesquiterpenes **198**–**201** has been thoroughly studied[79]. If the RDA fragments are generated via a concerted reaction the stereochemistry of the ring conjunction A/B should influence the intensity of the RDA fragments. Following the rules of orbital symmetry one should expect that the *trans* isomer gives a lower intensity for **202** than the *cis* isomer. The experimental data show that there is no unique correlation between the stereochemistry of these compounds and the reaction mechanism. The detailed mechanism has still to be revealed.



(192)

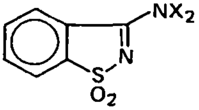


(193)

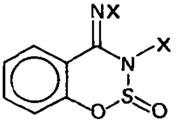


(194)

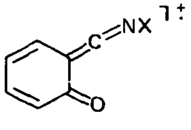
X = O, S



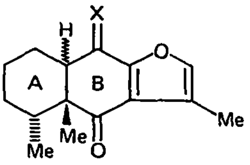
(195)



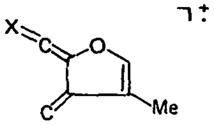
(196)



(197)



(198)–(201)

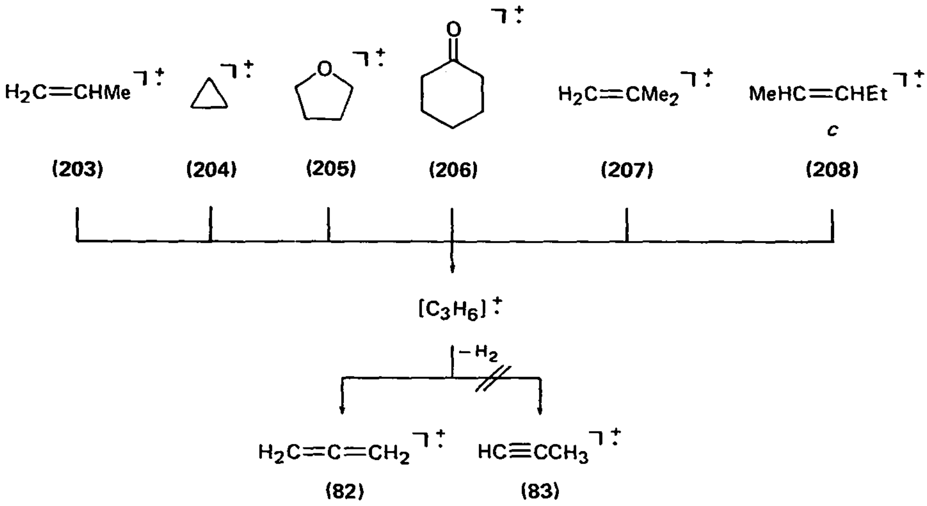


(202)

	X	A/B	Rel. intensity 202
198	H_2	*cis*	100%
199	H_2	*trans*	100%
200	O	*cis*	8%
201	O	*trans*	6%

C. Complex Multistep Rearrangements

A detailed analysis[80] of the $C_3H_4^{+\cdot}$ ion which is formed from the $C_3H_6^{+\cdot}$ ions of 203–208 showed clearly that ionized allene (82) is formed exclusively*. Appearance potential measurements, the activation energy determination and the peak-shape analysis exclude the formation of ionized propyne (83). The hydrogen abstraction leading to 83 would have an activation energy which is 20 kcal/mol higher than that for the formation of allene 82 (Scheme 35).



SCHEME 35.

Ionized allenes may be formed by fragmentation of acetylenic compounds, too. Hydrogen is transferred to the ionized triple bond via a six-membered transition

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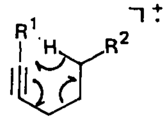
* A detailed description for the mechanism of $H^{\cdot}$ loss from 82 has been given by: R. Stockbauer and H. M. Rosenstock, *Int. J. Mass Spectrom. Ion. Phys.*, 27, 185 (1978).

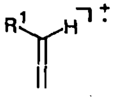
state. Reactions which correspond to this type of rearrangement have been thoroughly studied by Djerassi and coworkers[81]. Disubstituted acetylenes like **209**[81,82] react via a six-membered transition state, leading to **210**. Monosubstituted alkynes with longer alkyl chains, however, prefer hydrogen transfer via an eight-membered transition state (e.g. **211**)[83]. The structure of the resulting key fragment *m/e* 82 (C_6H_{10}) is still unknown.



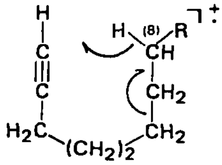
(209)

R^1 = H, alkyl

R^2 = alkyl, alkynyl



(210)

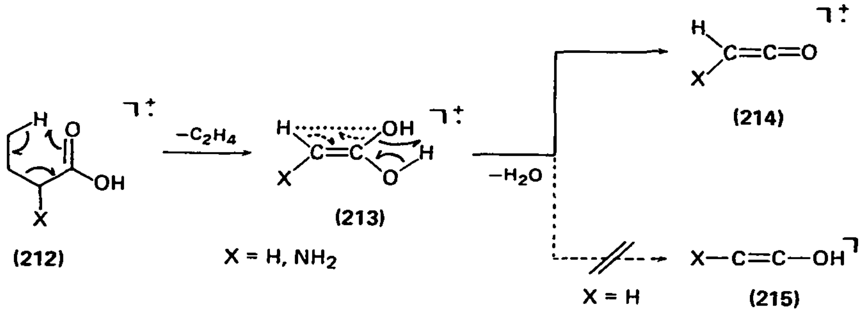


(211)

R = H, alkyl

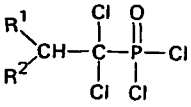
Unsubstituted ketene as well as its substituted derivatives and heterocumulenes may be formed from different classes of compounds*. Open- and closed-shell ketene cations can be observed.

The carboxylic acids **212** (X = H) as well as the α-amino acids (X = NH_2) give the fragment **213** (McLafferty rearrangement). For **213** (X = H) it can be proved by labelling that elimination of water gives exclusively **214**[84]. Whether this is also true for the fragmentation of the analogous NH_2-substituted ion is not yet known[85] (Scheme 36).



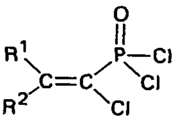
SCHEME 36.

Substituted ketene radical cations **218** are formed by a sequence of rearrangements from α,α-dichloroalkylphosphinic acid chloride (**216**)[86]. **217** is an important intermediate which forms **218** by transfer of an oxygen and the elimination of PCl_3.

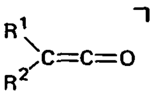


(216)

R^1, R^2 = H, alkyl, chlorine



(217)



(218)

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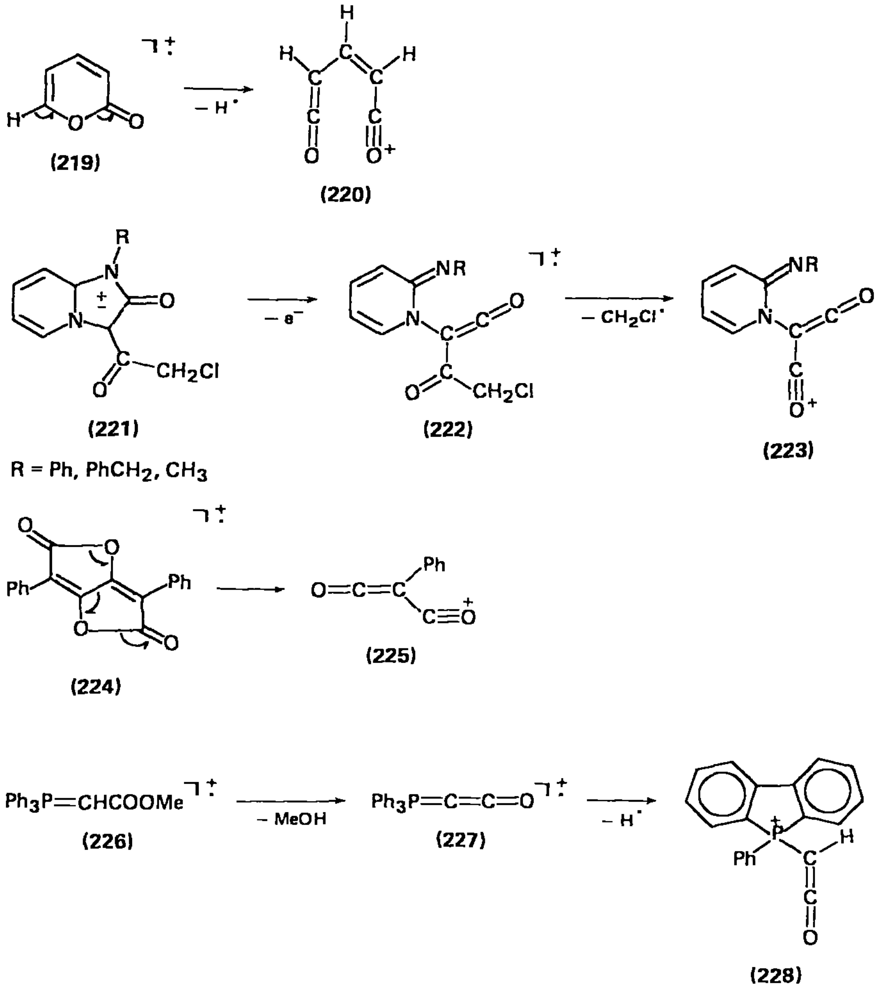
* An interesting mode of formation of ionized ketene via alkane elimination has been recently reported by J. F. Litton, T. L. Krüger and R. G. Cooks, *J. Amer. Chem. Soc.*, 98, 2011 (1976).

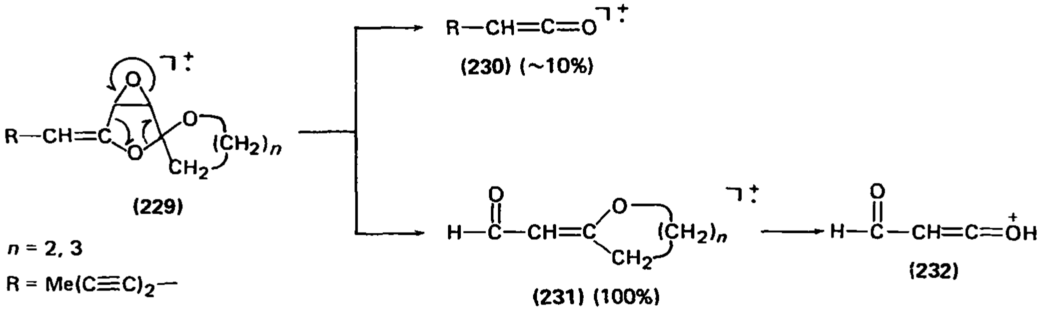
Starting with **217** as a molecular ion one also observes an intensive fragment **218** (100%).

Closed-shell cations with ketene structures may be formed from very different precursors (Scheme 37). 2-Pyrone (**219**) loses specifically the hydrogen from $C_{(6)}$ and forms **220**[87]. The mesoionic pyridine derivative **221** decomposes by elimination of a chloromethyl radical to **223**[88]. The pulvinic acid derivative **224** gives exclusively **225** (100%)[89]. Substituted ketenes are generated from alkylidenetriphenylphosphorone (e.g. **226**)[90]. The first step is a formal 1,2-elimination of methanol (**227**). **228** is formed by hydrogen abstraction and an extensive rearrangement (Scheme 37).



SCHEME 37.

The mass spectra of naturally occurring spiroketalenol ether polyynes (e.g. **229**)[91] give characteristic fragments of a high analytical significance (Scheme 38). The key fragment **232** may be formed by different mechanisms, the details of which are still unknown.

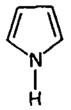


SCHEME 38.

Nitrogen-containing heterocumulenes may be generated from various precursors. The existence of four stable ion structures can be proved by extensive ^{2}H-labelling and collisional activation spectra[3] for the ion $C_2H_3N^{+\bullet}$. One of these structures is 233[92]. The mechanistic details of the formation of $C_2H_3N^{+\bullet}$ from 234–238 seem to be very complex. However, the azaallene 239 is formed by a simple α cleavage from 240 and 241[93,94].

$H_2C{=}C{=}\overset{+\bullet}{N}H$

(233)



(234)

MeHC=CHCN

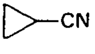
(235)

$H_2C{=}CHCH_2CN$

(236)

$H_2C{=}CMeCN$

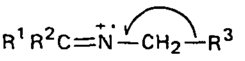
(237)



(238)

$R^1R^2C{=}\overset{+}{N}{=}CR^3R^4$

(239)

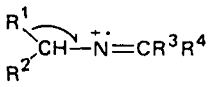


(240)

$R^1 = H$

R^2 = aryl

R^3 = alkyl



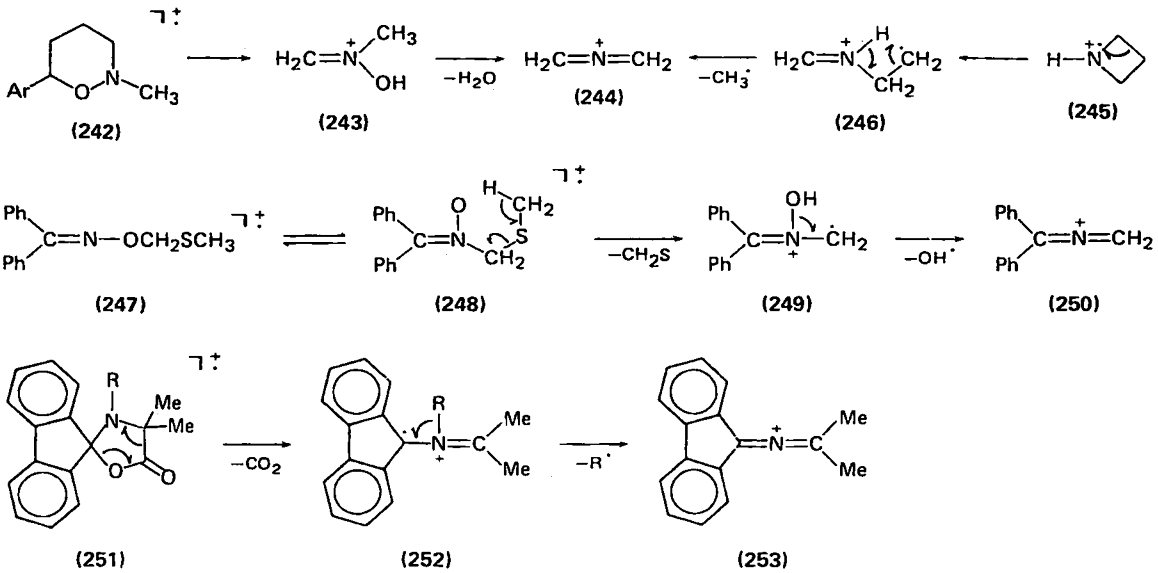
(241)

R^1 = alkyl

R^2 = aryl

R^3, R^4 = H, alkyl

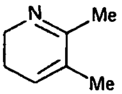
Species of the general structure 239 may be formed by a combination of many fragmentation processes. The 1,2-oxazine derivate 242 gives 243 and 244[95], the latter is also formed from isomerized azetidine 245 via 246[96]. The substituted azaallenes 250[97] and 253 result from a combination of McLafferty rearrangement and a consecutive loss of $OH^\bullet$ or alternatively cycloreversion followed by an alkyl elimination (Scheme 39)[98].



R = alkyl

SCHEME 39.

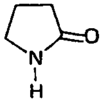
The existence of ionized heterocumulenes with more than one heteroatom or more than two cumulated double bonds has been postulated repeatedly. The dihydropyrazine **254** gives via ring-opening and consecutive elimination of methyl and acetonitrile the ion **255**[99]. Pyrrolidone (**256**)[100] and piperidone (**257**)[101] form **258** by α cleavage, H transfer and alkyl elimination. Aziridinones (**259**)[102] and the diaziridinone **260**[103] yield ions of the general structure **261**. The intensity of this ion depends highly on the kind of substitution.



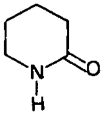
(254)

$H_2C{=}\overset{+}{N}{=}C{=}CH_2$

(255)



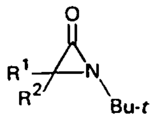
(256)



(257)

$H_2C{=}\overset{+}{N}{=}C{=}O$

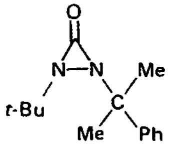
(258)



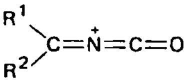
(259)

R^1 = H, alkyl, aryl

R^2 = alkyl, aryl

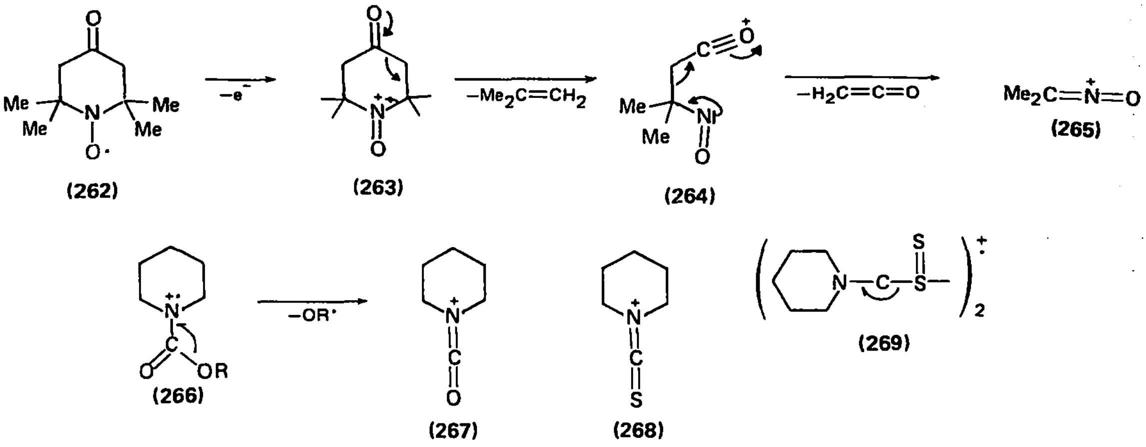


(260)



(261)

The nitroxide **262** fragments by heterolytic elimination of ketene to **265**[104] which shows a similar structure to the fragment **267**[105] from piperidine-*N*-carboxylate (**266**). The sulphur-containing compound **268** is formed by an α cleavage from **269**[106] (Scheme 40).



SCHEME 40.

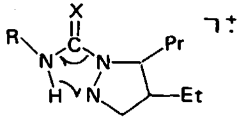
The radical cation **270** is formed from the pyrazoline derivative **271**[107] and substituted selenoureas **272**[108] (elimination of pyrazoline, respectively amine). Ionized carbodiimides (**273**) result from a combination of CO extrusion and elimination of alkyl nitrile from **274**. The intensity of this fragment depends highly on the electronic properties of the substituent R^1. Electron donors strongly facilitate the formation of this ion[109]. The cations **275**[110], **276**[110] and **277**[111] which are formed from **278**, **279** and **280** belong to the class of heterocumulenes, too [**278**: elimination of CONH and H$^\bullet$; **279**: elimination of NH_3; **280**: consecutive elimination of C_6H_4 (aryne) and H_2O].

$R{-}N{=}C{=}X^{\rceil +\cdot}$

(270)

R = aryl

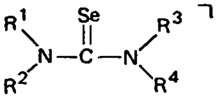
X = O, S, Se



(271)

R = aryl

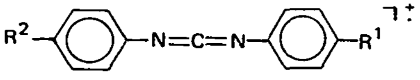
X = O, S



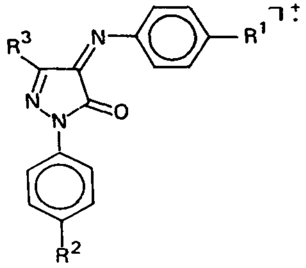
(272)

R^1, R^2 = H, alkyl

R^3, R^4 = H, alkyl, aryl



(273)



(274)

$Ph_2C{=}\overset{+}{N}{=}NH$

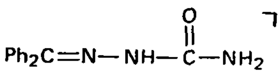
(275)

$Ph_2C{=}N{-}N{=}C{=}S^{\rceil +\cdot}$

(276)

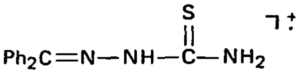
$Ph_3P{=}C{=}P{=}O^{\rceil +\cdot}$

(277)



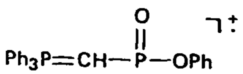
$[Ph_2C{=}N{-}NH{-}C({=}O){-}NH_2]^{+\cdot}$

(278)



$[Ph_2C{=}N{-}NH{-}C({=}S){-}NH_2]^{+\cdot}$

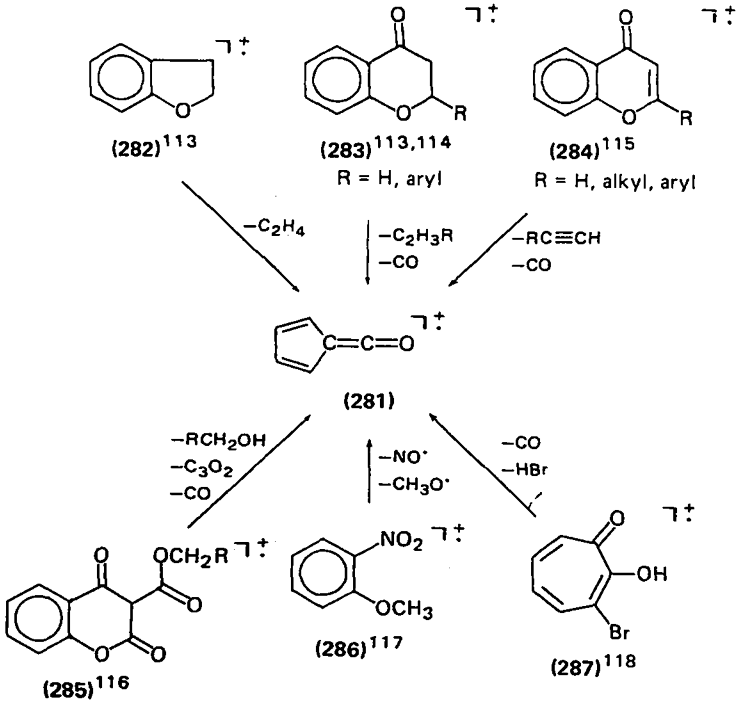
(279)



$[Ph_3P{=}CH{-}P({=}O){-}OPh]^{+\cdot}$

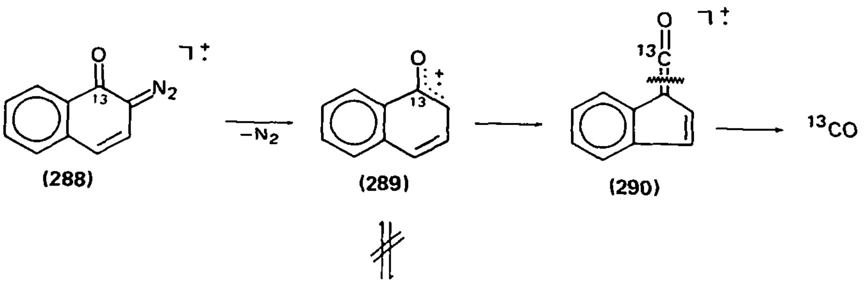
(280)

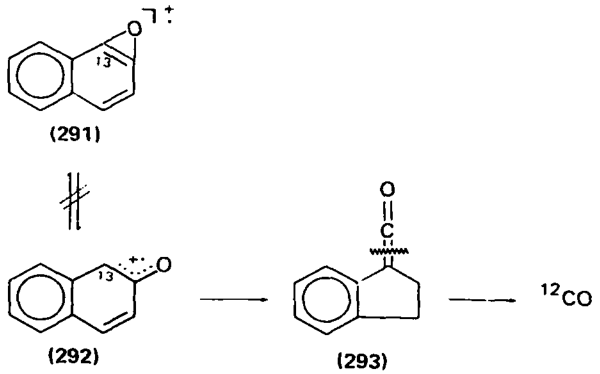
Scheme 41 gives some examples for the formation of the ionized heterocumu-ne **281**. It should be noted that the neutral species can be formed under thermal nditions, too. Identification was based on spectroscopic methods[112]. The mechan-tic details of the fragmentations given in Scheme 41 are not yet clear.



SCHEME 41.

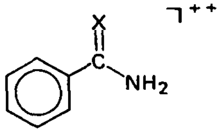
The elimination of N_2 from **288** leads to ring-contracted ketenes[119], in analogy the photochemical reaction. The fact that **289** loses exclusively ^{13}CO indicates at the ring-contraction does not proceed via the ionized oxirene **291**.





SCHEME 42.

Holmes and Benoit[120] suggested structures **295** with cumulated double bonds for those reactive M^{2+} ions of benzamide and thiobenzamide (**294**) which lose CX (X = O, S) subsequently.



(294)
X = O, S

$$X{=}C{=}\overset{+}{C}{-}CH{=}CH{-}CH{=}CH{-}CH{=}\overset{+}{N}H_2$$

(295)

$$H\overset{+}{C}{=}C{=}CH{-}CH{=}CH{-}CH{=}\overset{+}{N}H_2$$

(296)

Beynon and coworkers[121] have shown that the kinetic energy release of metastable ion decomposition processes correlates very well with the distance of the two positive charges. In a first approximation equation (2) is valid:

$$R(\text{Å}) = \frac{14.39}{T_{\text{kin}}(\text{eV})} \tag{2}$$

The value of R gives the *minimum* distance in Å between the centres carrying the positive charge. Beynon[122] suggested the structures **297** and **298** for the cations $(C_mH_2)^{++}$ (m = 2–5) and $(C_nH_6)^{++}$ ($n > 6$).

$$[C_mH_2]^{++} \qquad H{-}\overset{+}{C}{=}(C)_{m-2}{=}\overset{+}{C}{-}H$$

(297)
$m = 2–5$

$$[C_nH_6]^{++} \qquad H_3C{-}\overset{+}{C}{=}(C)_{n-4}{=}\overset{+}{C}{-}CH_3$$

(298)
$n > 6$

V. ACKNOWLEDGEMENTS

We wish to thank the *Gesallschaft von Freunden der Technischen Universität Berlin* and the *Fonds der Chemischen Industrie*, Frankfurt, for financial support.

H.S. gratefully acknowledges the receipt of a fellowship in the European Science Exchange Programme (Deutsche Forschungsgemeinschaft, Bonn – Bad Godesberg, The Royal Society, London) and a Fellow Commonership (1977/78) of Churchill College, Cambridge.

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The Chemistry of Ketenes, Allenes and Related Compounds
Edited by Saul Patai

CHAPTER 7

The preparation of ketenes

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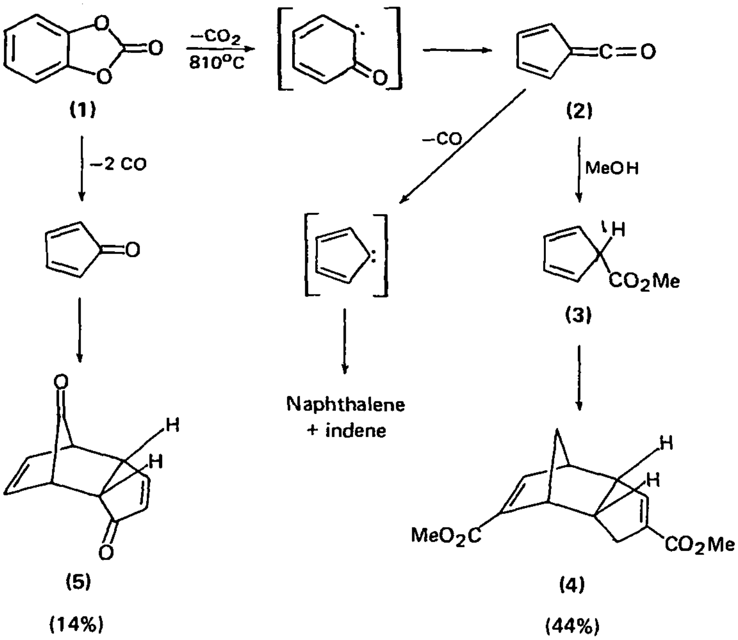
I. INTRODUCTION

The number of ketenes which have been isolated and characterized is in fact relatively small, but fortunately many more have been either generated *in situ* or identified as transient reactive intermediates. This chapter deals primarily with the methods which have been used to prepare stable ketenes and which have been used to generate ketenes *in situ*. However, reactions which have been shown to generate ketenes as fleeting reactive intermediates are also included, particularly where there is some evidence that a ketene is actually formed or where its subsequent reactions are of interest. The methods which have been used to prepare thioketenes are also described. Particular attention has been focused on recent developments and improvements which have been reported since the publication of the last chapter on ketenes in this series[1], and since the last major review of ketene chemistry[2]. A number of other reviews dealing with the preparation of ketenes and their generation *in situ* have also been published[3–5].

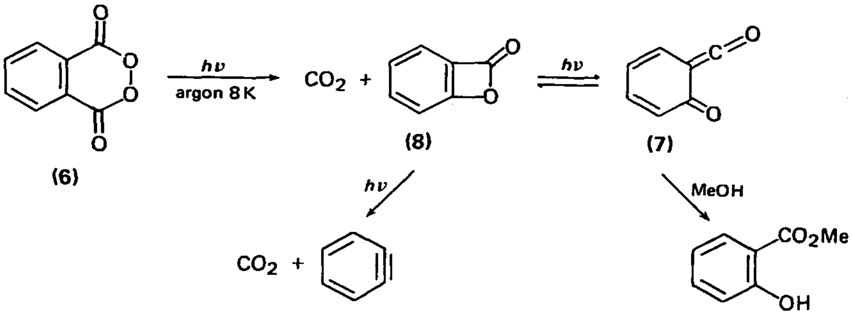
The ease of preparation and isolation of ketenes is very dependent upon their reactivity, particularly towards dimerization and oxidation. Monomethylketene, for example, can be kept at room temperature for only a few minutes before dimerization is complete, whilst dimethylketene dimerizes in about one hour at the same temperature. In contrast, diphenylketene can be stored for several months without dimerizing. Most ketenes are very sensitive to atmospheric oxidation.

The use of modern spectroscopic techniques and the development of other methods for studying reactive intermediates, such as flash thermolysis and matrix isolation, have considerably aided the task of generating and identifying reactive ketenes. Flash thermolysis in particular has found wide application in the synthesis of thermolabile compounds and in the investigation of thermolytic reactions[6]. Thermolabile products which cannot be isolated from conventional pyrolysis reactions can be obtained even on a preparative scale by flash thermolysis. Suffice it at this stage to consider briefly just two studies involving such techniques.

Flash thermolysis of *o*-phenylene carbonate (**1**), by passing it in a stream of nitrogen through a heated quartz tube gives indene and naphthalene as major products. If, however, methanol is introduced into the nitrogen stream the intermediate ketene **2** is trapped as the cyclopentadiene ester **3** which rearranges and dimerizes to give **4**[7]. A dimer (**5**) of cyclopentadienone, formed by loss of two molecules of carbon monoxide from (**1**), is also obtained[8].



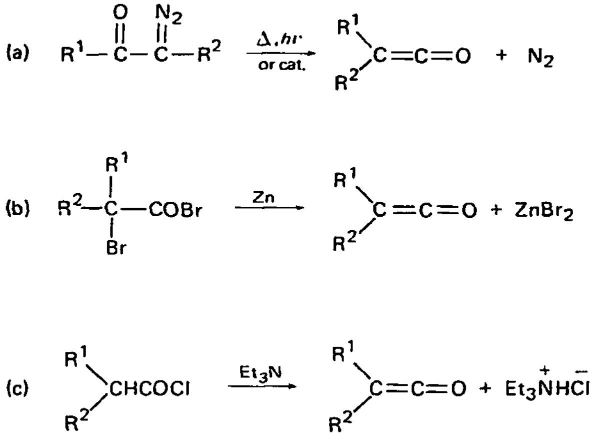
Irradiation of phthaloyl peroxide (6) as a matrix isolated in argon at 8 K gives infrared bands characteristic of the ketene 7 and the lactone 8[9]. The ratio of the ketene to the lactone is strongly dependent upon the wavelength used. The wavelength dependence is a consequence of the photochemical interconversion of the ketene and the lactone. Short wavelengths convert essentially all the lactone into the ketene while long wavelengths regenerate the lactone. Irradiation of phthaloyl peroxide in a matrix containing methanol initially gives infrared bands due to the ketene, but on warming these disappear and are replaced by bands characteristic of methyl salicylate. Prolonged irradiation of phthaloyl peroxide affords benzyne[10].



The first part of this chapter describes some general methods and procedures which have been used to prepare ketenes. The second part of the chapter considers individually the various types of ketenes (and thioketenes) which have been prepared and describes the specific methods which have been used to prepare them.

II. GENERAL METHODS AND PROCEDURES

Although improvements in experimental techniques and detection facilities have made possible the generation and identification of a wide variety of reactive ketenes, it is interesting to note that many of the methods widely used to prepare more stable ketenes were developed by Staudinger and others at the beginning of the present century. A summary of some of the more important general methods which have been used to prepare ketenes is shown in Figure 1.



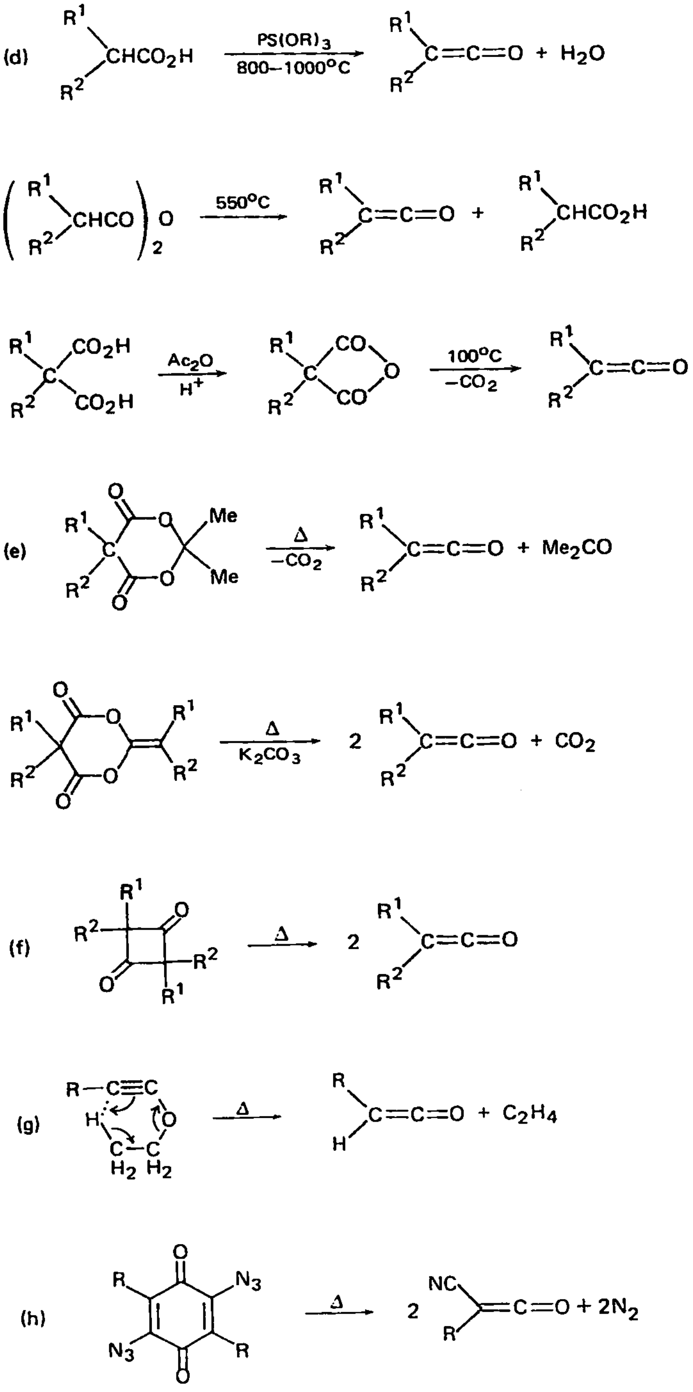
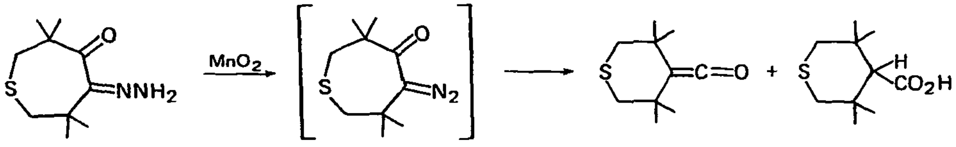

(d)
PS(OR)3
800–1000°C
H2O
550°C
Ac2O
H+
100°C
−CO2
(e)
Me
Me
Δ
−CO2
Me2CO
Δ
K2CO3
CO2
(f)
Δ
(g)
Δ
C2H4
(h)
Δ
2N2

FIGURE 1.

A. Wolff Rearrangement of α-Diazocarbonyl Compounds

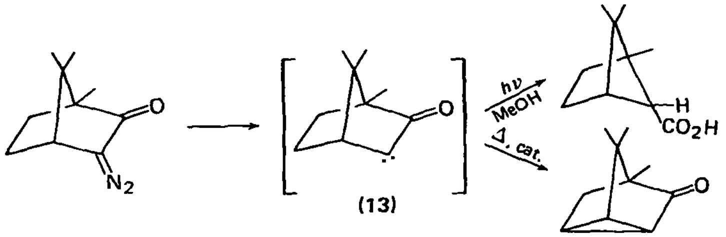
The Wolff rearrangement of α-diazocarbonyl compounds can be brought about thermally or photochemically and can also be brought about by a number of catalysts of which silver oxide is the most frequently used[11]. The preparative value of the reaction can be attributed to the reactivity and ready accessibility of α-diazocarbonyl compounds[12]. The Wolff rearrangement has proved particularly useful for the preparation of arylketenes (Section III.C), but is also widely used to prepare carboxylic acid derivatives by the Arndt–Eistert procedure and by ring-contraction.

The thermal stability of α-diazocarbonyl compounds is dependent upon both steric and electronic factors[11]. Oxidation of the ketohydrazone **9** with manganese dioxide gives the diazo ketone **10** which spontaneously decomposes to give the ketene **11** and the acid **12** in 49% yield[13]. The instability of the diazo ketone is in this case due to twisting of the $COCN_2$ group caused by ring strain. In other cases, where more severe conditions are required, there is always the risk of fragmentation of the ketene (see below).

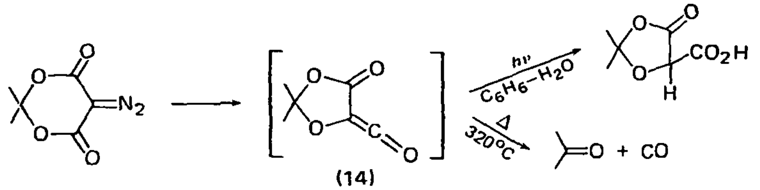


(9) (10) (11) (12)

The photochemically-induced Wolff rearrangement is frequently superior to other methods, especially in cases where the thermal and catalytic reactions merely lead to C–H insertion by the intermediate carbene (e.g. **13**)[14], or fragmentation of the ketene (e.g. **14**)[15].



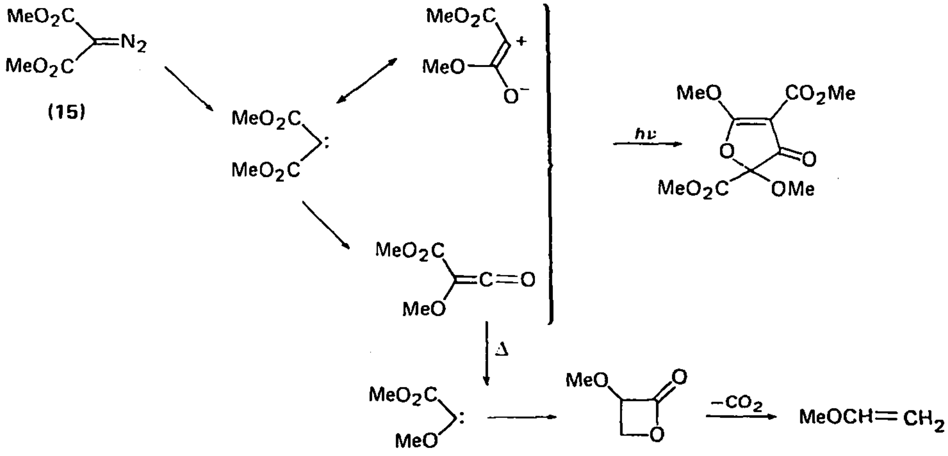
(13)



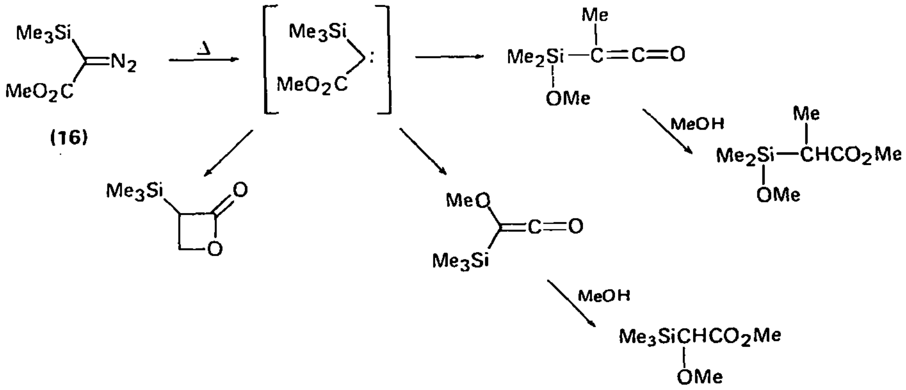
(14)

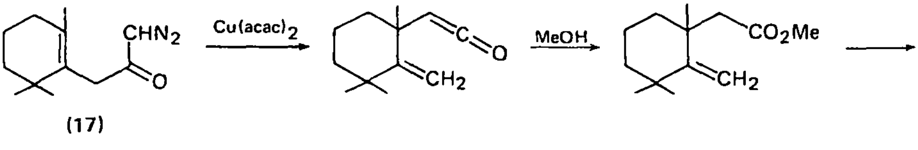
Many papers have been published on the Wolff rearrangement of α-diazo ketones. It is known for example that *t*-butyl groups display only a limited tendency to migrate[16]. The presence of other functional groups, particularly at the α position, or the introduction of a double or triple bond α,β to the carbonyl group, can interfere with the rearrangement or lead to the formation of secondary products[17].

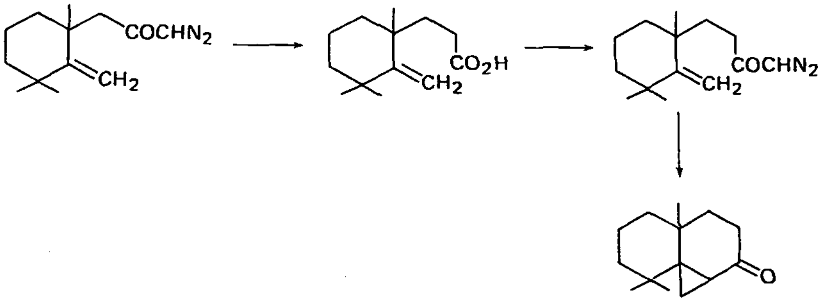
The Wolff rearrangement of the diazomalonate ester **15** has been studied both by photolysis in solution and by flash thermolysis. The product of the photolytic reaction is a dihydrofuranone, while in the thermolytic reaction methyl vinyl ether is the major product at high temperatures (500°C)[18].



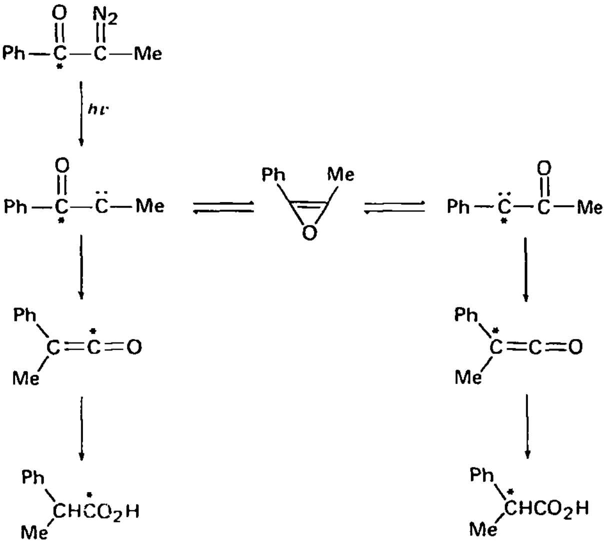
Evaporation of the diazo ester (**16**) through a pyrex tube heated to 360°C followed by treatment of the condensate with methanol gives three products, two of which clearly result from the trapping of ketene intermediates[19]. A vinylogous Wolff rearrangement occurs in the Cu^{2+}-catalysed reaction of **17** and forms part of an interesting synthesis of (±)-dihydromayurone involving three diazo ketone reactions[20].







Kinetic studies indicate that the Wolff rearrangement is a two-step reaction involving migration to an electron-deficient centre[21a]. Although 1,3-dipoles and diradicals have been suggested as possible intermediates most of the available evidence supports the conclusion that the key intermediate is a singlet carbene[11]. Carbene–carbene rearrangements via oxirenes have been demonstrated by carbon labelling (Scheme 1)[21b]. In the Ag$^+$-catalysed reaction, however, it is possible that loss of nitrogen and rearrangement may occur more or less simultaneously.



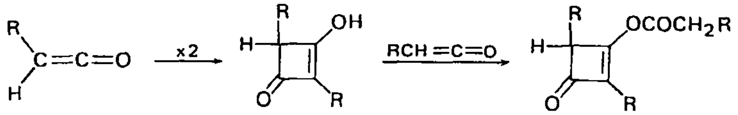
SCHEME 1.

B. Dehalogenation of 2-Haloacyl Halides

The oldest method for preparing ketenes, used by Staudinger in his classical synthesis of diphenylketene[22], involves treating an α-haloacyl halide with activated zinc. Ether or ethyl acetate are usually used as solvents since they dissolve the zinc bromide formed. The reaction gives excellent yields of stable ketenes but is less satisfactory for the preparation of dialkyl-, monoaryl- and monoalkylketenes. However a modified procedure for the preparation of dimethylketene has been described in which 2-bromoisobutyryl bromide is treated with zinc granules in ethyl acetate at reduced pressure. The dimethylketene codistils with the solvent in 46–54% yield[23]. More recently a modification of Staudinger's procedure (equation 1) which allows monoalkylketenes to be prepared free from starting materials and zinc salts, has been reported[24]. Using this procedure the α-bromoacyl bromide is treated with activated zinc dust suspended in dry tetrahydrofuran under reduced pressure. The alkylketene is formed immediately and codistils with the solvent.

$$\mathrm{RCHBrCOBr} \xrightarrow[\mathrm{THF}]{\mathrm{Zn}} \underset{(18)}{\mathrm{RCH{=}C{=}O}} + \mathrm{ZnBr_2} \qquad (1)$$

All attempts to isolate monoalkylketenes (18) prepared in this way free from the solvent have been unsuccessful[24]. The ketenes are obtained as a pale green solution showing an intense band at 2130 $\mathrm{cm^{-1}}$ in the infrared spectrum. The yield of the ketene can be estimated by treating the solution with excess aniline and determining the amount of unchanged aniline by back-titration. The yields of methyl- and ethylketene prepared by this method (equation 1) were 59.5 and 65.0% respectively. When a solution of methyl- or ethyl-ketene (18a,b) is allowed to stand at room temperature for 30 minutes or is kept at –30°C overnight the dimer (19) and trimer (20) are formed[24].



(18) (19) (20)

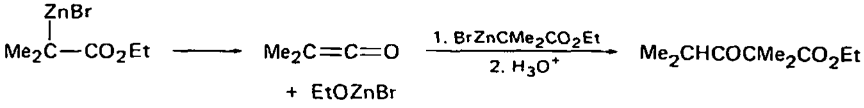
(a) R = Me

(b) R = Et

The dehalogenation of α-bromodiphenylacetyl bromide using triphenylphosphine has been reported[25]. The corresponding reaction of triphenylphosphine with bromoacetyl bromide at 0°C gives a solid enol phosphonium salt from which the ketene can be liberated on heating to 110°C (equation 2). When the whole reaction is carried out at 110°C the ketene is obtained directly.

$$\mathrm{Ph_3P} + \mathrm{BrCH_2COBr} \xrightarrow{0^\circ\mathrm{C}} \left[\begin{matrix}\text{enol phosphonium}\\ \text{salt}\end{matrix}\right] \longrightarrow \begin{matrix}\mathrm{H_2C{=}C{=}O}\\ + \mathrm{Ph_3PBr_2}\end{matrix} \qquad (2)$$

It has been suggested that ketenes could be generated under the conditions of the Reformatsky reaction[26]. Thus Vaughan has suggested the intervention of a ketene intermediate in the self-condensation of the zinc enolate of ethyl α-bromoisobutyrate (equation 3). Indeed it has been suggested that ketene intermediates may be involved in the self-condensation of other ester enolates. Certainly warming a tetrahydrofuran solution of the lithium enolate of *t*-butylbis(trimethylsilyl) acetate (21) produces the bis(trimethylsilyl)ketene (22)[27].

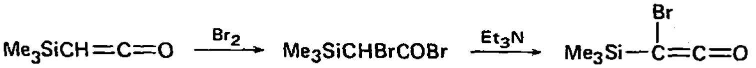


$$\mathrm{Me_2\overset{\overset{\displaystyle ZnBr}{|}}{C}{-}CO_2Et} \longrightarrow \begin{matrix}\mathrm{Me_2C{=}C{=}O}\\ + \mathrm{EtOZnBr}\end{matrix} \xrightarrow[2.\ \mathrm{H_3O^+}]{1.\ \mathrm{BrZnCMe_2CO_2Et}} \mathrm{Me_2CHCOCMe_2CO_2Et} \qquad (3)$$

$$\underset{(21)}{(Me_3Si)_2CHCO_2Bu\text{-}t} \xrightarrow[\substack{THF\\-78^{\circ}C}]{LDA} [\text{enolate}] \xrightarrow{r.t.} \underset{(22)}{(Me_3Si)_2C{=}C{=}O}$$

C. Dehydrohalogenation of Acyl Halides

This reaction has been widely used for the generation of ketenes and involves the elimination of a hydrogen halide from an acyl halide using a tertiary amine. The reaction is frequently used as a convenient method for generating ketenes *in situ* and is generally conducted in an ethereal solvent. However, this procedure can introduce additional complications which should not be overlooked[28]. For example, the dimerization of ketenes is catalysed by triethylamine hydrochloride and the method is not therefore ideally suited to the preparation of monoalkylketenes, which readily dimerize. However, in the absence of other methods, this reaction has been widely used for the preparation of ketenes. Indeed bromotrimethylsilylketene is stable in solution even at reflux temperatures in the presence of triethylammonium bromide (equation 4), but polymerizes immediately if the triethylammonium salt is removed[29]. Clearly in this case either an equilibrium exists or the triethylammonium salt exerts a stabilizing influence on the monomeric ketene.

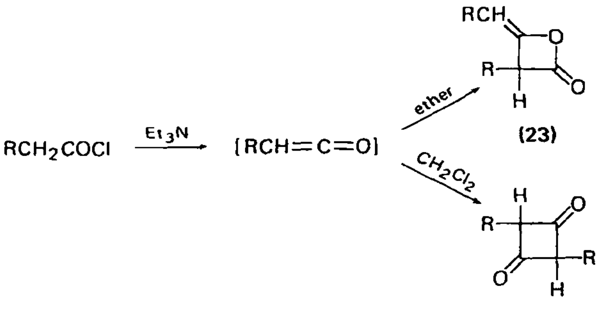


$$Me_3SiCH{=}C{=}O \xrightarrow{Br_2} Me_3SiCHBrCOBr \xrightarrow{Et_3N} Me_3Si{-}\overset{\displaystyle Br}{\overset{|}{C}}{=}C{=}O \qquad (4)$$

There is good evidence that the initial step in the dehydrohalogenation reaction involves the formation of an acylammonium salt. In the reaction of triethylamine with isobutyryl chloride the acylammonium salt has been detected by infrared and n.m.r. spectroscopy at low temperatures (equation 5)[30]. However, in the corresponding reaction of triethylamine with α-chloropropionyl chloride the intervention of an analogous acylammonium salt can only be inferred[31]. Another factor which complicates the preparation of some ketenes by this method is the formation of an α-halovinyl ester in a competing reaction involving an enolate anion (see Section III.D).

$$Me_2CHCOCl \xrightarrow{Et_3N} Me_2CHCO\overset{+}{N}Et_3\overset{-}{Cl} \longrightarrow Me_2C{=}C{=}O + H\overset{+}{N}Et_3\overset{-}{Cl} \qquad (5)$$

The dehydrohalogenation reaction has also been used to prepare monoalkylketene dimers (23) which are useful precursors for the preparation of β-keto esters[32]. If, however, the reaction is carried out in dichloromethane the dialkylcyclobutane-1,3-dione (24) is formed[33].

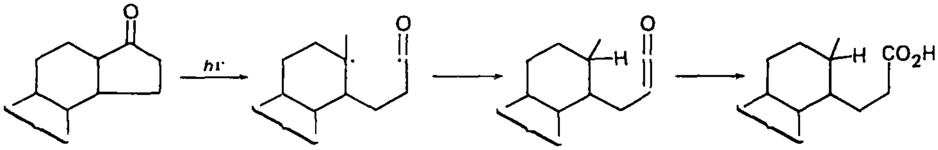


(24)

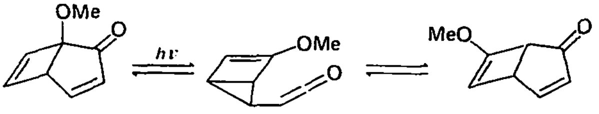
D. Decomposition of Ketones, Carboxylic Acids and Anhydrides

Ketene itself was first prepared by Wilsmore by the pyrolysis of acetone, ethyl acetate and acetic anhydride[34]. Ketene is in fact formed in varying amounts by pyrolysis of virtually any compound containing an acetyl group. In the laboratory it is usually prepared by decomposition of acetone vapour using an electrically heated nickel–chromium wire[35,36]. On an industrial scale ketene is usually prepared by pyrolysis of acetic acid.

Several photochemical reactions (equations 6–8) of ketones also yield ketenes either as transient intermediates or in some cases as stable products[37–40].



(6)



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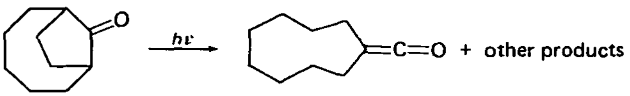


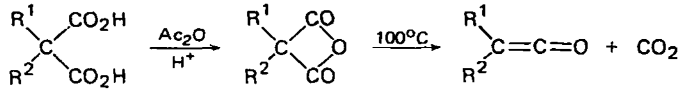
(8)

Mono- and di-alkylketenes have been prepared in yields ranging from 29–81.5% by heating the corresponding carboxylic acids in the presence of catalytic amounts of triethylthiophosphate (equation 9)[41]. Hasek and Elam have developed a method for making dialkylketenes in yields of 64–99% by pyrolysis of acid anhydrides (equation 10)[42]. Methylketene and dimethylketene can be readily prepared by pyrolysis of propionic and isobutyric anhydrides respectively[43,44], and dimethylketene can also be prepared by pyrolysis of isobutyric acid[45].

$$R^1R^2CHCO_2H \xrightarrow[800\text{–}1000^\circ C]{PS(OR)_3} R^1R^2C{=}C{=}O + H_2O \tag{9}$$

$$(R^1R^2CHCO)_2O \xrightarrow{550^\circ C} R^1R^2C{=}C{=}O + R^1R^2CHCO_2H \tag{10}$$

Ketenes can also be conveniently prepared by pyrolysis of the anhydrides of disubstituted malonic acids (26) which in turn can be prepared by treating the malonic acid (25) with acetic anhydride in the presence of a small amount of sulphuric acid[46]. The excess acetic anhydride and acetic acid are removed under reduced pressure, the sulphuric acid neutralized, and the residue heated to give the ketene. A disadvantage of this method is that the dialkylketene can react with any residual acetic anhydride to form a mixed anhydride (27) which disproportionates on heating to give the symmetrical anhydrides 28 and 29[47]. This problem can be



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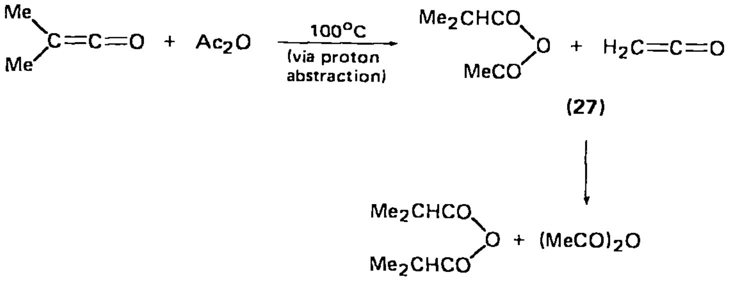


(27)

(28) (29)

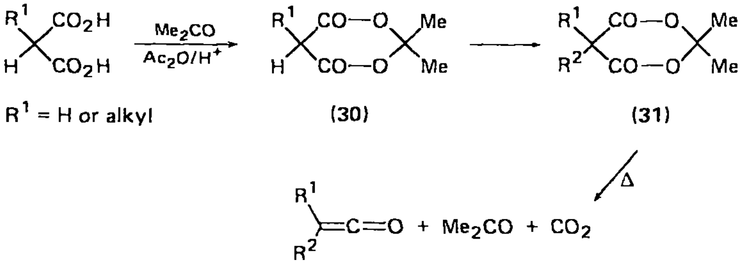
overcome by using isobutyric anhydride rather than acetic anhydride to bring about the initial dehydration. This has the advantage that it does not undergo proton abstraction by the dialkylketene.

An alternative route to ketenes from malonic acids involves heating a mixed anhydride of the acid. Mixed anhydrides of diphenylacetic acid have been frequently employed[46], but mixed anhydrides of trifluoroacetic acid can also be used (equation 11)[48]. Heating the mixed anhydride under reduced pressure converts it into the ketene.

$$R^1R^2C(CO_2H)_2 \xrightarrow{TFAA} R^1R^2C(CO_2COCF_3)_2 \xrightarrow[15-20\ Torr]{140-160^\circ C} R^1R^2C{=}C{=}O \qquad (11)$$

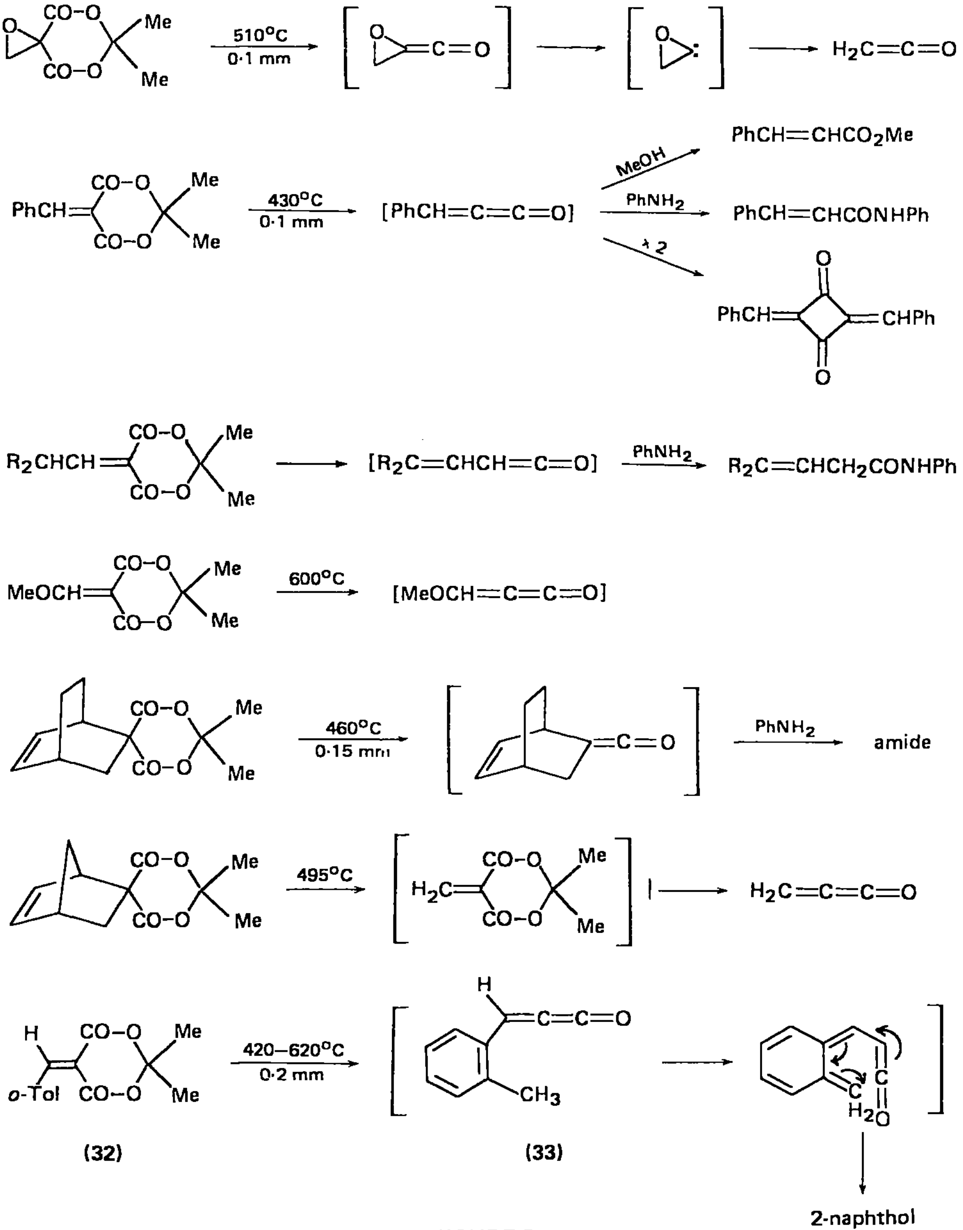
E. Decomposition of Ketone and Ketene Acylals

Acylals (30) are readily prepared by reacting monosubstituted (or unsubstituted) malonic acids with ketones in the presence of acetic anhydride and a trace of sulphuric acid. They can be alkylated to give the disubstituted (or monosubstituted) acylals (31). Heating such compounds then liberates the corresponding ketene[49].



R¹ = H or alkyl (30) (31)

Flash thermolysis of ketone acylals also affords ketenes (Figure 2). Thus flash thermolysis of the alkylidene and benzylidene derivatives affords methyleneketenes which readily dimerize to form cyclobutane-1,3-diones. Infrared measurements on the pyrolysis products collected at −196°C show absorptions attributable to the ketene, and reaction of the pyrolysate with methanol or aniline vapour affords the α,β-unsaturated ester or amide. Flash thermolysis of 32 affords β-naphthol in high yield, probably by way of the 2-methylbenzylideneketene (33), which undergoes a [1,5] hydrogen shift followed by cyclization[50].

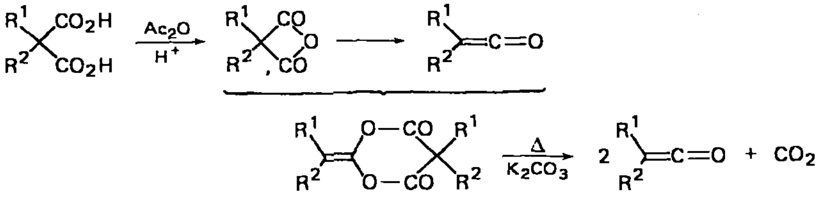


(32)

(33)

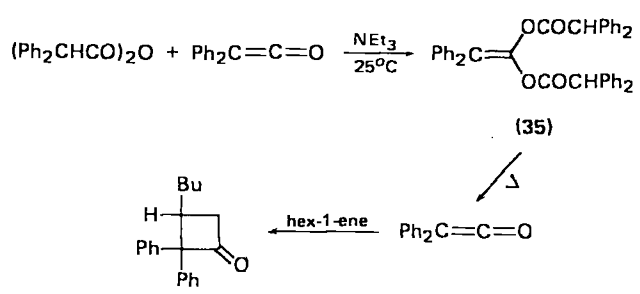
FIGURE 2.

Heating a dialkylmalonic acid with acetic anhydride at 60°C, with continuous removal of the acetic acid produced, affords the ketene acylal 34. This is a stable crystalline solid which serves as a convenient source of the dialkylketene, since it breaks down at relatively low temperatures in the presence of an alkaline catalyst to give the ketene in high yield[47].



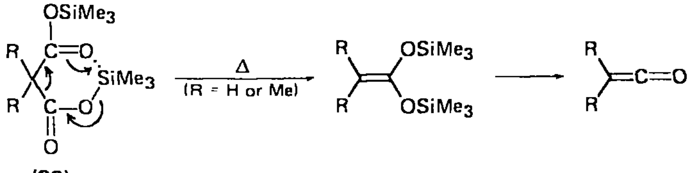
(34)

Huisgen and coworkers have recently reported the preparation of the acylal 35[51]. The formation of this compound by combination of diphenylacetic anhydride with diphenylketene is attributed to deprotonation of the anhydride by the tertiary amine followed by *O*-alkylation of the enolate so formed. The acylal can be used as an *in situ* source of diphenylketene. For example, heating it in hex-1-ene affords the corresponding cycloadduct in 63% yield.



(35)

Flash thermolysis of the trimethylsilyl esters of malonic and dimethylmalonic acids (36) affords ketene and dimethylketene respectively[52], but the analogous reaction of the trimethylsilyl ester of cyclopropane-1,1-dicarboxylic acid (37) follows a different course simply involving transfer of a trimethylsilyl group from oxygen to carbon.



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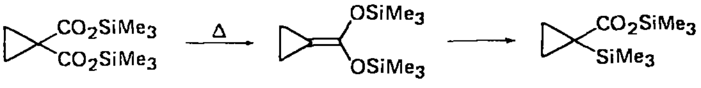
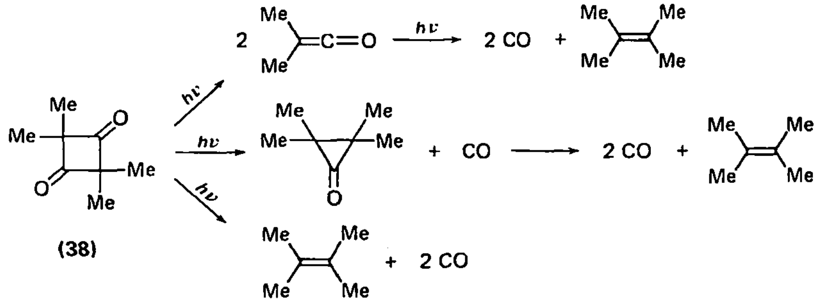


(37)

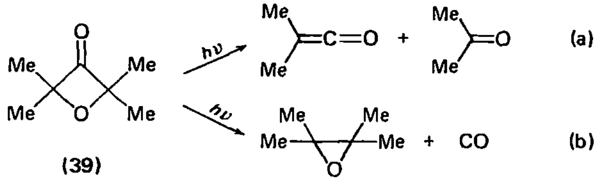
F. Decomposition of Ketene Dimers and Related Compounds

The thermal decomposition of cyclobutane-1,3-diones and alkylidenepropiolactones affords a convenient way of generating pure ketenes. Ketene itself can be obtained in quantitative yield and the dimers of methylketene and dimethylketene can be converted into the corresponding monomeric ketenes in 80–100% yield by passing them through a hot tube or over a hot filament.

The photochemical decomposition of ketene dimers is also a potential route to ketenes but side-reactions tend to detract from its value as a preparative method. Haller and Srinivasan have studied the photolysis of tetramethylcyclobutane-1,3-dione (38) in a nitrogen matrix at 4 K and in solution at room temperature. They found that in solution only a fifth of the molecules decompose to give dimethylketene while the rest decompose directly to give tetramethylcyclopropanone or tetramethylethene[53].


(38)

In the photolysis of the oxetanone 39 two competing modes of decomposition are observed. In polar solvents path (a) predominates, while in nonpolar solvents (a) and (b) are equally important[54]. Photolysis of cyclobutanones (40) and azetidinones (41) also afford ketenes[55].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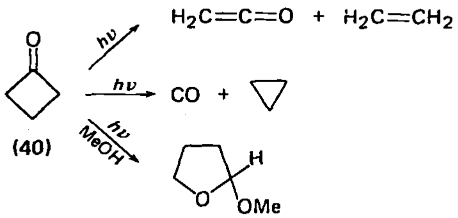
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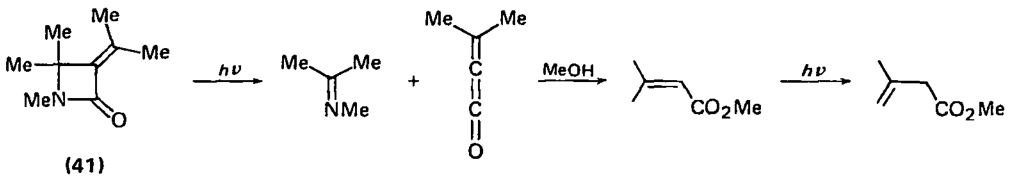
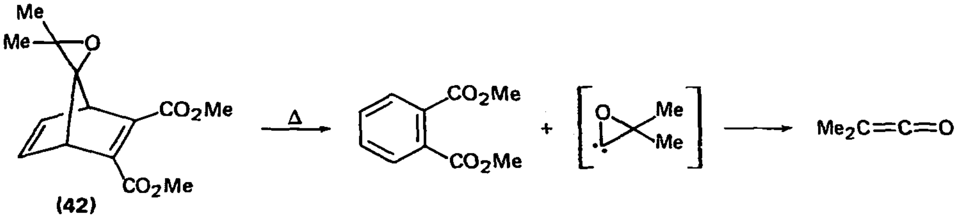

(41)

Other retrocycloaddition reactions which afford ketenes include thermal fragmentation of the epoxide 42, which probably proceeds via initial formation of a carbene[56]. Photolysis of the anthracene derivative 43 gives the elusive dimethyleneketene 44 as a transient intermediate, while thermolysis affords the isomeric vinylketene 45[57a]. By analogy, photolysis of 46 affords benzylideneketene which reacts with methanol to give *cis-* and *trans*-methyl cinnamate in 42% yield[57b].



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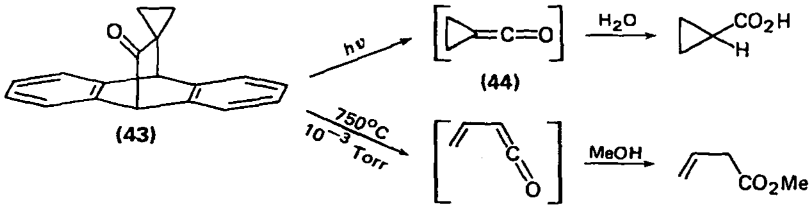

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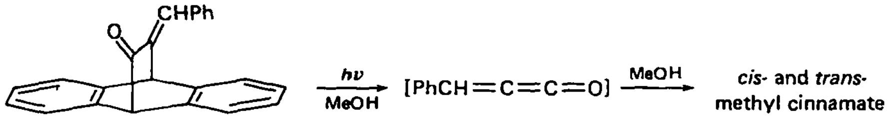
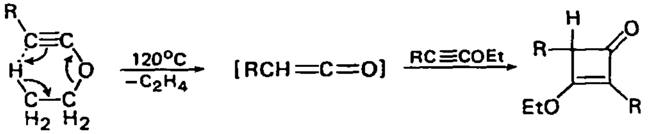


(46)

G. Thermal Cleavage of Alkoxyalkynes

It has been known for many years now that acetylenic ethers having at least one β-hydrogen atom are thermally unstable and, when heated, eliminate an alkene to form a ketene by a concerted process involving an intramolecular hydrogen shift (equation 12). The intermediate ketenes usually then react with the parent alkyne to afford a cyclobutenone[58]. A recent example is the preparation of 2,3,4-tri-*t*-butoxycyclobutenone (47) from di-*t*-butoxyethyne which proceeds in quantitative yield[59].



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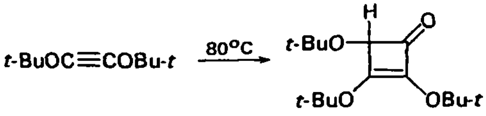
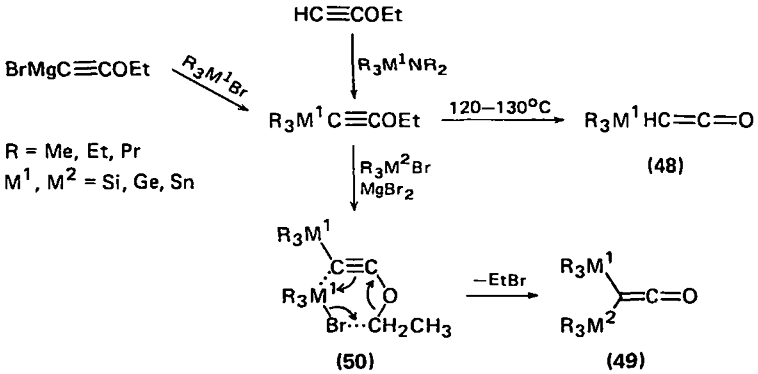


(47)

This reaction forms the basis of a general method for preparing monoalkylketenes and has proved particularly useful for the preparation of thioketenes (Section III.L), and silyl-, germyl- and stannyl-ketenes[60–63]. The infrared and n.m.r. spectra of the silicon-containing ketenes (48) confirm that they possess the ketene structure rather than the alternative siloxyalkyne structure. The reaction leading to the bimetalated ketenes (49) probably proceeds via a six-membered cyclic transition state (50)[61].



(48)

(50)

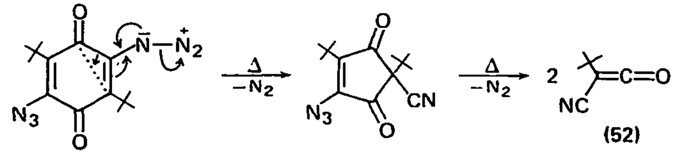
(49)

Optically active (methyl-1-naphthylphenylsilyl)ketene has been prepared and its absolute configuration established (equation 13) on the basis of its reactions with water and ethanol to give products of known configuration[64].

$$(-)\text{-}R_3\overset{*}{Si}Cl \xrightarrow{BrMgC\equiv COEt} (+)\text{-}R_3\overset{*}{Si}C\equiv COEt \xrightarrow{\Delta} (+)\text{-}R_3\overset{*}{Si}CH{=}C{=}O \qquad (13)$$

H. Decomposition of 2,5-Diazidoquinones

2,5-Diazido-3,6-di-*t*-butyl-1,4-benzoquinone (51) undergoes a facile cleavage on refluxing in benzene to give *t*-butylcyanoketene (52)[65]. The ketene is formed in nearly quantitative yield and is stable in benzene solution at room temperature. However, it is quite reactive towards cycloaddition with alkenes and cumulenes, and reacts with alcohols to give esters. All attempts to isolate the ketene have failed. Removing the solvent or cooling the solution to low temperatures causes polymerization. Interestingly, although the ketene has a half-life of more than seven days in benzene at 25°C, in cyclohexane at the same temperature it has a half-life of only a few hours.



(52)

(51)

1,1-Dimethylpropylcyanoketene, methylcyanoketene and phenylcyanoketene can also be prepared by heating appropriately substituted 2,5-diazidoquinones.

III. PREPARATION OF DIFFERENT TYPES OF KETENES

Some of the most recent developments in ketene chemistry have involved the synthesis of ketenes having heteroatoms attached to $C_{(2)}$. Thus a large number of

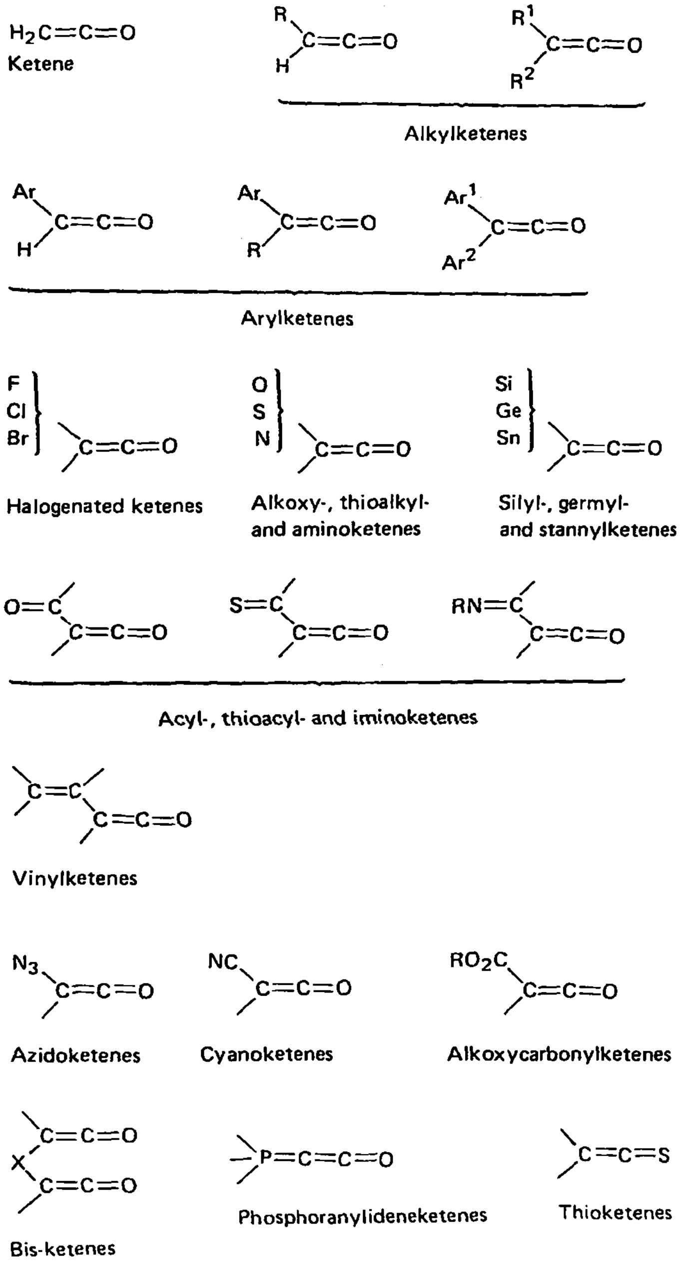


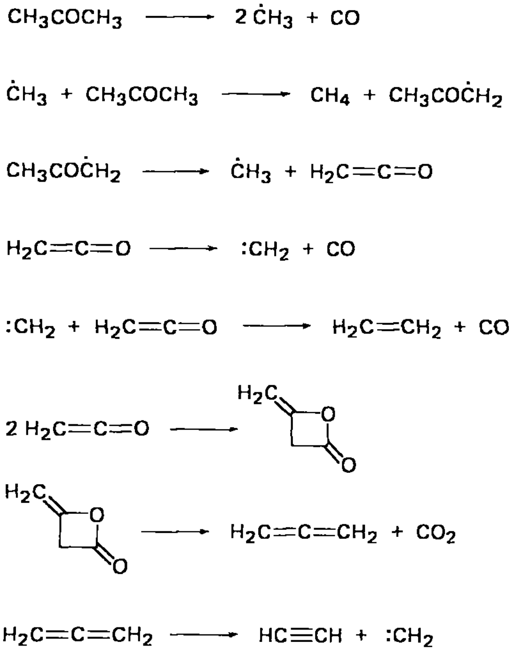
FIGURE 3.

papers have been published dealing with the chemistry of halogenated ketenes (Section III.D), and silyl-, germyl- and stannyl-ketenes (Section III.F). Furthermore, improved experimental techniques and detection facilities have led to the generation and identification of many reactive acyl-, imino- and vinylketenes (Sections III.G and III.I). In this section the preparation of each of these various types of ketenes (see Figure 3) is considered individually. Methyleneketenes and ketene imines are not considered however, since each of these groups is the subject of a separate chapter in this volume.

A. Preparation of Ketene Itself

Ketene (m.p. −134°C, b.p. −41°C) can be most conveniently prepared in the laboratory by the thermal decomposition of acetone, diketene or acetic anhydride[66-68]. Many different and ingenious designs for 'ketene generators' and 'ketene lamps' have been devised, frequently tailored to individual needs or commercial objectives.

The thermal decomposition of acetone can be achieved either by passing acetone vapour through a red-hot silica tube or over an electrically heated nickel—chromium wire. When the latter method is used the current should be adjusted so that the wire glows dull red. If the wire is allowed to get too hot yellow by-products are formed and may be swept into the reaction vessel or receiver. If a red-hot tube is used then lower temperatures are recommended in order to avoid further decomposition of the ketene to carbon monoxide and alkenes (see Scheme 2). The major disadvantage of both of these methods for preparing ketene is the contamination of the



SCHEME 2.

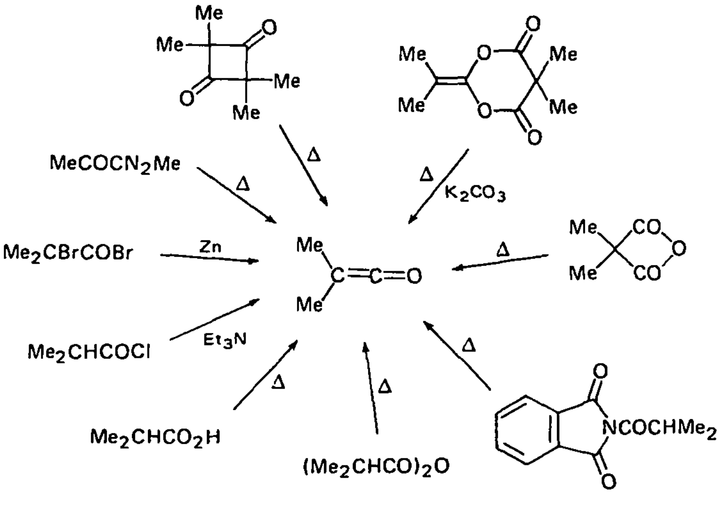
ketene by large amounts of methane and carbon monoxide. Pure ketene can only be obtained by low-temperature condensation followed by fractional distillation. Pure ketene can, however, be obtained directly by pyrolysis of diketene or acetic anhydride. The latter method affords a stream of ketene of greater than 99% purity[69].

The thermal decomposition of acetyl chloride to ketene has been studied by photoelectron spectroscopy[70].

B. Preparation of Alkylketenes

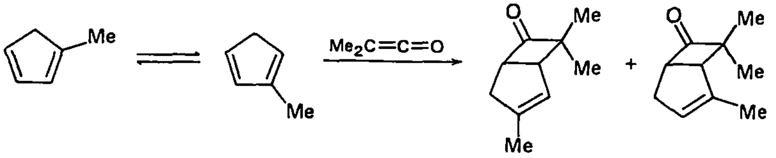
The many methods which have been used to prepare dialkylketenes are conveniently summarized by considering the various routes to dimethylketene (Scheme 3)[41,71–73]. The most frequently used procedures involve dehalogenation of 2-bromoisobutyryl bromide[23], dehydrohalogenation of isobutyryl chloride[72], or the thermal decomposition of isobutyric anhydride[73], dimethylmalonic anhydride[47], or dimethylketene acylal[48]. Pyrolysis of isobutyric anhydride yields essentially pure dimethylketene[73]. However, a more convenient method for preparing dimethylketene in solution is by dehalogenation of 2-bromoisobutyryl bromide[23]. Dehydrohalogenation is useful for generating the ketene *in situ*[72], or for preparing the dimer, which is itself a very efficient source of dimethylketene[2]. The generation of dimethylketene from dimethylmalonic anhydride suffers from the disadvantage that it seems to be almost impossible to remove the last traces of acetic anhydride from the dimethylmalonic anhydride, with the result that a mixture of products is obtained (see Section II.D).

Dimethylketene (m.p. −97°C, b.p. 34°C) can be purified by low-temperature fractionation. It can be stored for several weeks under nitrogen at −78°C. The formation of peroxides can be prevented by adding a small amount of an aluminium trialkyl[73].



SCHEME 3.

In a study of the reactions of dimethylketene, generated *in situ* by two different methods, with methylcyclopentadiene, a marked variation in the ratio of the two major products was observed (equation 14)[74]. The differences were attributed to differing degrees of competition between the interconversion of the methylcyclopentadiene isomers and their cycloaddition to dimethylketene. Similarly, dimethylketene, generated *in situ* by two different methods, reacts with *cis*- and *trans*-but-2-ene with different degrees of stereospecificity (equation 15)[75]. The *cis* alkene reacts with at least 95% retention of configuration while the *trans* alkene reacts more slowly and gives only 60–80% of the *trans* product. It may also be noted that in several instances the isolation of dimethylketene prior to reaction is reported to give higher yields in cycloaddition reactions.



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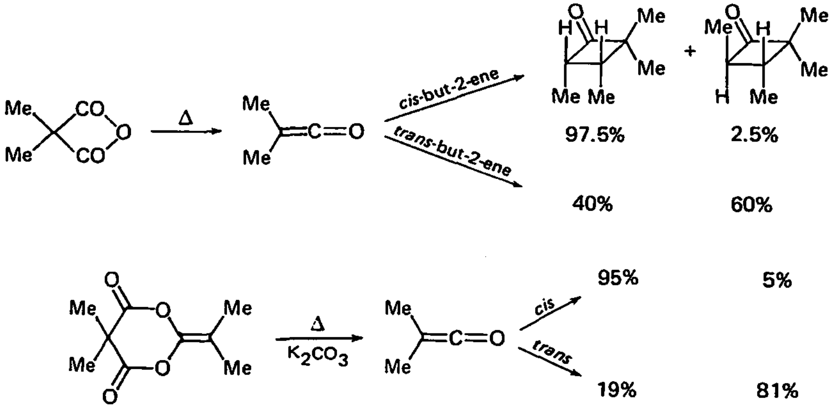
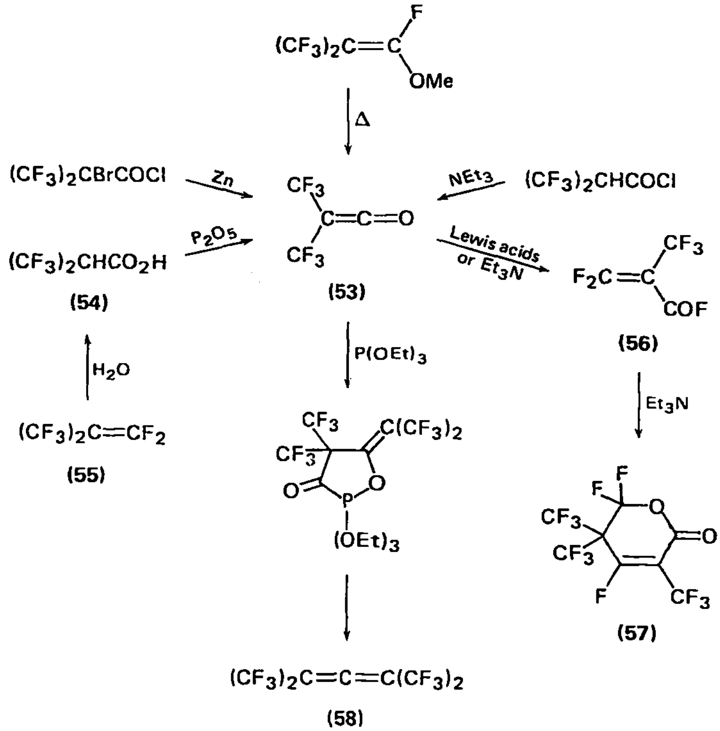


(15)

Bis(trifluoromethyl)ketene (**53**) can be prepared by dehalogenation of α-halohexafluoroisobutyryl halides[76]. If the reaction is carried out in diethyl ether the major product is ethyl hexafluoroisobutyrate formed by cleavage of the diethyl ether by the acyl halide. The best yield of the ketene is obtained when a less basic solvent such as ethyl acetate is used. Alternatively, bis(trifluoromethyl)ketene can be prepared by dehydration of bis(trifluoromethyl)acetic acid (**54**), which is in turn readily obtained by hydration of octafluoroisobutene (**55**)[77]. The ketene has also been prepared by dehydrohalogenation of hexafluoroisobutyryl halides and by pyrolysis of methyl perfluoroisobutyryl ether[78].

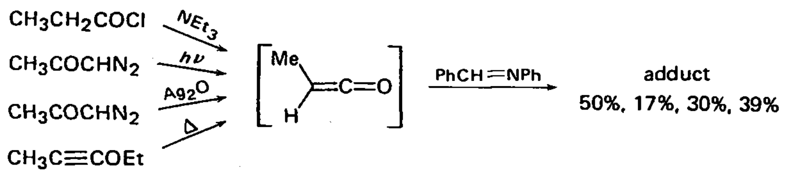
Bis(trifluoromethyl)ketene (b.p. 5°C) does not dimerize spontaneously but is susceptible to nucleophilic attack. Under the action of Lewis acids it undergoes isomerization to perfluoromethacrylyl fluoride (**56**). Triethylamine also causes isomerization, but the end-product is a dimer of the acid fluoride (**57**). In the presence of weaker bases the more usual β-lactone dimer is obtained, while triethyl phosphite converts the ketene into an allene (**58**).



Other dialkylketenes are usually prepared either by pyrolysis of the corresponding acid anhydride[79], or by dehydrohalogenation of the acid chloride[80,81]. Di-*t*-butylketene, for example, is readily prepared by dehydrohalogenation of di-*t*-butylacetyl chloride[82,83]. Polymethyleneketenes of various ring-sizes are well known[84–86].

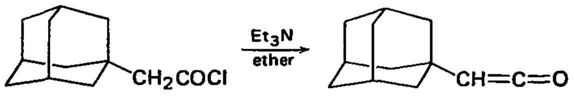
The usual method for the preparation of low molecular weight monoalkylketenes is by the dehydrohalogenation of acyl halides[87–90]. However, this reaction is usually carried out *in situ* and suffers from a number of disadvantages which have already been mentioned (Section II.C). A more satisfactory method for the preparation of such compounds is by the modification to Staudinger's procedure whereby 2-bromoacyl halides are treated with activated zinc dust suspended in tetrahydrofuran[24]. The ketene codistils with the solvent and can therefore be separated from starting materials and zinc salts. Methylketene has also been obtained in high yield by pyrolysis of propionic anhydride[38,50,91]. According to the original procedure[91] the propionic anhydride was vaporized by dripping it into an evacuated flask heated to 150°C. The vapour was then drawn through a quartz tube heated to 400–600°C. The contact time was ca 10^{-2} sec and the emergent gases were immediately condensed in a trap cooled in liquid nitrogen. Trap-to-trap distillation then gave the pure ketene as a pale-green liquid (b.p. −56°C at 760 mm).

The yields of cycloadducts obtained by reacting monoalkylketenes, prepared by several different methods, with imines show considerable variation (equation 16)[92]. The best yields of product were in fact obtained by carrying out a Reformatsky reaction on the corresponding α-bromo ester (see Section II.B).



(16)

The preparation of a number of ketenes containing the adamantane skeleton have been reported[93]. Thus when an ether solution of (1 adamantyl)acetyl chloride is heated under reflux with triethylamine the ketene **59** is formed. Attempted isolation of the pure ketene was unsuccessful, since concentration of the ether solution gave only a polymer. The solution of the monomer displays a sharp band at 2120 cm^{-1} in its infrared spectrum. Reaction of (2-adamantyl)acetyl chloride with triethylamine gives the ketene **60** which also shows a band at 2100 cm^{-1} in its infrared spectrum but undergoes rapid polymerization.



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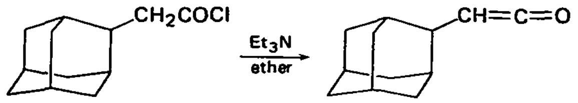
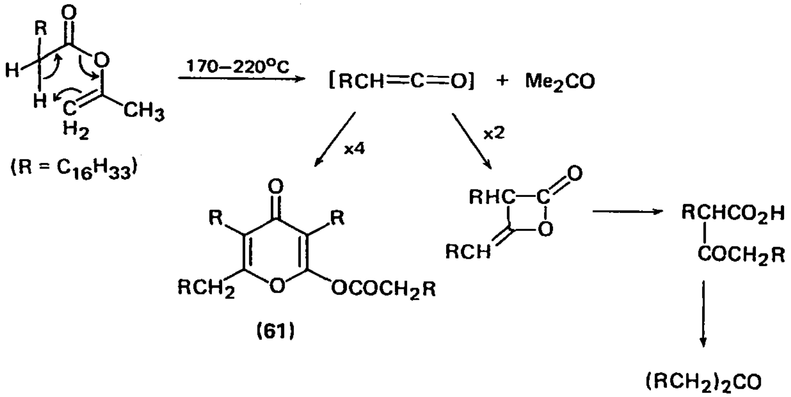


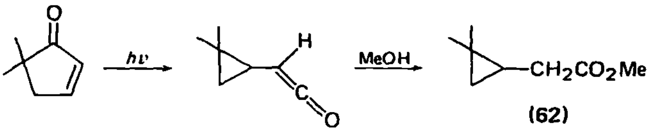
(60)

Hexadecylketene can be efficiently generated by heating isopropenyl stearate. The monomeric ketene cannot be isolated but reacts with alcohols and amines to give high yields of the corresponding esters and amides[94]. In the absence of nucleophiles the fate of the liberated ketene is determined by the conditions under which it is generated. When the thermolysis is carried out in the absence of solvent the product is an acyclic ketone, but when an inert hydrocarbon is used as solvent the tetramer **61** is obtained.



(61)

In addition, a number of monoalkylketenes have been generated by photochemical rearrangement of cyclic ketones, lactones and diazo ketones. Irradiation of 5,5-dimethylcyclopentenone, for example, affords a ketene which reacts with methanol to give the ester 62[95]. Irradiation of the tricyclic ketone **63** affords the ketene **64** which is stable in solution, exhibits a characteristic band in its infrared spectrum at 2155 cm^{-1} and reacts with methanol to give the ester **65**[96]. Irradiation of dihydrocoumarin (**66**) at – 190°C as a thin film or glass containing methanol affords the ketene **67** which exhibits a band at 2115 cm^{-1} in its infrared spectrum and on warming gives the ester **68**[97]. Finally Wolff rearrangement of the diazo ketones **69** and **70** affords initially monoalkylketenes which subsequently rearrange as indicated to more stable products[98,99].



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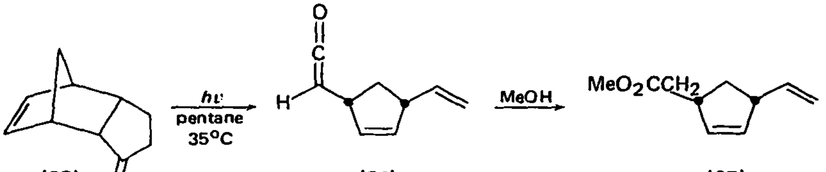

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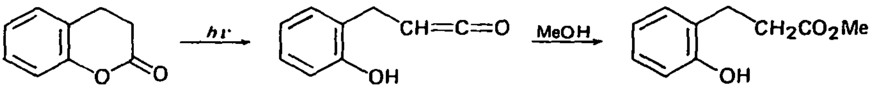

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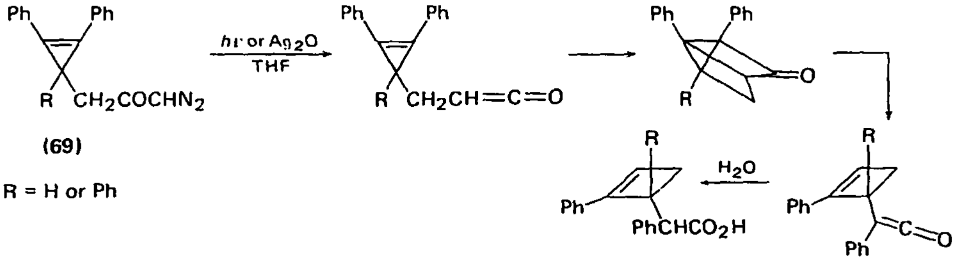

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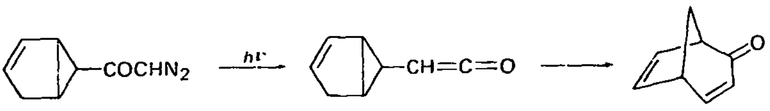
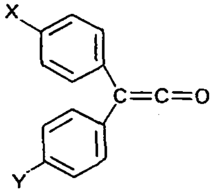
R = H or Ph



(70)

C. Preparation of Arylketenes

Diphenylketene (b.p. 120°C at 3.5 mm) is usually prepared either by dehydrohalogenation of diphenylacetyl chloride[100], or by Wolff rearrangement of azibenzil[101]. The latter method usually involves heating a benzene solution of azibenzil to 70°C or allowing the solution of azibenzil to drip into a flask heated to 105–110°C. Both methods suffer from the disadvantage that they involve heating the diphenylketene once formed until all the azibenzil has been decomposed. This tends to reduce the yield of the reaction since diphenylketene polymerizes when heated and may also undergo a number of other side-reactions. A simple apparatus which avoids this problem has been described in which the ketene formed is immediately removed from the hot zone[71]. In this way a yield of over 80% can be consistently obtained. A wide variety of other arylketenes (71–73) have also been prepared by Wolff rearrangement of the corresponding diazo ketones[102-7].

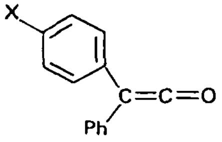


(71)

X = Y = OMe

X = Y = NO$_2$

X = NO$_2$, Y = OMe



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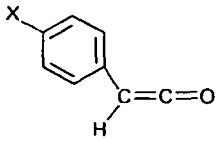
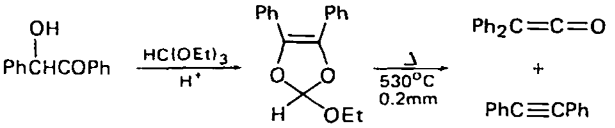
X = OMe, Me, Cl, Br, CO$_2$Et, NO$_2$



(73)

X = F, Cl, Me, OMe, CN, NO$_2$

Diphenylketene has also been prepared from benzoin and benzil by treating them with triethyl orthoformate and triethyl phosphite respectively[108,109] and from diphenylethyne by oxidation[110] (equations 17–19).



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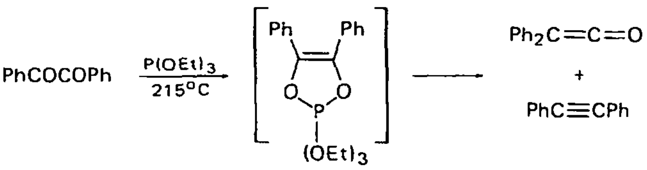

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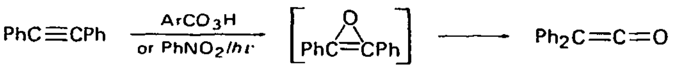
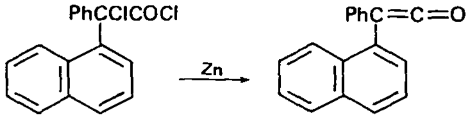


(19)

Arylketenes have also been prepared by dehalogenation of α-haloacyl halides[111,112], by dehydrohalogenation of acyl halides[113-115] and by heating malonic anhydrides[116] or ketene alkyltrimethylsilylacetals[117] (equations 20–24).

Decafluorodiphenylketene has been prepared by heating the corresponding diarylacetic acid with phosphorus pentoxide. The ketene can be distilled from the reaction mixture (b.p. 120°C at 3 mm, m.p. 48–51°C)[118].



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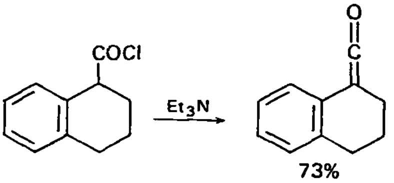

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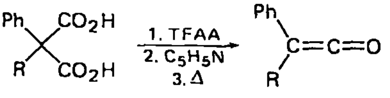

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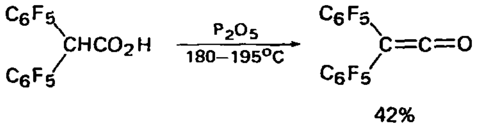
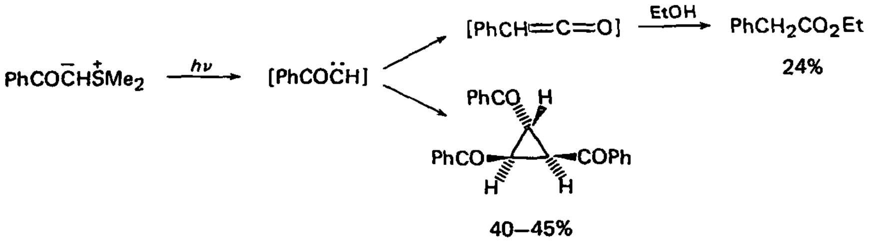


(24)

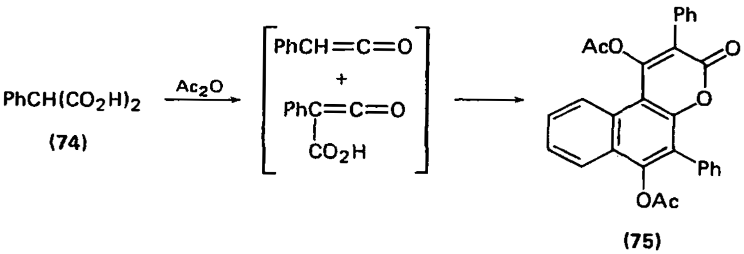
The formation of phenylketene by Wolff-type rearrangement of the carbene generated by irradiation of benzoyldimethylsulphonium methylide has been demonstrated by trapping the ketene by addition of ethanol, which results in the formation of ethyl phenylacetate (equation 25)[119].

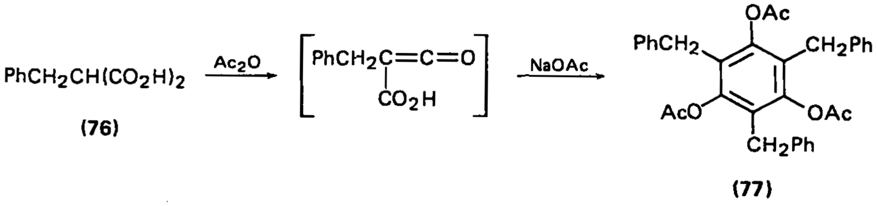


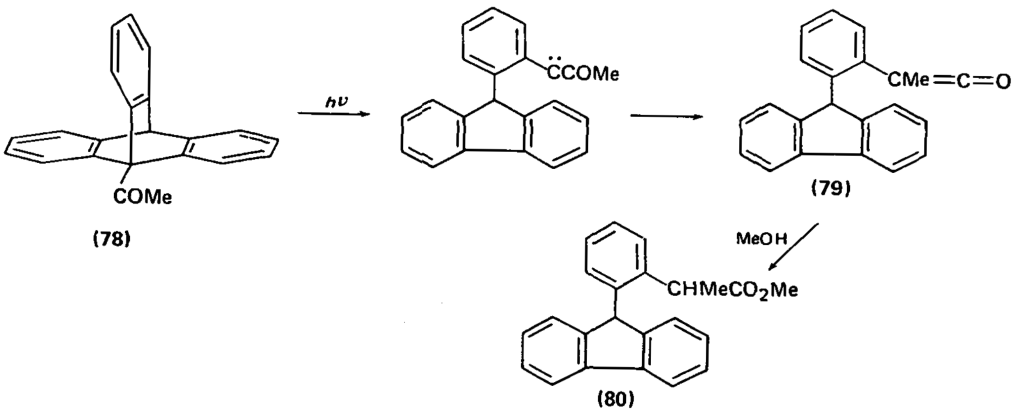
(25)

The reaction of phenylmalonic acid (74) with acetic anhydride gives the benzocoumarin 75. A mechanism for this reaction involving ketene intermediates has been proposed[120]. The analogous reaction of benzylmalonic acid (76) gives a phloroglucinol derivative (77) and a ketene intermediate has again been suggested.

The formation of an interesting monoarylketene (79) by photolysis of the

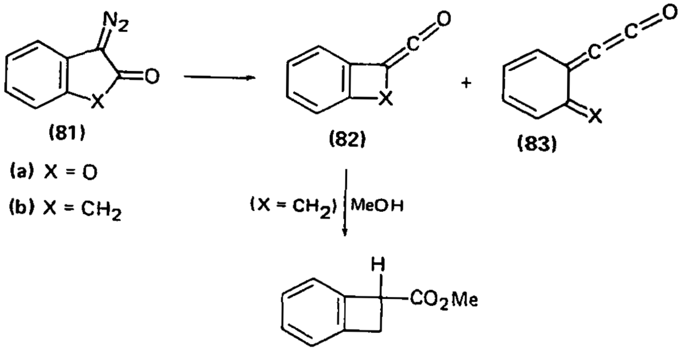






trypticene derivative **78** has been demonstrated by trapping the ketene by reaction with methanol to give the ester **80**[121].

Irradiation of the diazobenzofuranone (**81a**) at low temperatures affords two ketenes (**82a**) and (**83a**)[122]. Long wavelengths favour the former product while short wavelengths favour the latter. Irradiation of the diazoindanone (**81b**) gives



two similar products of which 82b can be identified by allowing an argon matrix containing methanol to warm up to room temperature when a benzocyclobutene carboxylate ester is obtained.

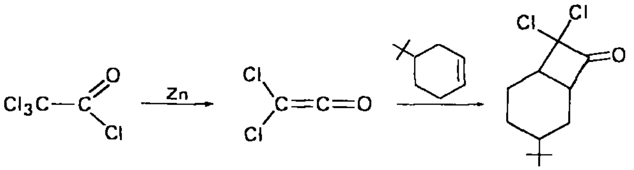
D. Preparation of Halogenated Ketenes

Since many of the early attempts to prepare halogenated ketenes were unsuccessful it was concluded that they were probably unstable compounds which polymerize readily even at low temperatures[123]. Despite the publication of many papers on halogenated ketenes they still cannot be isolated but are usually generated *in situ* by dehalogenation or dehydrohalogenation[124]. Halogenated ketenes are indeed very susceptible to polymerization and reactions involving them are usually accompanied by the formation of tarry by-products.

The preparation of difluoroketene was first reported in 1957[125] but several attempts to repeat this work have been unsuccessful[124,126]. More recently, however, difluoroketene has been successfully prepared by dehalogenation of bromodifluoroacetyl halides with zinc[127]. Difluoroketene dissociates above 35°C forming carbon monoxide and tetrafluoroethylene.

Dichloroketene was first prepared in 1966 by the addition of trichloroacetyl bromide to activated zinc dust in ether or ethyl acetate. The evidence for its existence was based on the observation of a peak at 1940 cm^{-1} in the infrared spectrum (probably misassigned) and reaction with aniline to give dichloroacetanilide[128]. Other workers have prepared dichloroketene by dehydrochlorination of dichloroacetyl chloride with triethylamine, and suggest that this is a superior method of preparation since it gives higher yields and more reproducible results[129,130].

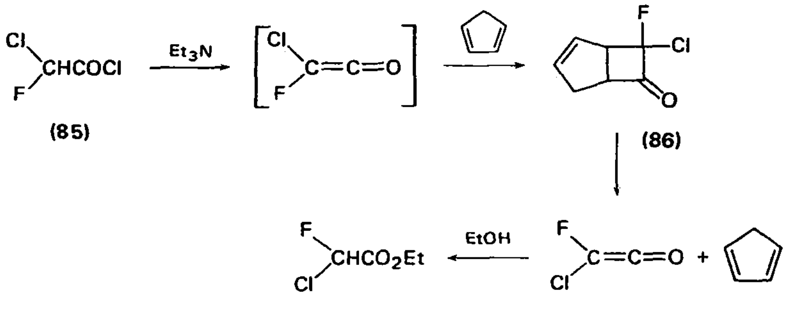
However while generation of dichloroketene by dehalogenation of trichloroacetyl chloride by zinc in the presence of ketones results in the formation of oxetanones, dichloroketene does not undergo cycloaddition to simple ketones when it is generated by dehydrochlorination of dichloroacetyl chloride by triethylamine, unless zinc or zinc chloride are also added to the reaction mixture. It has been suggested that the zinc and/or zinc chloride activate the carbonyl group of the ketone and thus facilitate the cycloaddition reaction[131]. Similarly, while generation of dichloroketene by dehalogenation in the presence of 4-*t*-butylcyclohexene produced the expected adduct (84), generation of the ketene by dehydrohalogenation gave none of this product[132].



(84)

Chlorofluoroketene has been prepared by dehydrochlorination of chlorofluoroacetyl chloride (85)[133]. The adduct 86, formed in the presence of cyclopentadiene, decomposed on heating to give volatile products which fumed in air and reacted with ethanol to give ethyl fluorochloroacetate. Bromochloroketene has also been generated *in situ* by dehydrochlorination of bromochloroacetyl chloride.

Dibromoketene itself has been prepared by both of the above methods[134], and



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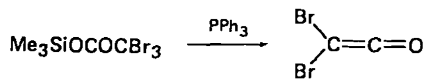
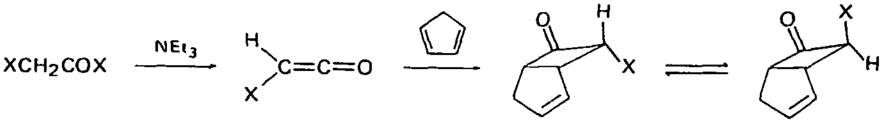


(26)

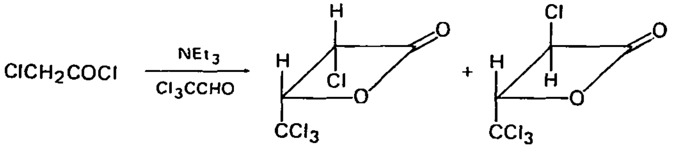
also by treatment of the trimethylsilyl ester of tribromoacetic acid with triphenylphosphine (equation 26)[135].

The dehydrohalogenation of haloacetyl halides in the presence of cyclopentadiene produces the corresponding 1,2-cycloadducts of fluoro-, chloro- and bromoketenes[87,89]. The unsymmetrically substituted ketenes undergo cycloaddition to cyclopentadiene to give only the *endo* isomer (87), but in the presence of excess triethylamine some of the more stable *exo* isomer (88) is also produced, probably as a result of isomerization via the enol tautomer of the initial adduct[136].



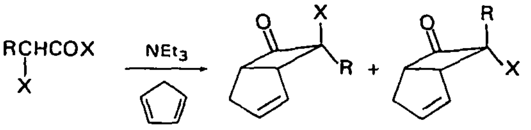
(87) (88)

When chloroketene is generated by dehydrohalogenation of chloroacetyl chloride, in the presence of chloral, a mixture of the *cis* and *trans* oxetanones **89** and **90** is obtained[137]. However, when the chloroketene is generated by dehalogenation of dichloroacetyl chloride, in the presence of chloral, it reacts preferentially with the acyl halide to give a dichlorovinyl ester (see below).



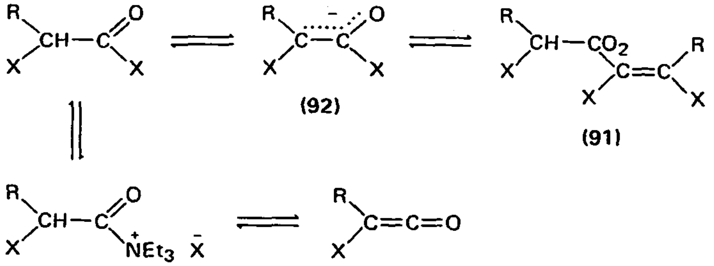
(89) (90)

Alkylhaloketenes have also been prepared and reacted *in situ* with alkenes[138]. The proportions of the *exo* and *endo* isomers obtained are strongly dependent upon the solvent polarity, the substituents attached to the ketene and the reaction temperature (equation 27)[139–141].



(27)

Another reaction which competes with ketene formation when triethylamine is added to α-haloacyl halides is the formation of an α-halovinyl ester (91)[142–144]. The α-halovinyl esters are believed to be formed by acylation of an intermediate enolate anion[145]. The reaction can be minimized or even eliminated if the acyl halide is slowly added to the amine. It has in fact been demonstrated that the formation of the enolate (92) is reversible[31]. It is therefore clear that a complex series of equilibria are involved in the dehydrohalogenation of α-haloacyl halides (see Section II.C), and that the order of addition of the reagents can be very important.

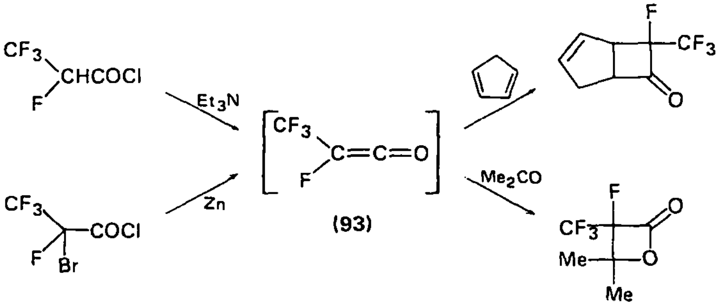


(92)

(91)

Phenylchloro- and phenylbromo-ketenes have been prepared by dehydrochlorination of α-chloro- and α-bromo-phenylacetyl chlorides[146–8]. Once again the ketenes cannot be isolated but can be trapped by alkenes.

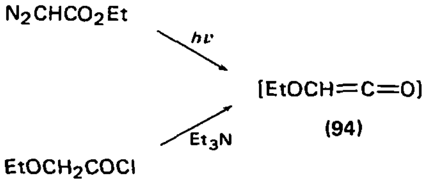
Dehydrochlorination of 2,3,3,3-tetrafluoropropionyl chloride in the presence of cyclopentadiene yields the appropriate adduct of trifluoromethylfluoroketene (93)[133]. Evidence for the transitory existence of trifluoromethylfluoroketene during the dehalogenation of 2-bromo-2,3,3,3-tetrafluoropropionyl chloride is also provided by the formation of an adduct with acetone in 6% yield[149].



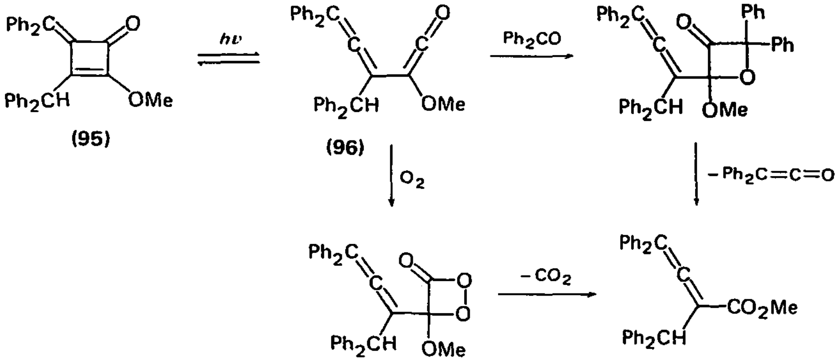
(93)

E. Preparation of Alkoxy-, Thioalkyl-, and Amino-ketenes

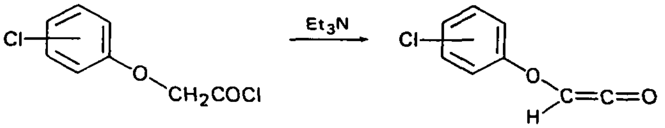
Ethoxyketene (94) has been generated *in situ* by irradiation of ethyl diazoacetate and by treatment of ethoxyacetyl chloride with triethylamine[150]. The ketene can be trapped by cycloaddition to alkenes.



The methoxyketene (**96**) has been postulated as the key intermediate in the photolysis of 2-methoxy-3-diphenylmethyl-4-diphenylmethylenecyclobut-2-enone (**95**) in the presence of benzophenone or oxygen[151].

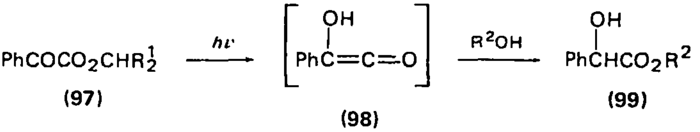


Phenoxyketene and phenoxymethylketene can be generated *in situ* from the corresponding acid chlorides by dehydrohalogenation[148]. Several other aryloxyketenes have also been generated in this manner (e.g. equation 28)[152-4].



(28)

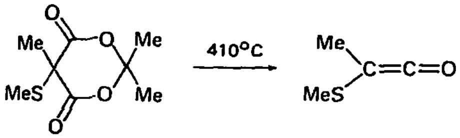
It has been claimed that the hydroxyketene **98** may be an intermediate in the photochemical reaction of the α-keto ester **97** since in the presence of an alcohol the α-hydroxy ester **99** is produced[155].



$$\underset{(97)}{PhCOCO_2CHR^1_2} \xrightarrow{h\nu} \underset{(98)}{\left[PhC(OH)=C=O\right]} \xrightarrow{R^2OH} \underset{(99)}{PhCH(OH)CO_2R^2}$$

Several thioalkylketenes have been prepared either by dehydrohalogenation of acyl halides[156,157], or by flash thermolysis of appropriately substituted derivatives of isopropylidene malonate (equation 29)[50]. Dithioethylketene, prepared *in situ* from dithioethylacetyl chloride and triethylamine, reacts with *N,N*-disubstituted 2-aminomethylenecycloalkanones to give the expected 1,4-cycloadducts (**100**)[158].

A number of phthalimidoketenes have also been prepared either by dehydrohalogenation or by Wolff rearrangement (equation 30)[153,154].



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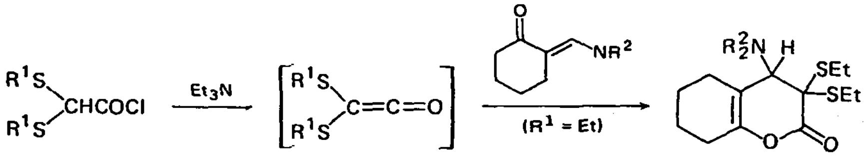

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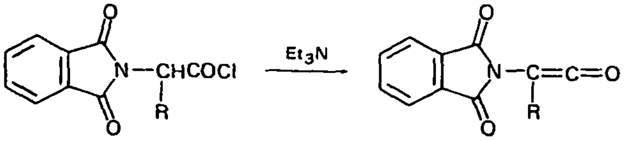
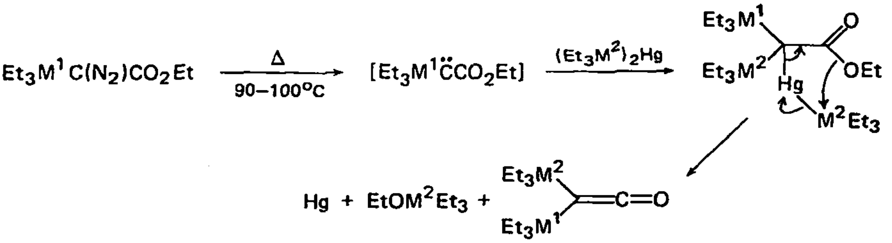


(30)

(R = H, Ph, PhCH$_2$, *i*-Pr, *t*-Bu, Me)

F. Preparation of Silyl-, Germyl- and Stannyl-ketenes

Several silyl-, germyl- and stannyl-ketenes have been prepared by rearrangement of appropriately substituted alkoxyalkynes (Section II.G). Dimetalated ketenes have also been prepared by insertion of carbenes into Si–Hg or Ge–Hg bonds of bis(triethylsilyl)- and bis(triethylgermyl)-mercury compounds, followed by rearrangement (equation 31)[159].



(31)

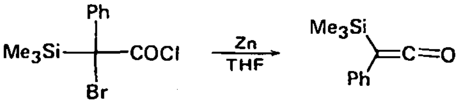
M^1 = Si, M^2 = Ge (92%)
M^1 = M^2 = Si (58%)
M^1 = Sn, M^2 = Ge (73%)

Ketenes with Si, Ge or Sn as substituents can also be prepared by more conventional methods such as heating the corresponding carboxylic acid anhydride (equation 32), dehalogenation of an α-bromoacyl halide (equation 33) or via the appropriate alkyltrimethylsilyl acetal (equation 34)[160–162].

$$(R_3MCH_2CO)_2O \xrightarrow{\Delta} R_3MCH{=}C{=}O + R_3MCH_2CO_2H \qquad (32)$$

M = Si (80%)
M = Ge (40%)

Finally, such compounds can also be prepared by replacement of the trimethylstannyl group in Sn-substituted ketenes (equation 35)[163].



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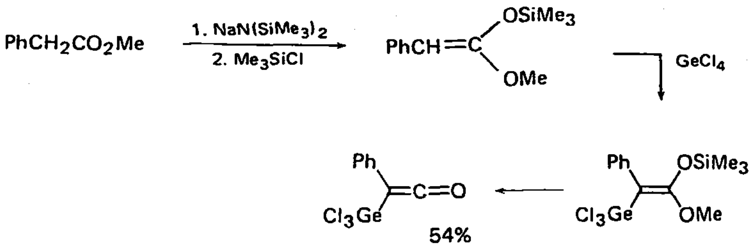

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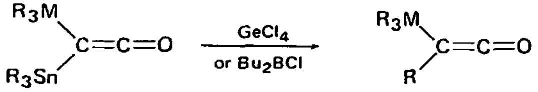


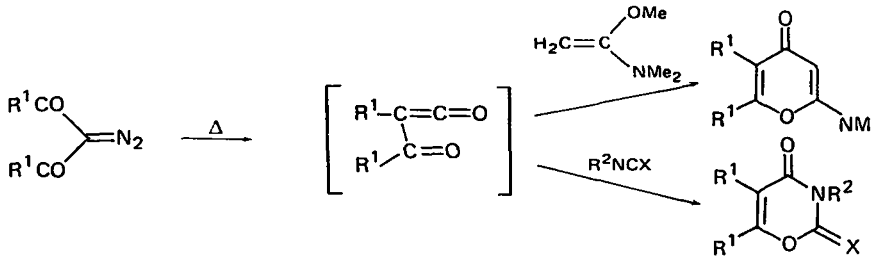
(35)

M = Si or Ge

R = Cl_3Ge or Bu_2B

G. Preparation of Acyl-, Thioacyl- and Iminoketenes

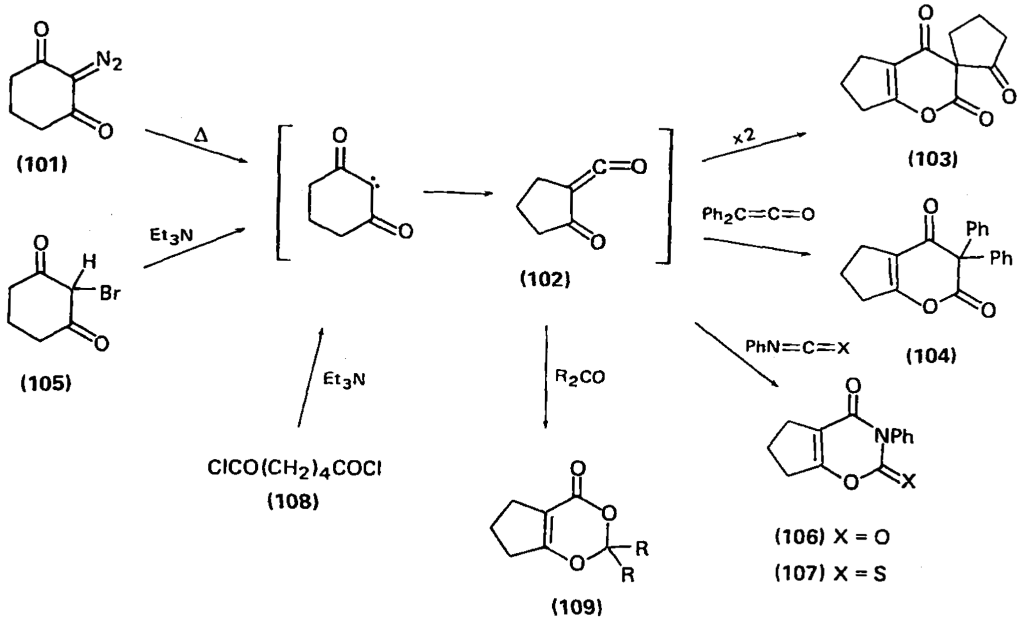
Thermolysis of 2-diazo-1,3-diketones affords acylketenes which readily undergo cycloaddition reactions with various dienophiles (equation 36)[164].

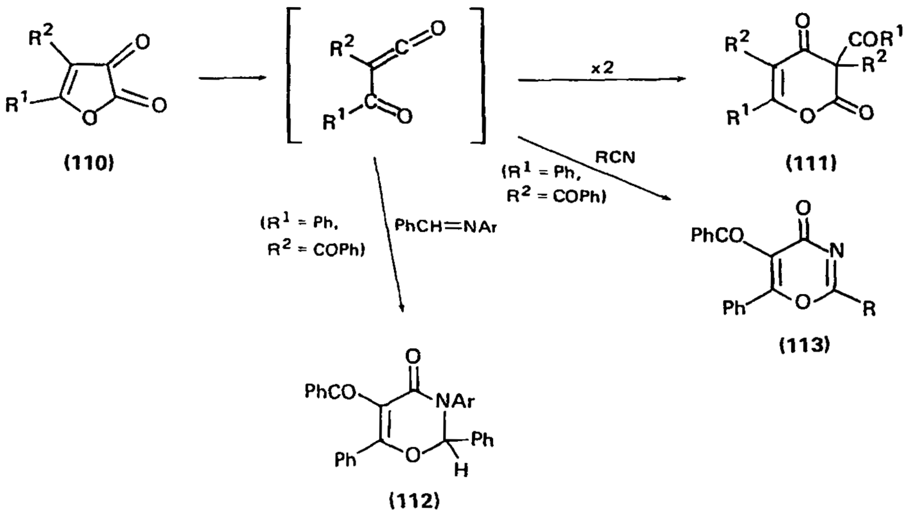


(36)

Thermolysis of 2-diazocyclohexane-1,3-dione (**101**) affords the acylketene **102** which spontaneously dimerizes to give **103** but can be trapped by diphenylketene as the adduct **104**[165]. The same acylketene can also be generated by α-dehydrohalogenation of 2-bromocyclohexane-1,3-dione (**105**) and in this case the ketene has been trapped by reaction with phenyl isocyanate and phenyl isothiocyanate giving adducts **106** and **107** respectively[166]. Dehydrochlorination of adipoyl chloride (**108**) in the presence of aldehydes and ketones affords adducts **109** which are presumed to arise by cycloaddition of the same acylketene **102**[167]. In the presence of isocyanates, 1,3-oxazin-2,4-diones (e.g. **106**) are formed.

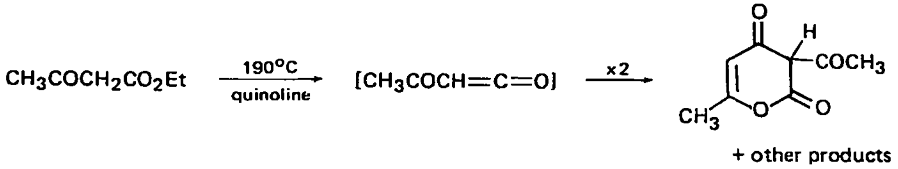
Acylketenes have also been generated by thermal decomposition of furan-2,3-diones (**110**)[168,169]. The acylketenes spontaneously dimerize to give pyran-2,4-





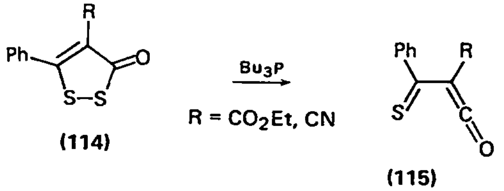
diones (**111**) but in at least one case can be trapped by reaction with imines and nitriles to give cycloadducts **112** and **113** respectively.

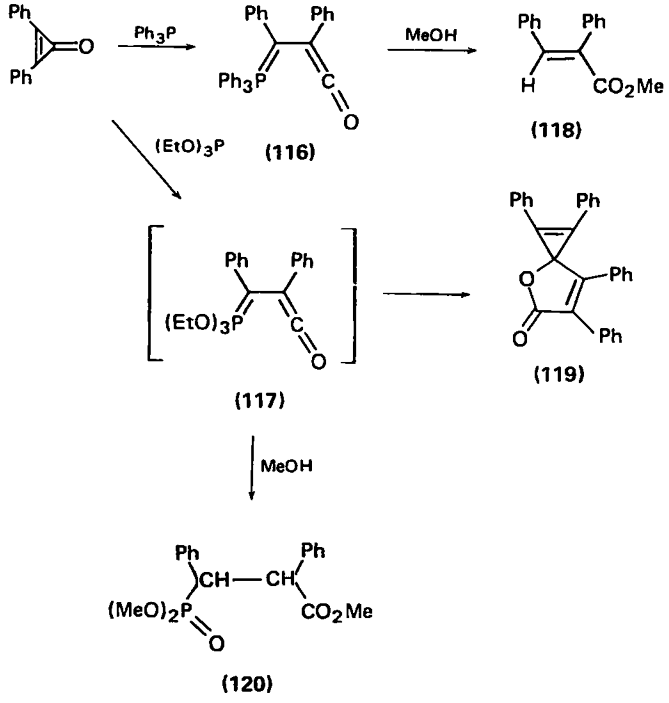
Acylketenes have also been postulated as intermediates in several reactions of β-keto esters. For example, thermolysis of ethyl acetoacetate in the presence of quinoline affords a number of products whose formation can be rationalized in this way (equation 37)[170].



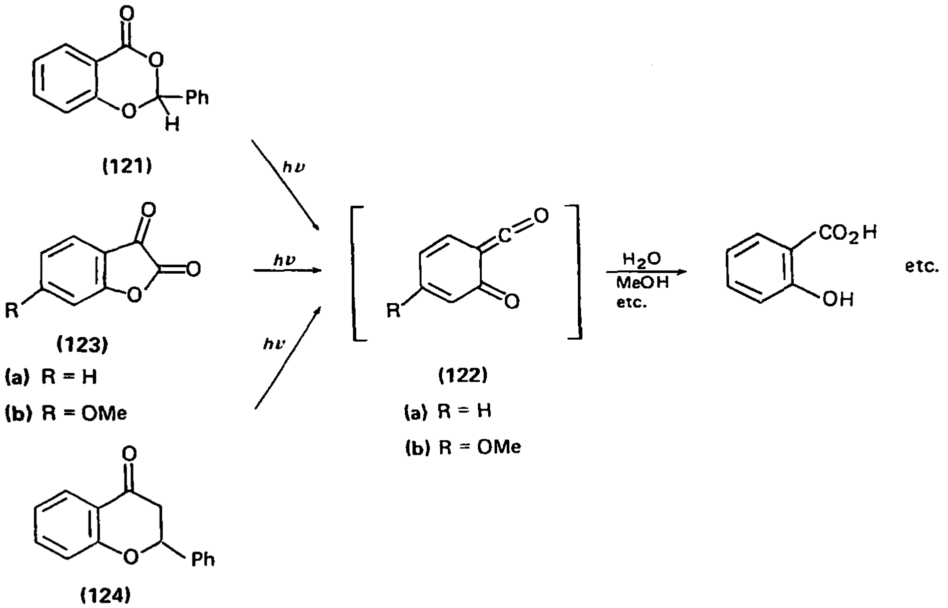
(37)

It is also worth drawing attention to the structurally related thioacylketenes (**115**)[171] and the ketene phosphoranes **116** and **117**[172]. Triphenylphosphine reacts with diphenylcyclopropenone to give **116** which can be isolated and characterized, and reacts with methanol to give the ester **118**. Triethylphosphite on the other hand reacts with diphenylcyclopropenone to give the lactone **119**. The intermediate ketene **117** can, however, be intercepted by methanol to give the ester **120**.





The acylketene **122a** has been generated from several different precursors. It has been observed spectroscopically and trapped by reaction with nucleophilic reagents. Irradiation of **121** at low temperatures (77 K) gave bands in the infrared spectrum characteristic of the ketene (2118 cm^{-1}) but no bands attributable to the isomeric β-lactone (cf. Section I)[173]. Reaction with methanol afforded methyl salicylate. Similarly irradiation of benzofuran-2,3-dione (123a)[174a] and flavanone (124)[174b] in solution at room temperature gave, in the presence of nucleophiles, products resulting from nucleophilic addition to the acylketene. Attempts to trap the methoxy-substituted ketene **122b** by cycloaddition to styrene and β-ethoxystyrene have as yet proved unsuccessful yielding instead products resulting from cycloaddition to the ketene's precursor (123b)[175].



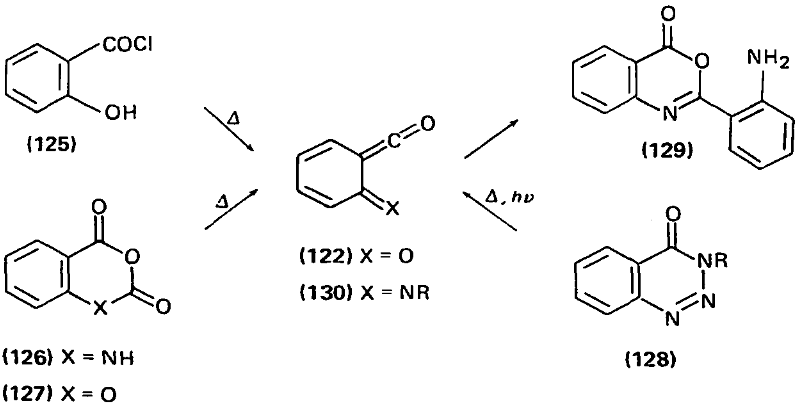
(121)

(123)
(a) R = H
(b) R = OMe

(122)
(a) R = H
(b) R = OMe

(124)

Thermal decomposition of salicyloyl chloride (125), isatoic anhydride (126) and 2,4-dioxobenzo-1,3-dioxane (127) leads to acyl- and imino-ketenes which have been observed by infrared spectroscopy[176]. Benzotriazinone (128; R = H) also decomposes in high boiling solvents to give the dimer (129) of iminoketene (130; R = H) which can also be trapped by cycloaddition to benzyne and 4-methoxybenzaldehyde[177].



(125)

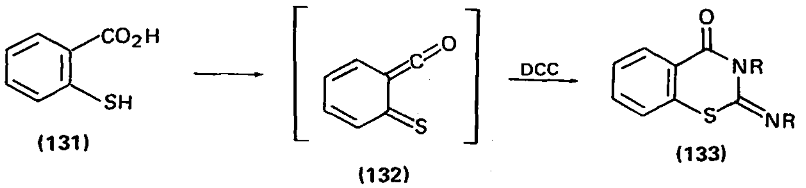
(126) X = NH
(127) X = O

(122) X = O
(130) X = NR

(129)

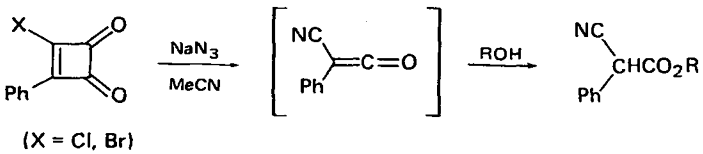
(128)

The iminoketene **130** has also been postulated as an intermediate in the photolysis of benzotriazinones and indeed irradiation of **128** in aqueous tetrahydrofuran, methanol or $C_6H_{11}NH_2$–C_6H_6 gives the expected adducts in 80–90% yield[178]. Kametani and coworkers have recently reported the synthesis of several quinazolones by a route which is thought to involve cycloaddition to the iminoketene **130** (R = H or Me)[179], and DeMayo and collaborators have generated the same iminoketenes by flash thermolysis of anthranilic acid derivatives[180]. An analogous thioacylketene (**132**) has been generated from 2-mercaptobenzoic acid (**131**) and trapped by cycloaddition to a carbodiimide to give the adduct **133**[181].



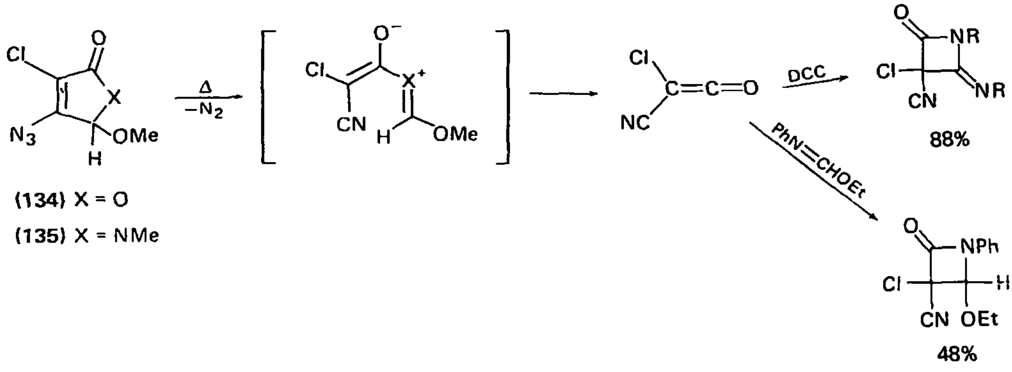
H. Preparation of Cyano-, Azido- and Alkoxycarbonyl-ketenes

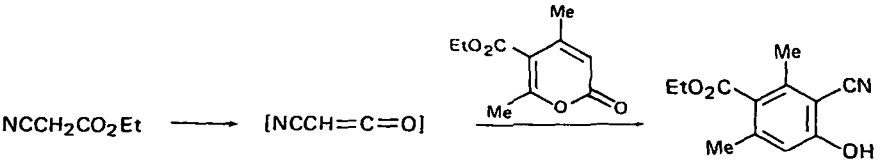
Cyanoketenes have been prepared by thermal decomposition of azidoquinones (Section II.H). Phenylcyanoketene has also been prepared by treating 3-halo-4-phenylcyclobutene-1,2-diones with sodium azide in acetonitrile[182]. The ketene reacts *in situ* with alcohols to give α-cyano esters (equation 38).



(38)

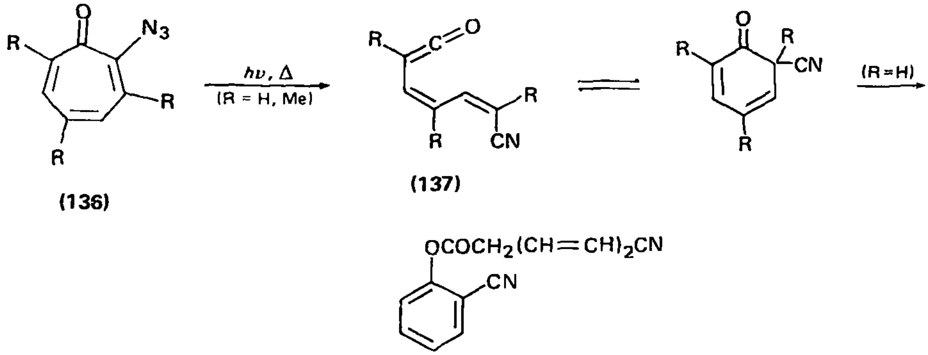
Chlorocyanoketene can be generated by thermolysis of the lactone **134** or the lactam **135** and affords a useful precursor for the preparation of β-lactams[183]. Cyanoketenes have also been proposed as intermediates in the thermal reactions of α-cyano esters with ethyl 4,6-dimethylcoumalate (equation 39)[184].





(39)

Thermal or photochemical decomposition of the azidotropone (**136**) yields the ketene **137** which exhibits an appropriate band at 2100 cm^{-1} in its infrared spectrum and reacts immediately with methanol. The ketene (**137**, R = H) is slowly converted into the dimer **138** in the absence of added reagents[185].

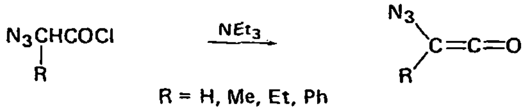


(136)

(137)

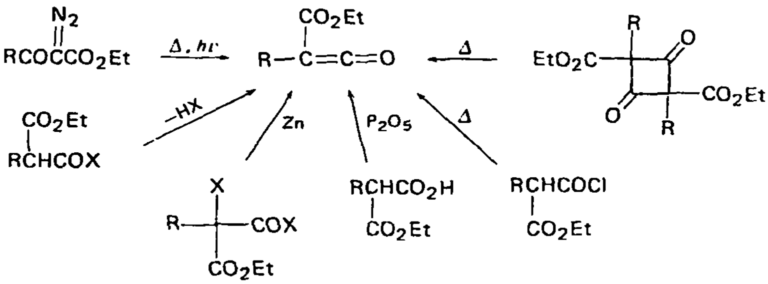
(138)

Azidoketenes have been prepared *in situ* by dehydrohalogenation of the corresponding acyl halides (equation 40)[186].



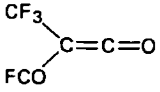
$$N_3\underset{R}{\underset{|}{C}}HCOCl \xrightarrow[R\,=\,H,\,Me,\,Et,\,Ph]{NEt_3} \begin{matrix}N_3\\ R\end{matrix}\!\!>C{=}C{=}O \qquad (40)$$

Alkoxycarbonylketenes are in fact well known and have been prepared by a variety of different methods including Wolff rearrangement, dehydrohalogenation, dehalogenation and dehydration (Scheme 4)[187–190].

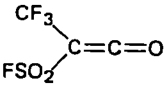


SCHEME 4.

Three new α-functionalized trifluoromethylketenes (**139**–**141**) have recently been reported[191]. For example, **139** can be obtained by dehydrofluorination of trifluoromethylmalonyl fluoride with sulphur trioxide. It is a colourless fuming liquid (b.p. 58–59°C) which is only moderately stable to storage.



(139)



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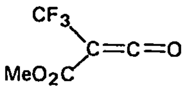
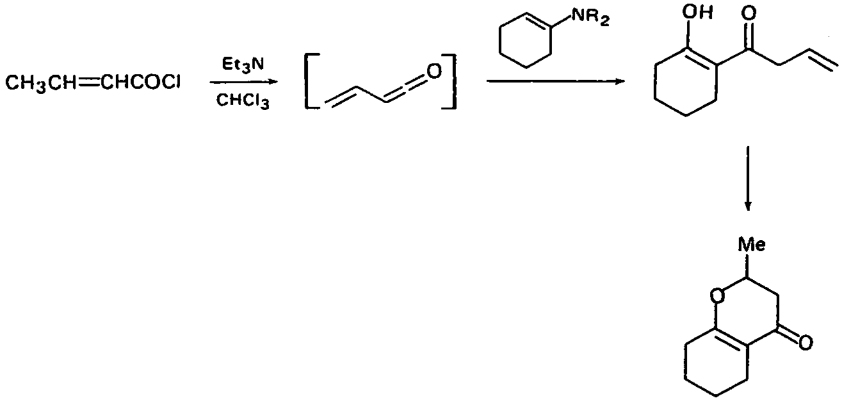


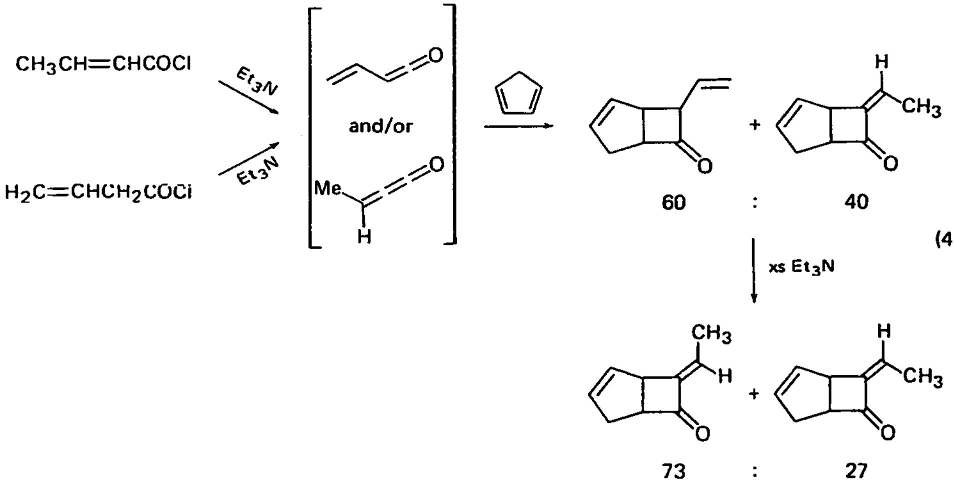
(141)

I. Preparation of Vinylketenes

Vinylketenes (and isomeric methyleneketenes) have been prepared by a wide variety of methods including dehydrohalogenation of α,β- and β,γ-unsaturated acyl halides (equations 41 and 42)[192,193].

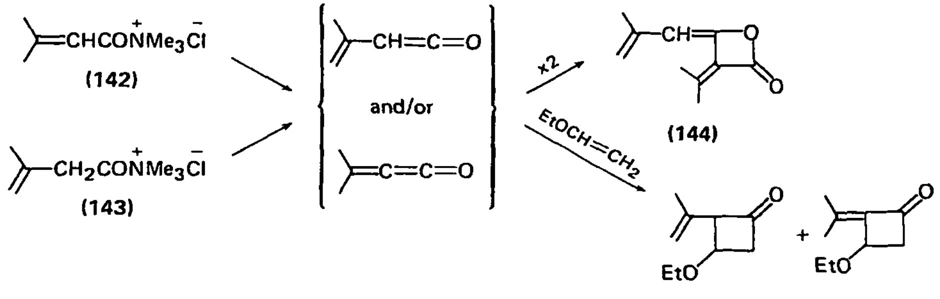


(41)



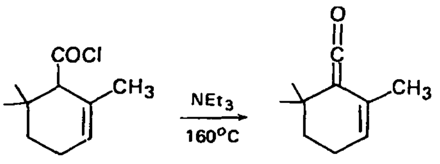
(42)

Solvolysis of the acylammonium salts **142** and **143** affords the β-lactone dimer (**144**) in 62 and 20% yield respectively[194]. In the presence of ethyl vinyl ether the 3-ethoxycyclobutanones **145** and **146** are obtained.

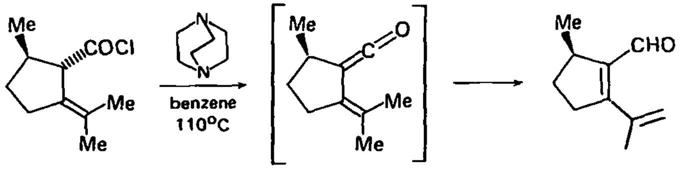


(142) (143) (144) (145) (146)

The vinylketene **147** has in fact been isolated, but attempts to prepare the vinylketene (**148**) in a similar manner resulted in the isolation of the rearrangement product **149** rather than the ketene[195].

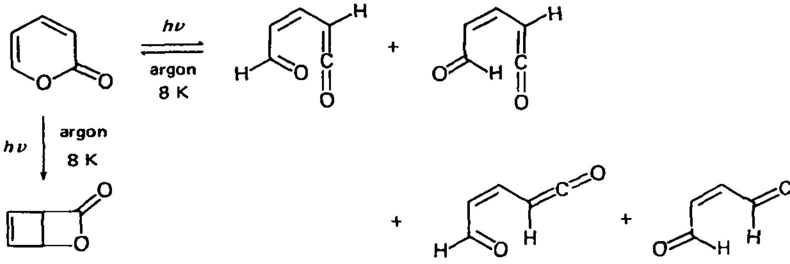


(147)



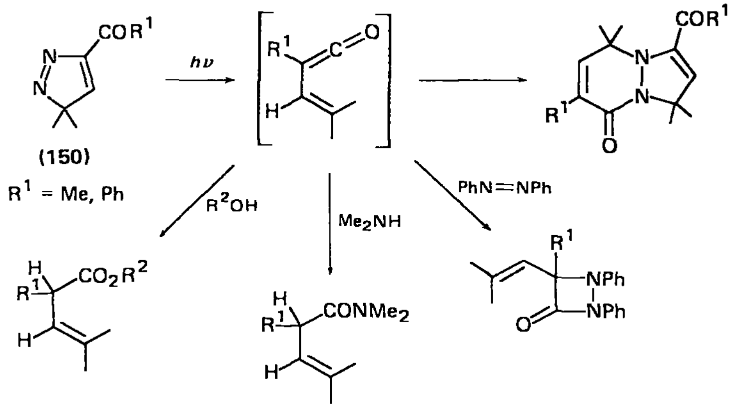
(148) (149)

Irradiation of an α-pyrone matrix isolated in argon at 8 K leads rapidly to the formation of a β-lactone and a ketene, of which several rotamers can be identified (equation 43)[196,197]. Irradiation of 4,6-dimethyl-2-pyrone in argon at 8 K also gives a β-lactone and a mixture of ketene rotamers. Flash photolysis at room temperature shows that the ketene has a half-life of less than 50 μsec.

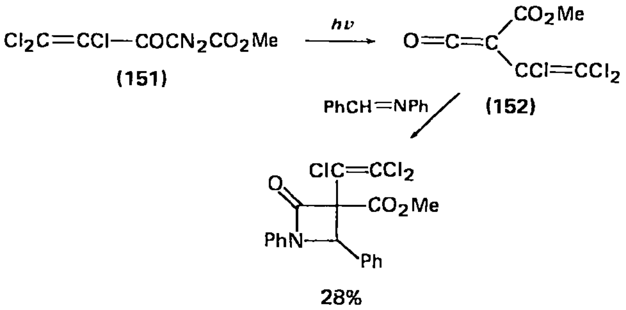


(43)

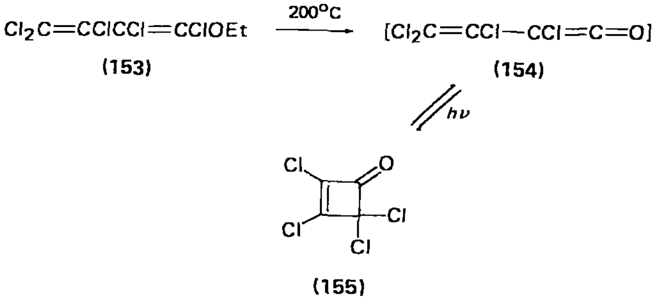
Vinylketenes have also been obtained by Wolff rearrangement of the 5-acyl-3,3-dimethyl-3*H*-pyrazoles (**150**) by irradiating them in an inert solvent[198,199]. The ketenes undergo cycloaddition to azo compounds and react with alcohols and amines to give esters and amides by nucleophilic addition.



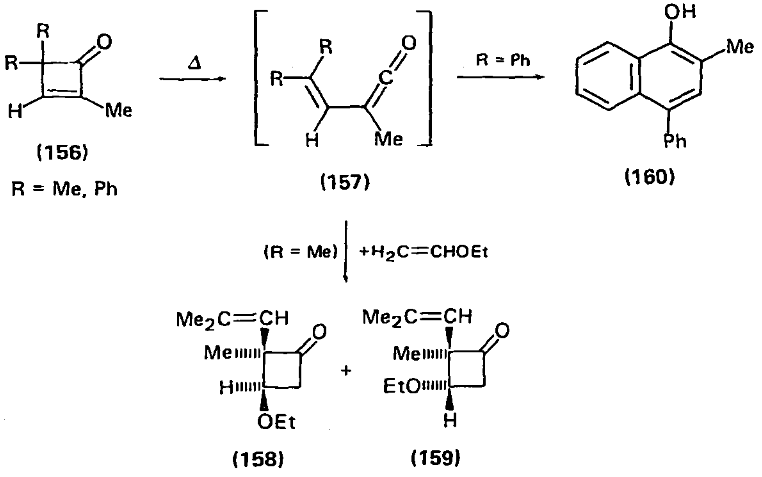
Wolff rearrangement of **151** also affords a vinylketene (**152**) which can be trapped by reaction with imines[200].

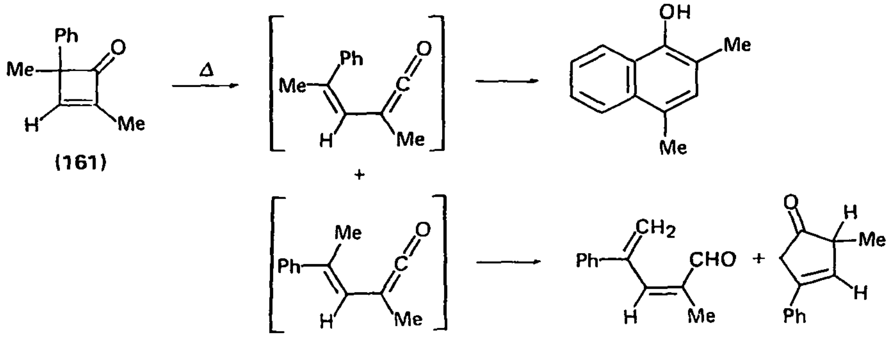


1-Ethoxypentachloro-1,3-butadiene (**153**) is converted into the tetrachlorocyclobutenone (**155**) by heating at 200°C, a reaction which is presumed to proceed via the vinylketene **154**[201]. Irradiation of the tetrachlorocyclobutenone regenerates the ketene, as evidenced by the observation of a band at 2145 cm^{-1} in the infrared spectrum[38].

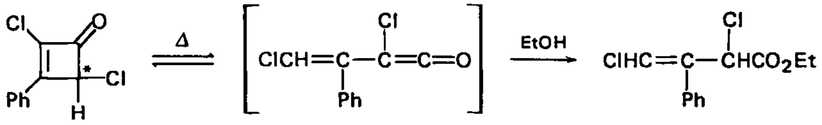


The cyclobutenone **156** (R = Me) undergoes ring-opening in boiling cyclohexane to form a vinylketene (**157**, R = Me), as demonstrated by the appearance of a yellow colouration which disappears on addition of alcohol. The vinylketene can be trapped *in situ* by ethyl vinyl ether to give a 63% yield of cyclobutenones **158** and **159**. Alternatively irradiation of **156** (R = Me) in carbon tetrachloride at 10°C leads to a yellow solution displaying a characteristic ketene band at 2097 cm^{-1} in the infrared spectrum. The 4,4-diphenylcyclobutenone **156** (R = Ph) undergoes quantitative conversion into the α-naphthol **160** on boiling for one hour in cyclohexane. The appearance of β,γ-unsaturated esters and amides in the presence of ethanol and aniline suggests that the vinylketene **157** (R = Ph) is an intermediate in the reaction[202,203]. Thermolysis of **161** affords two isomeric vinylketenes which undergo further reaction to give distinctly different products.

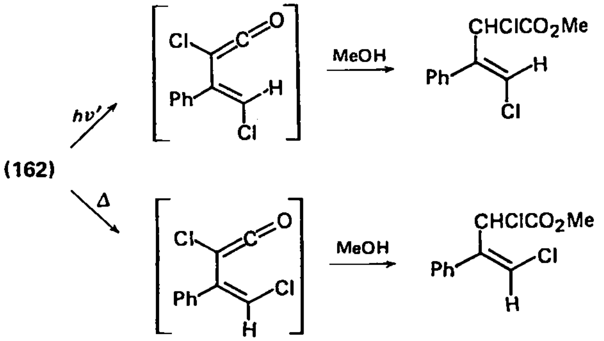




Racemization of the optically active 2,4-dichloro-3-phenylcyclobutenone (**162**) on heating in chloroform or acetic acid is interpreted as involving a vinylketene intermediate[204]. This conclusion is further supported by the observation that in ethanol the rate of loss of optical activity is equal to the rate of formation of the ester **163**. Furthermore the different stereochemical courses of the thermal and photochemical reactions of 2,4-dichloro-3-phenylcyclobutenone are revealed by examining the configuration of the double bond in the esters produced (equation 44)[205].

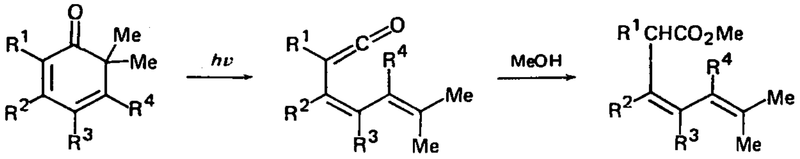


(162) (163)



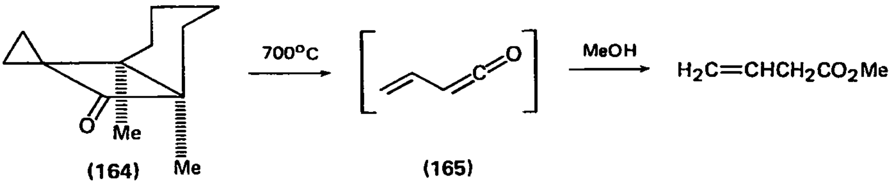
(44)

Vinylketenes can also be generated by photolytic cleavage of cyclohexa-2,4-dienones (equation 45)[206,207].



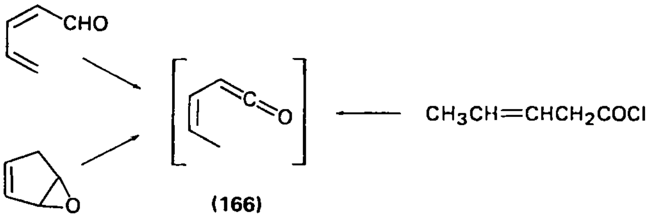
(45)

Flash thermolysis of the tricyclic ketone **164** gives the vinylketene **165** which is stable below −160°C. When a matrix containing the ketene in methanol is allowed to warm up, the red colour of the ketene slowly disappears and methyl but-3-enoate is formed[208].



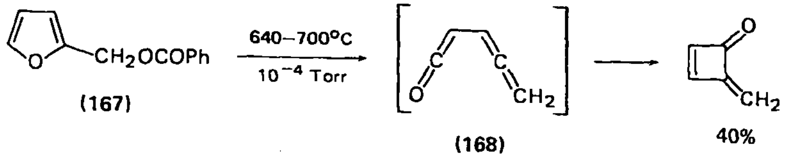
(164) (165)

Vapour-phase pyrolysis of a number of different compounds can be used to generate the vinylketene **166** which has in fact been identified by n.m.r. spectro-

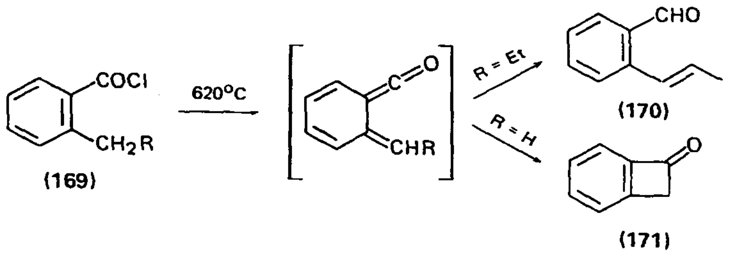


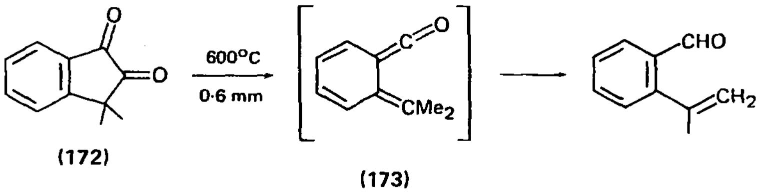
(166)

scopy[209a]. The ketene allene **168** is presumed to be an intermediate in the flash thermolysis of the furan **167**[209b].

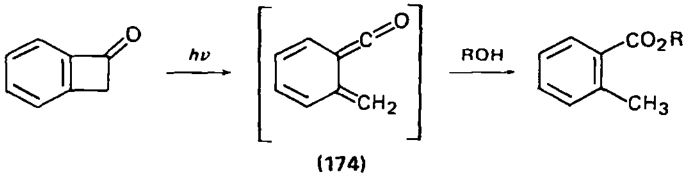


When the aroyl chlorides **169** are distilled at 12 Torr through a quartz tube packed with quartz chips heated to 620°C and the pyrolysate condensed at −78°C the aldehyde **170** or benzocyclobutenone **171** are obtained[210]. A similar ketene (**173**) is involved in the thermolysis of the indanedione **172**[211].

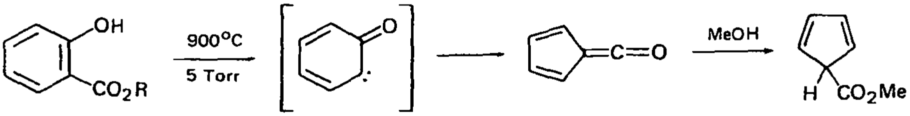




Irradiation of benzocyclobutenones in alcoholic solution gives toluates as the major products formed via the vinylketene **174**[212].



The pyrolysis of esters of *o*-hydroxy aromatic acids in the gas phase gives derivatives of ketenes formed by ring contraction of the intermediate carbenes (equations 46–48)[213].



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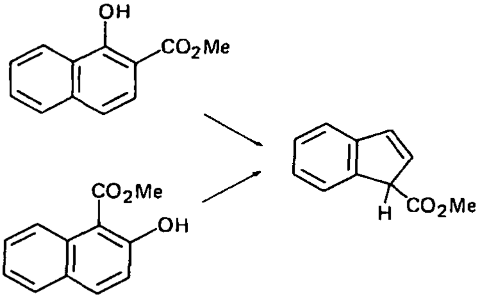
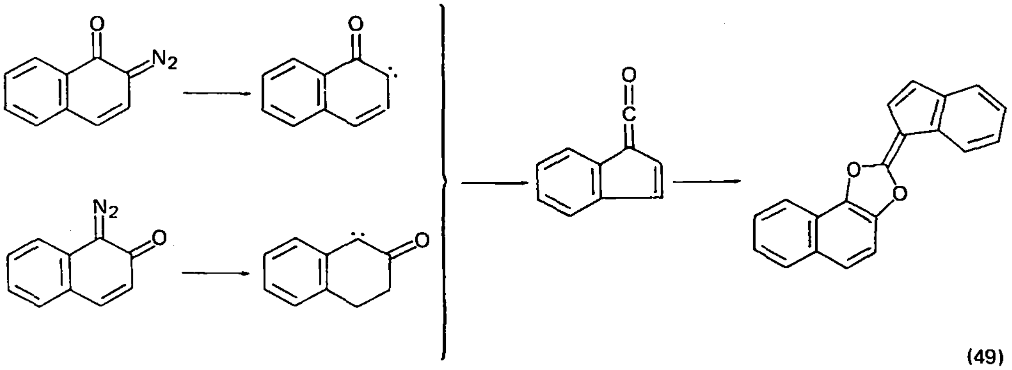


(47)

(48)

There is also good evidence that the same ketenes are produced during the thermal decomposition of naphthalenediazooxides and related compounds (equation 49)^{214}.



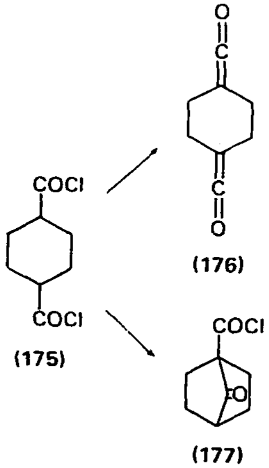
(49)

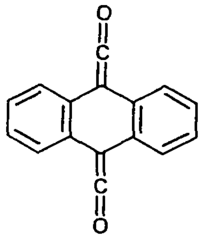
J. Preparation of Bis-ketenes

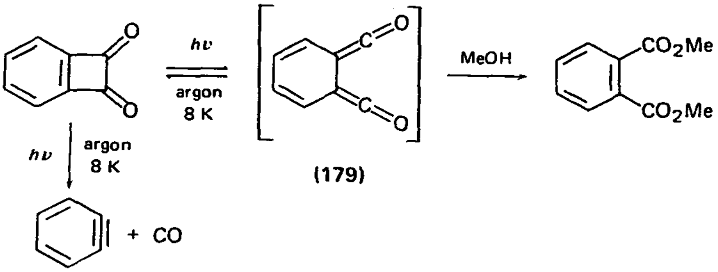
Addition of the acid chloride **175** to excess triethylamine at room temperature gives the bis-ketene **176**^{215}. It is a yellow crystalline compound and can be purified by sublimation, but it polymerizes on warming and reacts with water. The reverse addition of one equivalent of triethylamine to a refluxing ether solution of the acid chloride gives the β-keto acid halide **177**.

The bis-ketene **178** can be prepared from the corresponding acid chloride by dehydrohalogenation. It is an orange-red crystalline compound which reacts with water, methanol and aniline to give the expected products^{216,217}.

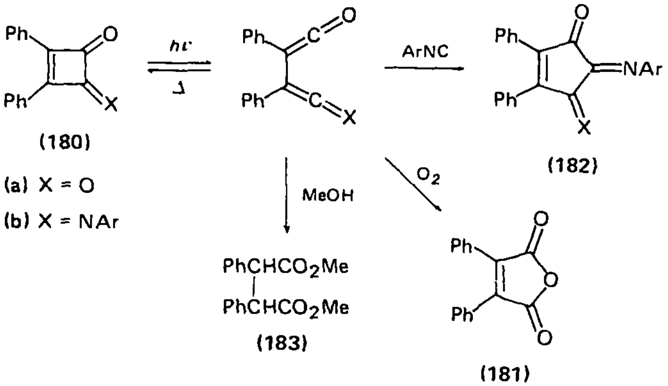
Irradiation of a benzocyclobutenedione matrix isolated in argon at 8 K gives benzyne, carbon monoxide and a bis-ketene **179** as primary photoproducts. The identity of the bis-ketene has been established by allowing an argon–methanol matrix containing the ketene to warm up and observing the gradual disappearance of the infrared spectrum of the ketene and its replacement by that of dimethyl phthalate^{218}.


(175) (176) (177)


(178)

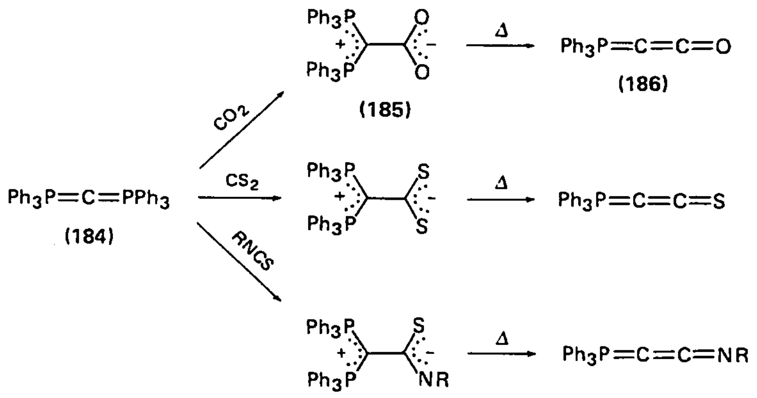

(179)

The photolysis of **180a** and **180b** in the presence of oxygen or an isocyanide affords **181** and **182** respectively[219]. The participation of ketene intermediates has been confirmed by low-temperature infrared spectroscopy and by photolysis in methanol which affords both *meso* and racemic isomers of the succinate ester **183**.

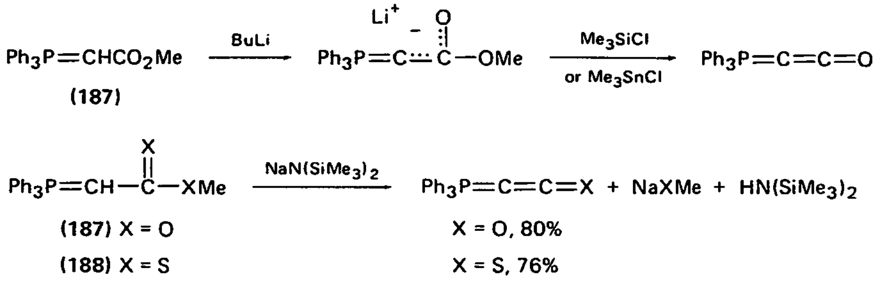

(180) (181) (182) (183)

K. Preparation of Phosphoranylideneketenes and Related Compounds

Phosphoranylideneketene (**186**) is prepared by heating the inner salt (**185**) in diglyme[220]. The phosphoranylidenethioketene and ketene imines are similarly prepared. The inner salts are themselves prepared by reacting the diphosphorane **184** with carbon dioxide, carbon disulphide or isothiocyanates.



Phosphoranylideneketene can also be prepared by treating the lithiated derivative of carbomethoxymethylenetriphenylphosphorane (**187**) with trialkyl-tin or -silicon halides[221]. The ketene can also be prepared by treating the same ylid with the sodium salt of hexamethyldisilazane. The phosphoranylidenethioketene can be prepared in a similar manner from **188**[222].



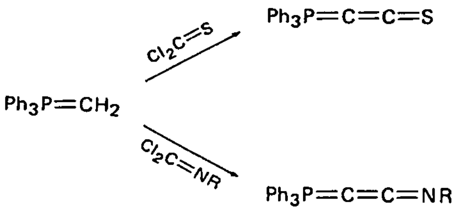
$$\underset{(187)}{Ph_3P{=}CHCO_2Me} \xrightarrow{BuLi} Ph_3P{=}C{\cdots}\overset{\overset{Li^+\ -\ O}{\vdots}}{C}{-}OMe \xrightarrow[\text{or } Me_3SnCl]{Me_3SiCl} Ph_3P{=}C{=}C{=}O$$

$$Ph_3P{=}CH{-}\overset{\overset{X}{\|}}{C}{-}XMe \xrightarrow{NaN(SiMe_3)_2} Ph_3P{=}C{=}C{=}X + NaXMe + HN(SiMe_3)_2$$

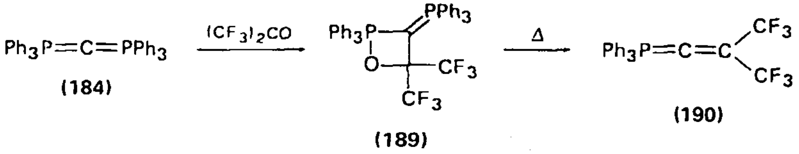
(187) X = O X = O, 80%

(188) X = S X = S, 76%

The phosphoranylidenethioketene and ketene imines can also be prepared by reacting methylenetriphenylphosphorane with thiophosgene or an isocyanide dichloride (equation 50)[223]. Furthermore the diphosphorane **184** reacts with hexafluoracetone to give the cycloadduct **189** which on warming in an inert solvent gives the vinylidenephosphorane **190**[220].

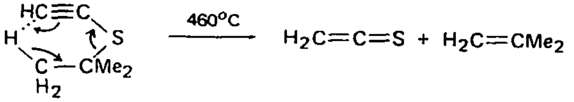


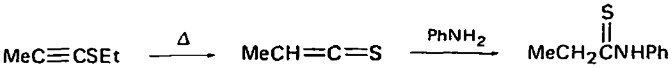
(50)


(184) (189) (190)

L. Preparation of Thioketenes

Many early attempts to prepare thioketenes were unsuccessful, giving only dimers or polymers. However, in 1962 Howard prepared thioketene itself by pyrolysis of *t*-butyl ethynyl sulphide (equation 51)[224]. He found that it was stable below −80°C but polymerized above this temperature. Boonstra and coworkers also prepared monomethylthioketene and showed that it reacted with aniline to give a thioamide (equation 52)[225]. More recently the trimethylsilylthioketenes (**191**) have been prepared by means of a similar rearrangement[226]. In this case the thioketenes have been isolated and their ^{1}H and ^{13}C-n.m.r. spectra measured.


(51)


$$\mathrm{MeC{\equiv}CSEt} \xrightarrow{\Delta} \mathrm{MeCH{=}C{=}S} \xrightarrow{\mathrm{PhNH_2}} \mathrm{MeCH_2\overset{\overset{\large S}{\|}}{C}NHPh} \qquad (52)$$

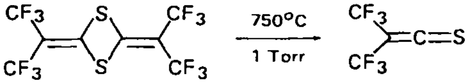

(191)

$R^1 = R^2 = Me$, $R^3 = H$

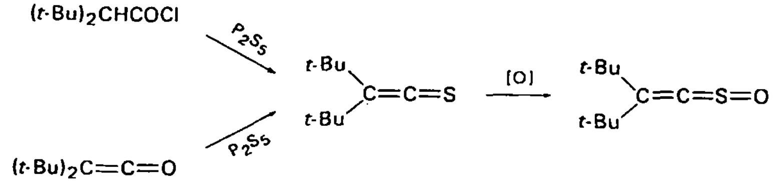
$R^1 = Me$, $R^2 = R^3 = H$

$R^1 = H$, $R^2 + R^3 = -(CH_2)_3-$

Raasch has prepared bis(trifluoromethyl)thioketene by pyrolysis of its dimer (equation 53), and found that it is stable for many months at room temperature[227]. It is an orange-red liquid (b.p. 52–53°C). Di-*t*-butylthioketene may be prepared by heating di-*t*-butylacetyl chloride or di-*t*-butylketene with phosphorus pentasulphide in pyridine (equation 54)[228]. This particular thioketene shows no tendency to dimerize or polymerize at room temperature. However, oxidation with hydrogen peroxide or monoperoxyphthallic acid converts it into the *S*-oxide.

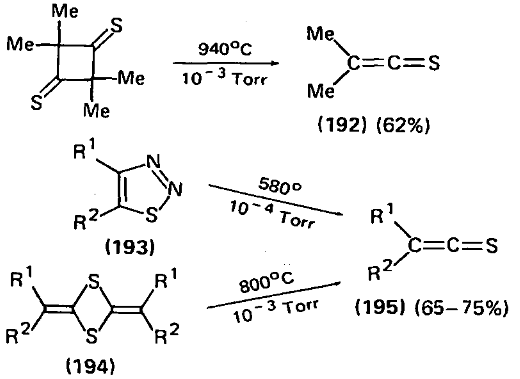

(53)

70%



(54)

The thermally unstable dimethylthioketene **192** was first obtained by flash thermolysis of tetramethylcyclobutanedithione[229]. A general synthesis of thioketenes by flash thermolysis of 1,2,3-thiadiazoles (**193**) and 1,3-dithietane derivatives (**194**) has been described[230]. In this instance the preparative advantage of flash thermolysis is convincingly demonstrated since if 1,2,3-thiadiazoles are simply heated in a high-boiling solvent only secondary products are obtained.



(192) (62%)

(193)

(194)

(195) (65–75%)

(a) $R^1 = R^2 = 4\text{-}ClC_6H_4$

(b) $R^1 = R^2 = Ph$

(c) $R^1 = Ph, R^2 = H$

(d) $R^1 = t\text{-}Bu, R^2 = H$

(e) $R^1 = Me, R^2 = Ph$

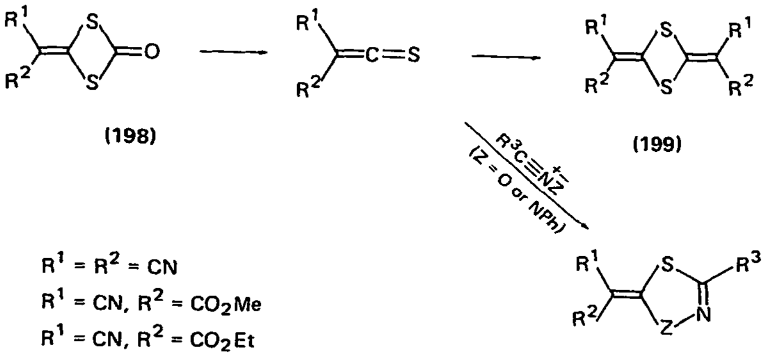
(f) R^1, R^2 = 2,2-biphenylenyl

On warming to 30°C the diarylthioketenes **195a** and **195b** dimerize to give 1,3-dithietanes **194**. In contrast **195c**, **195d** and **195e** oligomerize at room temperature to give complex mixtures of products. Flash thermolysis of **196** affords the thioketene **197** but it begins to polymerize even at – 120°C and can only be detected indirectly.

(196) (197)

The 1,3-dithietanes **198** decompose to thioketenes under catalysis by Lewis bases, surface active agents and polar solvents, as well as on heating. In the absence of a suitable reactant the thioketenes dimerize to give 1,3-dithietanes (**199**) but in the presence of nitrile oxides or imines they undergo 1,3-dipolar cycloaddition to give heterocyclic products (**200**)[231].

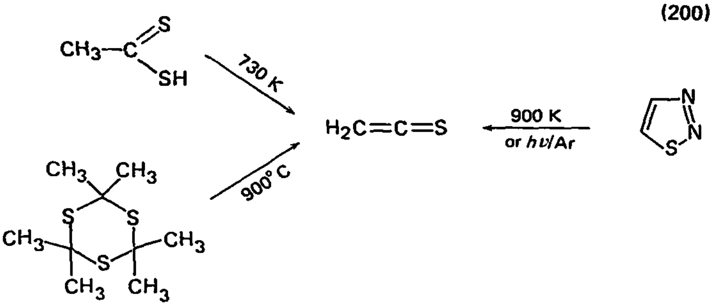
The photoelectron spectrum of thioketene itself has been recorded by generating it from dithioacetic acid at 730 K or from 1,2,3-thiodiazole at 900 K (equation 55)[232]. Thioketene has also been generated by photolysis of the thiadiazole in an argon or nitrogen matrix[233]. The microwave spectrum of thioketene has been recorded by generating it by pyrolysis of hexamethyltrithian at 900°C[234].



(198)

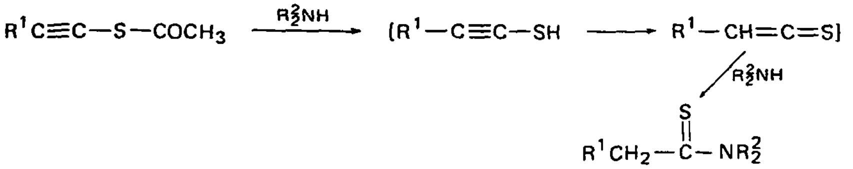
(199)

(200)



(55)

Finally, thioketenes have been postulated as intermediates in the reactions of acetylthioalkynes with nucleophiles (equation 56)[235].



$$R^1C\equiv C-S-COCH_3 \xrightarrow{R^2_2NH} [R^1-C\equiv C-SH \longrightarrow R^1-CH=C=S] \xrightarrow{R^2_2NH} R^1CH_2-\overset{\overset{\displaystyle S}{\|}}{C}-NR^2_2 \qquad (56)$$

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The Chemistry of Ketenes, Allenes and Related Compounds
Edited by Saul Patai

CHAPTER 8

Synthetic uses of ketenes and allenes

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I. INTRODUCTION

This chapter has been divided into two distinct parts dealing with the synthetic utility of ketenes and allenes separately. An attempt has been made to focus attention on ketene and allene reaction products rather than reaction classifications or starting reactants. Many of the functionally-substituted reaction products of ketenes and allenes may be converted into important compounds and these transformations are included. The emphasis has been placed on synthetic developments which have occurred in the past 10–12 years.

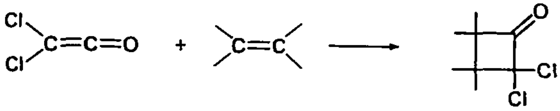
II. SYNTHETIC USES OF KETENES

Clearly the most synthetically useful reaction of ketenes is the [2 + 2] cycloaddition reaction to form a four-membered ring. This reaction constitutes one of the few routes to synthetically versatile four-membered rings. Ketenes undergo this cycloaddition reaction with a wide variety of unsaturated compounds thus yielding a vast array of four-membered ring compounds. The developments in the past few years involving halogenated ketenes have greatly widened the scope and utility of this important synthetic reaction. The halogenated ketenes are generally more reactive in cycloaddition reactions than alkyl- or aryl-ketenes. The cycloadducts from halogenated ketenes are useful synthetic intermediates because the halogen atom(s) is easily replaced by hydrogen. Also, since the halogen is a good leaving group, substitution and ring-contraction reactions of the ketene cycloadducts become important. Another significant consideration is that the starting materials for the preparation of halogenated ketenes are inexpensive and readily available.

Ketenes undergo nucleophilic addition reactions with nucleophiles such as alcohols, amines and carboxylic acids to yield esters, amides and anhydrides. However, there are usually simpler routes to these compounds and therefore the ketene acylation reactions are generally not useful synthetically and are not covered in this chapter. Consequently, this section is concerned with the synthetic applications of ketene cycloaddition reactions and conversion of the resultant cycloadducts into important compounds.

A. Cyclobutanones

The cycloaddition of ketenes and olefins provides an elegant synthetic route to cyclobutanones. Dichloroketene readily reacts with various olefinic compounds to yield α,α-dichlorocyclobutanones (equation 1). Some examples of the variety of olefins which undergo cycloaddition to dichloroketene to yield a vast array of α,α-dichlorocyclobutanones include cyclopentadiene[1], indene[2], cyclohexene[3], styrene[3], 1-pentene[3], 1,5-cyclooctadiene[3], ethyl vinyl ether[3], steroid olefins[4], diphenylfulvene[5], diphenylbenzofulvene[5], *cis*- and *trans*-cyclooctene[6], norbornene[7], norbornadiene[7], dicyclopentadiene[7], cyclopentene[8], dihydropyran[9], cyclohexadiene[9], dimethylfulvene[10], 1-*t*-butylcyclopentadiene[11], 2-methylcyclopentadiene[12] and trimethylsilylcyclopentadiene[13].



(1)

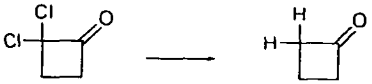
Dichloroketene is more reactive in ketene–olefin cycloaddition reactions than most nonhalogenated ketenes. A general comparison of the reactivity of variously substituted ketenes in cycloaddition reactions with olefin compounds gives the following order:

$$Cl_2C{=}C{=}O > Ph_2C{=}C{=}O > Me_2C{=}C{=}O > H_2C{=}C{=}O$$

The behaviour of dichloroketene with unactivated olefins such as cyclopentene and cyclohexene contrasts sharply with the relative inertness of ketene, alkyl- or even aryl-substituted ketenes under the same mild experimental conditions. The reactivity of olefins in ketene cycloaddition reactions parallels the nucleophilicity of the olefin.

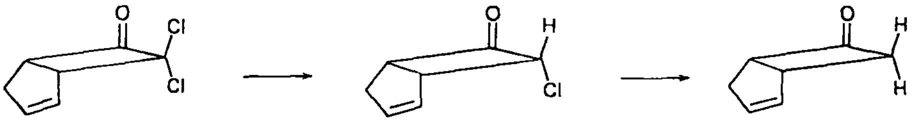
Dichloroketene reacts with unsymmetrical olefins in a regiospecific manner, i.e. the most nucleophilic carbon atom of the olefin is always bonded to the sp-hybridized carbon atom of the ketene molecule. The reaction is rather general and the yields moderate to good. Dichloroketene generation and subsequent cycloaddition reactions require only mild experimental conditions. Although dichloroketene has a high tendency to polymerize and cannot be isolated, this ketene readily enters into cycloaddition reactions. The precursors to dichloroketene, dichloroacetyl chloride and trichloroacetyl chloride, are readily available.

The chlorine atoms may be easily removed from the α,α-dichlorocyclobutanones by zinc in acetic acid or tri-*n*-butyltin hydride in near quantitative yields (equation 2)[7,14,15]. The α,α-dichlorocyclobutanones may even be selectively reduced to the



(2)

monochlorocyclobutanones, i.e. 7,7-dichlorobicyclo[3,2,0]hept-2-en-6-one preferentially reduces to yield only the *endo*-chloro isomer (equation 3)[14,15]. The resultant halogen-free cyclobutanones possess the same structure as would be obtained by the cycloaddition of ketene itself with the olefin. The advantage of dichloroketene over ketene is the much greater reactivity of this ketene. Hence, the use of dichloroketene followed by the reductive halogen removal described significantly broadens the scope of cyclobutanone synthesis.

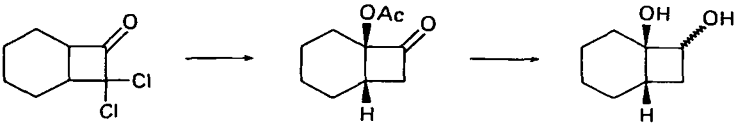


(3)

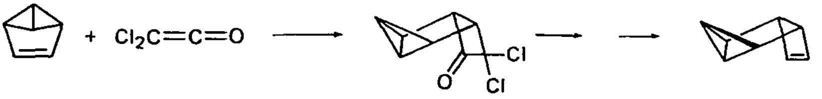
Bicyclo[3,2,0]hept-2-en-6-one is readily obtained in good yield by the cycloaddition of dichloroketene and cyclopentadiene followed by the removal of the chlorine atoms as described above. This bicyclic compound has been found to be a versatile intermediate in prostaglandin synthesis[16-22] and also has been used to achieve a short high yield synthesis of *cis*-jasmone[23]. There are numerous other examples involving the use of bicyclo[3,2,0]heptan-6-ones in synthetic schemes leading to compounds of chemical and/or biological interest. An excellent review on these bicyclic compounds has recently appeared in the literature[24].

The synthesis of bicyclo[*n*,2,0]alkanediols has been described utilizing the cycloaddition of dichloroketene to a cycloalkene[25,26]. Cyclohexene was treated with dichloroketene to give the corresponding cycloadduct which was treated with triethylammonium acetate and chromium dichloride to give the ketoacetate which was reduced with lithium aluminium hydride to give the bicyclooctanediol (equation 4). Bicycloheptanediol was similarly prepared.

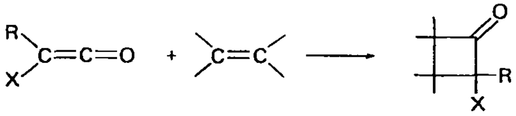
Tetracyclo[4,2,0,0^{2,4},0^{3,5}]oct-7-ene was prepared from benzvalene utilizing a cycloaddition of dichloroketene as a key step in the synthesis[27]. Dichloroketene

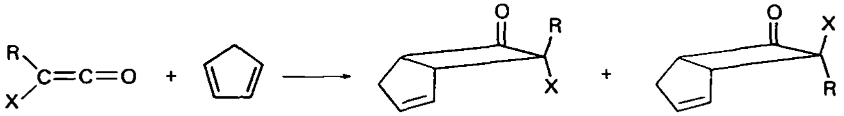

(4)

undergoes cycloaddition in good yield to benzvalene and this cycloadduct is dehalogenated with triphenyltin hydride (equation 5). Conversion of this dechlorinated ketone to the *p*-toluenesulphonylhydrazone and reaction with lithium 2,2,6,6-tetramethylpiperidide yielded the tetracyclo compound.

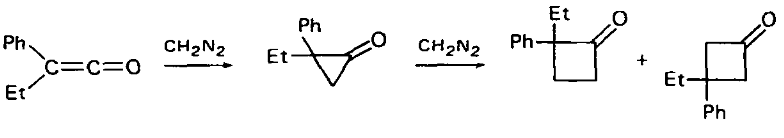

(5)

Alkylhaloketenes also react with a wide variety of olefinic compounds under mild conditions to yield α-halo-α-alkylcyclobutanones (equation 6)[28–33]. The yields are generally as good or better than the cycloadditions with dichloroketene. Cycloaddition with cyclic olefins produces both *endo*- and *exo*-halo-1,2-cycloadducts (equation 7). The isomer distributions are dependent upon the nature of the substituents on the alkylhaloketene, the solvent media and the reaction temperature[32].

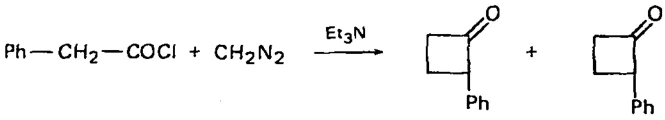

(6)


(7)

Another synthetic method for the preparation of cyclobutanones involves the reaction of diazomethane with ketenes. At low temperatures, the reaction of ketenes and diazomethane yields cyclopropanones. This is illustrated with phenylethylketene (equation 8) and reveals that the reaction of the cyclopropanone yields both isomers of the cyclobutanone. This reaction has been reported with dimethylketene[34–36], trimethylsilylketene[37,38], trimethylgermylketene[37], phenyltrimethylsilylketene[38] and phenylethylketene[38].


(8)

A recent report indicates that the reaction of triethylamine and phenylacetyl chloride in the presence of excess diazomethane at low temperature yields a mixture of 2- and 3-phenylcyclobutanones from which the latter can be isolated in 48% overall yields (equation 9)[39].



(9)

B. Tropolones and Tropones

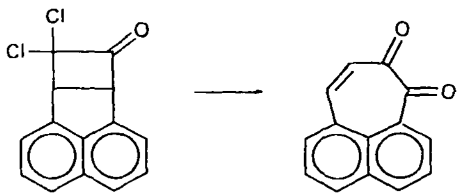
One of the most interesting synthetic applications of halogenated ketenes is the synthesis of tropolones and 2-alkyltropones from readily available starting materials. Tropolone can be obtained in good yield simply by hydrolysis of the dichloroketene–cyclopentadiene adduct, 7,7-dichlorobicyclo[3,2,0]hept-2-en-6-one (equation 10)[1,40]. The cycloadducts of dibromo- and bromochloroketenes with cyclopentadiene have also been solvolysed to tropolone and these proceed as smoothly as the dichloroketene cycloadduct[12]. In a similar fashion the hydrolysis of the cycloadduct of dichloroketene and 1-*t*-butylcyclopentadiene affords β-*t*-butyltropolone and hydrolysis of the dichloroketene and 1-methylcyclopentadiene cycloadduct yields 4-methyltropolone[11,12]. The cycloaddition product of dichloroketene and indene has been solvolysed to 4,5-benzotropolone[2]. The hydrolysis of the cycloadducts of dichloroketene with 1- and 2-isopropylcyclopentadienes afforded Thujaplicin (isopropyltropolones)[41]. Also, this reaction has been utilized in an elegant synthetic route to an established colchicine precursor[42]. Solvolysis of the cycloadduct of dichloroketene and 6,6-dimethylfulvene yields α-dolabrin (3-isopropenyltropolone) in excellent yield[10].

(10)

In a more recent synthetic application utilizing dichloroketene, cycloaddition with 1,6-dihydroazulene occurred in good yield and hydrolysis with triethylammonium acetate in acetone–water resulted in the formation of 8*H*-cyclohepta[*d*]tropolone in excellent yield (equation 11)[43].

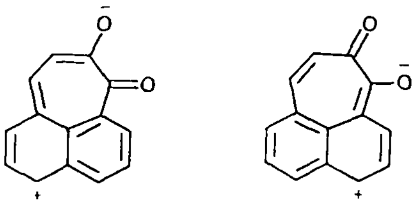
(11)

The hydrolysis of the cycloadduct of dichloroketene–acenaphthalene yields pleiadiene-7,8-dione (equation 12)[44]. The spectral data suggest that this dione has

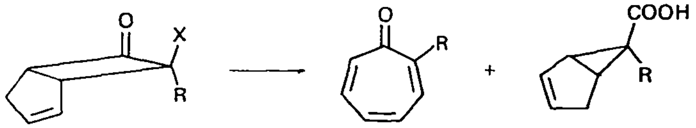


(12)

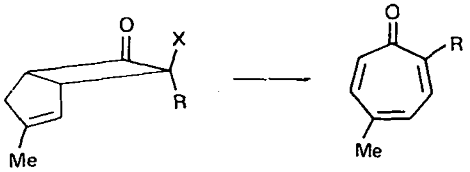
contributions from the following two tropolone structures:



The solvolysis of the cycloadducts of dichloroketene with cyclopentadiene and cyclopentadiene derivatives has been extended to include the adducts of alkylhaloketenes and cyclopentadiene resulting in the development of a new general method for the preparation of 2-alkyltropones. It is quite noteworthy that only the *exo*-7-halo-*endo*-7-alkylbicyclo[3,2,0]hept-2-en-6-ones undergo conversion to the 2-alkyltropones (equation 13). There is a competing Favorskii-type ring contraction reaction which accompanies these solvolysis reactions yielding 6-alkyl-6-carboxybicyclo[3,1,0]hex-2-enes. The relative amounts of 2-alkyltropones and ring contraction produced are strongly dependent on both the nature of the halogen and the steric size of the alkyl substituent on the alkylhaloketene. The *exo*-alkyl isomers of the alkylhaloketene–cyclopentadiene cycloadducts undergo only the ring-contraction reaction under the reaction conditions to produce 2-alkyltropones as will be discussed later[45,46].


(13)

Also, the solvolysis of the cycloadducts of methylchloroketene and 1-methylcyclopentadiene and isopropylchloroketene and 1-methylcyclopentadiene (the *exo*-halo isomers) yield 2,5-dimethyltropone and 2-isopropyl-5-methyltropone respectively (equation 14)[12].

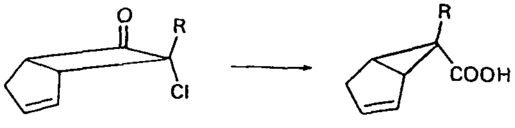

(14)

The preparations cited above represent the first convenient synthesis of tropone derivatives from readily available and inexpensive starting materials.

C. Cyclopropane Derivatives

The ring-contraction of α-halocyclobutanones with aqueous base to yield cyclopropane derivatives has been known for many years and has recently been reviewed[47]. The cycloadducts of halogenated ketenes and olefinic compounds provides an excellent synthesis of α-halocyclobutanones from readily available starting materials. Consequently, halogenated ketenes become pertinent intermediates in the synthesis of cyclopropane derivatives.

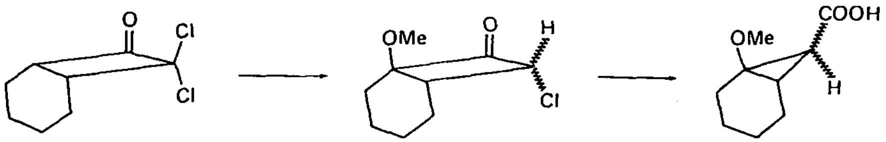
The cycloadducts of cyclopentadiene and alkylhaloketenes, 7-halo-7-alkylbicyclo[3,2,0]hept-2-en-6-ones, undergo a stereospecific base-catalysed ring-contraction reaction to yield 6-alkyl-6-carboxybicyclo[3,1,0]hex-2-enes (equation 15)[46,48-51]. The *endo*-chloroketones yield the corresponding *endo* acids and the *exo*-chloro ketones the *exo* acids. The *exo*-halo isomers also yield 2-alkyltropones as previously mentioned. Because of conformational effects in the cyclobutanone ring, 7-*exo*-chloro-7-*endo*-isopropylbicyclo[3,2,0]hept-2-en-6-one rearranges abnormally on base treatment and gives three hydroxycyclohexenecarboxylic acids[52].



(15)

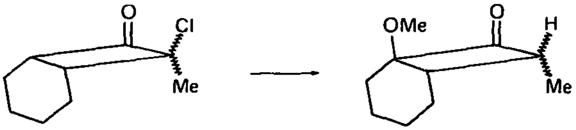
R = Me, Et, *n*-Pr, *i*-Pr, *n*-Bu

In the presence of strong base the cycloadduct of dichloroketene and cyclopentadiene undergoes a ring-opening reaction in contrast to the ring-contraction with the monochloro cycloadducts[7,8,40,53]. However, the cycloadduct of dichloroketene and cyclohexene upon treatment with sodium methoxide in methanol undergoes substitution and then ring-contraction (equation 16)[54].



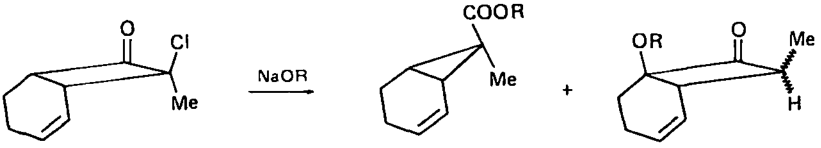
(16)

Treatment of the cycloadduct of methylchloroketene and cyclohexene with sodium methoxide in refluxing methanol yields only the substitution product since a second leaving group is not present for ring-contraction as in the dichloroketene case (equation 17). The adducts of methylchloro- and methylbromo-ketenes and cyclopentadiene also yield substitution at $C_{(5)}$ when treated with sodium methoxide in methanol at 0–5°C. However, treatment of these adducts with sodium methoxide in refluxing methanol afforded ring-contraction rather than substitution[46].



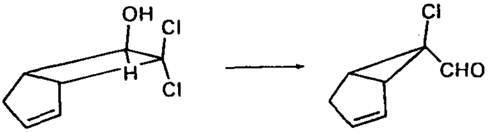
(17)

The isomeric *endo*- and *exo*-chlorobicyclic ketones obtained from the cycloaddition of methylchloroketene and 1,3-cyclohexadiene were separately treated with various bases (equation 18)[55]. A stereospecific ring-contraction and an allylic substitution involving the enol form of the bicyclic ketone were found to be dependent on the base.



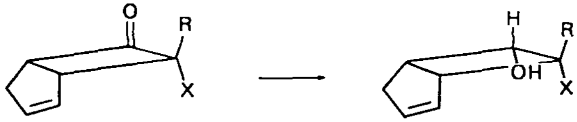
(18)

An interesting rearrangement of cyclobutanols, obtained by the sodium borohydride reduction of adducts of halogenated ketenes and cyclopentadiene, has been reported. The reduction of the dichloroketene cyclopentadiene adduct gave two epimeric alcohols in a ratio of 4:1 with the 6-*endo* alcohol assigned as the predominate isomer. The *exo* alcohol of the adduct of dichloroketene and cyclopentadiene, 7,7-dichlorobicyclo[3,2,0]hept-2-en-6-*exo*-ol, upon treatment with base yielded the *endo* carboxaldehyde which could be easily oxidized to the corresponding acid. The *endo* alcohol analogously produced the *exo* aldehyde (equation 19). This stereospecific base-catalysed ring-contraction involves the chlorine atom *trans* to the hydroxyl group[56,57].



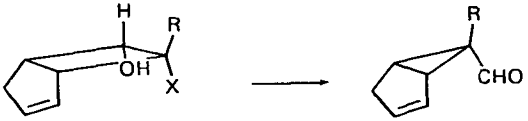
(19)

The lithium aluminium hydride or sodium borohydride reduction of the 7-*endo*-halo-7-alkylbicyclo[3,2,0]hept-2-en-6-ones proceeded stereospecifically to give the corresponding 7-*endo*-halo-7-alkylbicyclo[3,2,0]hept-2-en-6-*endo*-ols (equation 20).



(20)

No evidence for even small amounts of the *exo* alcohols could be found. Conversely, the *exo*-halo ketones gave a mixture of 6-*exo* and 6-*endo* alcohols. The 7-*endo*-halo-7-alkylbicyclo[3,2,0]hept-2-en-6-*endo*-ols upon treatment with base gave the bicyclo[3,1,0]hex-2-en-6-*endo*-carboxaldehydes (equation 21). However, the base treatment of the 7-*exo*-chloro-6-*exo*-alcohol produced no aldehyde (equation 22). A hydride shift was demonstrated to have occurred, thus producing the methyl ketone. Ring contraction, the normally favoured reaction course, is not observed because the required conformation produces a bad interaction between the 7-*endo*-methyl and $C_{(4)}$ hydrogen atom[58,59].



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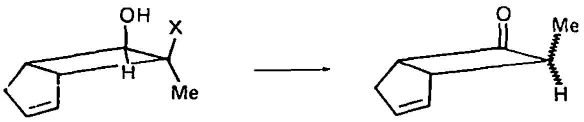
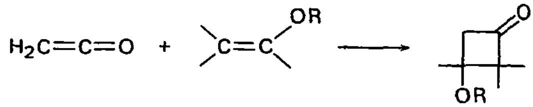
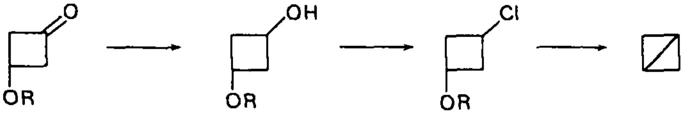


(22)

Ketene adds to simple vinyl ethers to give 3-alkoxycyclobutanones (equation 23) which are convenient entries into the 1,3-disubstituted cyclobutane series and


(23)

particularly the bicyclobutane series. The 3-alkoxycyclobutanones are suitable intermediates for the preparation of bicyclobutanes by the following reaction sequence:

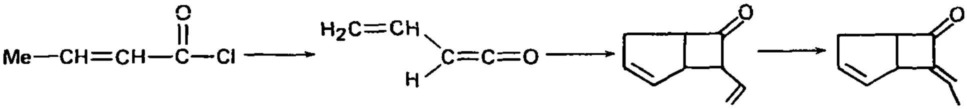


Several syntheses of this type have been described providing an easy access to a variety of bicyclobutanes[60].

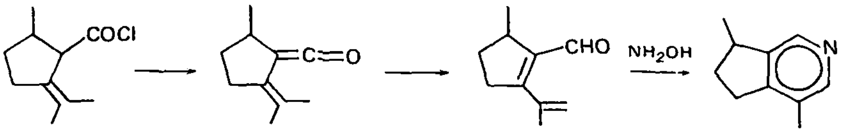
D. Alkylidenecyclobutanones

2-Alkylidenecyclobutanones are readily obtained by the regiospecific cycloaddition of ketenes and allenes. These cycloadditions are discussed in Section III.A.

Another method for the preparation of 2-ethylidenecyclobutanones involves the preparation of vinylketene by a 1,4-elimination of hydrogen chloride from crotonyl chloride. The cycloaddition of this ketene with cyclopentadiene produced the vinyl cycloadduct which isomerized to the conjugated ethylidenecyclobutanone when additional triethylamine was added (equation 24)[61].


(24)

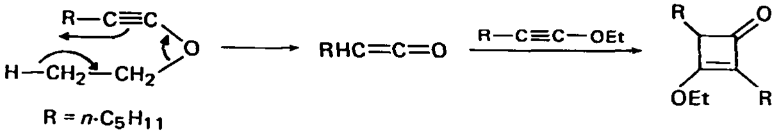
(+)-Actinidine is a rare monoterpenoid alkaloid which has been prepared by a synthetic sequence utilizing a vinylketene (equation 25). The vinylketene, 5-methyl-2-(1-methylethylidine)-1-carbonylcyclopentane, was not stable and quickly rearranged by a [1,5] sigmatropic migration of hydrogen to the aldehyde. The aldehyde could be converted directly to actinidine[62].


(25)

A new synthesis of 2-pyrones has been developed which probably involves the cycloaddition of a vinylketene to an acid chloride which will be discussed in Section II.J[63]. *8-Oxoheptafulvene is a vinylketene and cycloadditions will be discussed in* connection with spiro compounds (Section II.F)[64].

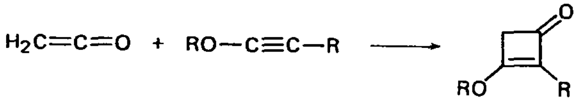
E. Cyclobutenones

The first reported example of a cycloaddition reaction between a ketene and an alkoxyalkyne was rather unusual. 1-Ethoxy-1-heptyne underwent an elimination reaction upon heating to 120°C to yield *n*-pentylketene which immediately underwent cycloaddition with the acetylenic ether (equation 26)[65,66].



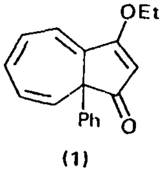
(26)

Several 3-alkoxy-2-alkylcyclobutenones have since been prepared by the cycloaddition of ketene with alkoxyalkynes (equation 27)[67,68]. 2,2-Dialkyl-3-ethoxycyclobutenones have been synthesized by reacting dialkylketenes with ethoxyacetylene[69–73].



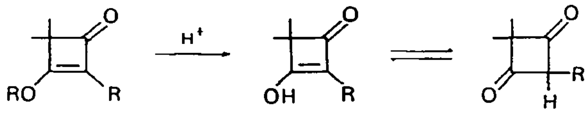
(27)

The cycloaddition of diphenylketene with ethoxyacetylene yields the unexpected hydroazulene (1)[74–76]. This cycloadduct undergoes isomerization with gentle heating to a 1-naphthol.



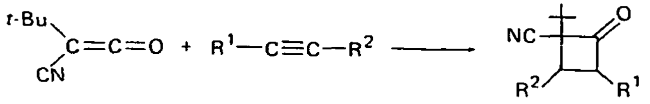
(1)

The hydrolysis of 3-alkoxycyclobutenones gives the 1,3-cyclobutanediones which may also exist in the enol form (equation 28)[70,73,77]. The 1,3-cyclobutanediones prepared in this manner have been converted to a series of 3-substituted derivatives by reaction with a variety of nucleophiles, either directly or through the monoenol ether[73].



(28)

The *in situ* cycloaddition of dichloroketene with 2-butyne has been reported, but this reaction occurs in very low yield[78]. *t*-Butylcyanoketene cycloadds to phenylacetylene and *t*-butylacetylene in 40–80% yields (equation 29). Since two possible relative orientations of the reacting molecules in the cycloaddition are possible and only one product isomer is found, the reaction is regiospecific[79].

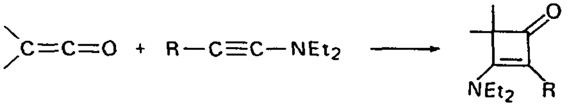


(29)

$R^1 = H, R^2 = Ph$
$R^1 = H, R^2 = t\text{-Bu}$
$R^1 = Ph, R^2 = t\text{-Bu}$

Bis(trifluoromethyl)ketene undergoes cycloaddition with 1-hexyne, 2-butyne, phenylacetylene and diphenylacetylene to yield the expected cyclobutenones[80,81].

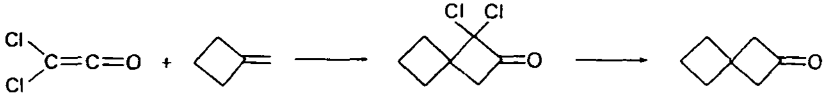
The cycloaddition of a variety of ketenes with ynamines (diethylaminoalkynes) yields the expected diethylaminocyclobutenones (equation 30)[82-84].



(30)

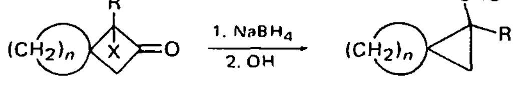
F. Spiro Compounds

The cycloaddition of ketenes with methylenecycloalkanes yields [3,*n*]spiro ketones. Dichloroketene undergoes cycloaddition with methylenecyclobutane to yield the dichlorospiro[3,3]heptanone which can be dechlorinated to yield the spiro[3,3]heptanone (equation 31)[85]. The cycloaddition of dichloroketene with methylenecyclohexane and subsequent dechlorination yields the spiro[3,5]-nonanone[86].



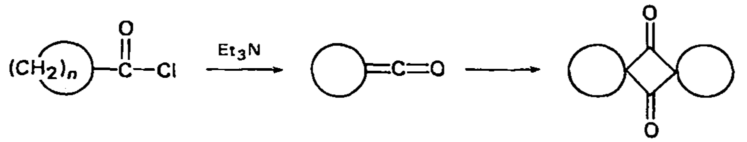
(31)

The cycloaddition of methylchloroketene with methylenecyclohexane, methylenecyclobutane, β-pinene and 5-methyl-2-norbornene yields the corresponding spiro[3,5] and spiro[3,3] ketones in moderate to good yields under the appropriate conditions[87]. The halogenated ketenes give much better yields of cycloadducts than the nonhalogenated ketenes[88]. The sodium borohydride reduction of the halospiro ketones to the corresponding alcohols and subsequent base-catalysed ring-contraction occurs smoothly to the spiro aldehyde thus yielding spiro[*n*,2] compounds (equation 32)[85,87]. Another method for the preparation of spiro compounds utilizing ketenes as synthetic intermediates involves the *in situ* dimerization



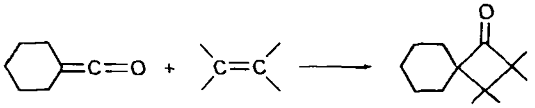
(32)

of polymethylene ketenes (equation 33). These polymethyleneketene dimers can be treated with base and converted to polymethyleneketene trimers[89,90].



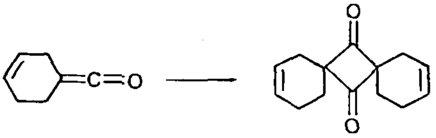
(33)

The cycloaddition of a ketene such as pentamethyleneketene with an olefinic compound yields spiro[3,5]ketones (equation 34). The preparation and dimerization of this ketene has been known for some time[89–93]. Cycloaddition reactions of pentamethyleneketene to cyclopentadiene, dihydropyran, tetramethylallene, diisopropylcarbodiimide, *N-t*-butylbenzylimine and chloral have been described as routes to spiro[3,5]nonanes[94]. Because the dimerization of pentamethyleneketene is a serious competing reaction, reactive cycloaddition partners are necessary to successfully compete for the ketene in the *in situ* reaction.



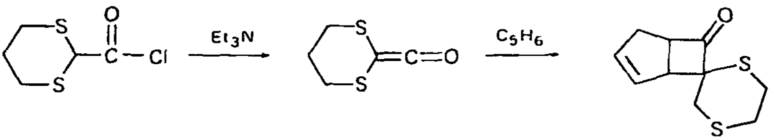
(34)

The triethylamine dehydrochlorination of 3-cyclohexenylcarboxylic acid chloride yields the corresponding ketene which like pentamethyleneketene readily dimerizes to the dispiro compound (equation 35)[95].



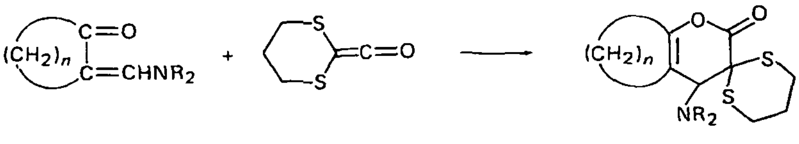
(35)

A sulphur analogue of pentamethyleneketene has been prepared by the dehydrochlorination of 2-chlorocarbonyl-1,3-dithiane and cycloadded to cyclopentadiene (equation 36)[96]. Several spiro 1,3-dithiane-2,3′-(5′,6′-polymethylene)dihydropyranones were obtained by the *in situ* reaction of 2-carbonyl-1,3-dithiane with the



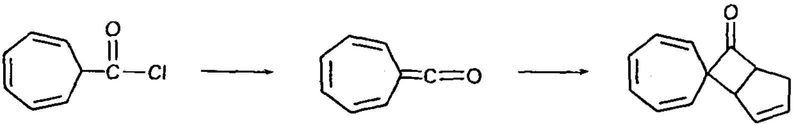
(36)

2-(aminomethylene)cycloalkanones (equation 37)[97]. This is a rare example of a 1,4-cycloaddition reaction involving a ketene.



(37)

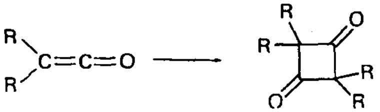
The reaction of 1,3,5-cycloheptatrienyl-7-carbonyl chloride with triethylamine in the presence of cyclopentadiene or indene gave the spirobicyclo[3,2,0]heptane-6,7′-cyclohexatrieneones (equation 38). The intermediate 8-oxoheptafulvene was confirmed[64].



(38)

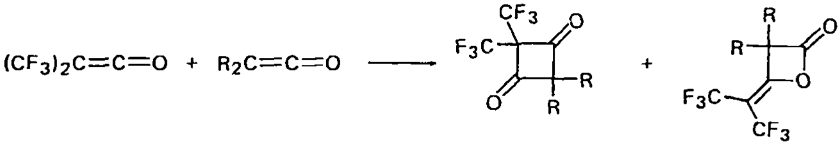
G. 1,3-Cyclobutanediones and Derivatives

1,3-Cyclobutanediones are readily available by the dimerization of dialkylketenes (equation 39). A wide variety of tetraalkylcyclobutanediones have been prepared by the triethylamine dehydrohalogenation of appropriately substituted acid halides.



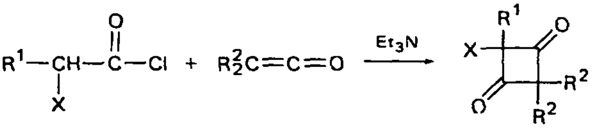
(39)

Mixed dimers of ketenes to yield unsymmetrical 1,3-cyclobutanediones have rarely been studied because in addition to the mixed ketene dimers the two homodimers are produced. However, bis-(trifluoromethyl)ketene does not thermally homodimerize and forms mixed dimers with various other ketenes in good yield (equation 40)[98]. Both dimers of the 1,3-cyclobutanedione structure and 2-oxetanones have been observed. The 2-oxetanone dimers were derived only from cycloaddition to the carbon–carbon double bond and not to the carbon–oxygen double bond of the nonfluorinated ketene.



(40)

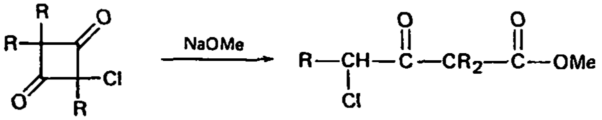
Numerous efforts to homodimerize halogenated ketenes to 1,3-cyclobutanediones have been unsuccessful. However, halogenated ketenes will undergo mixed dimerization with nonhalogenated ketenes to yield halo-1,3-cyclobutanediones (equation 41)[99-101]. The alkylhaloketenes have been generated *in situ* in the presence of dialkylketenes to yield the *unsym*-1,3-cyclobutanediones. Also, the mixed dimers have been prepared by the simultaneous generation of the two ketenes from



(41)

their respective acid halides. A wide variety of these compounds have been prepared in this manner[100].

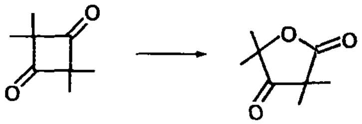
Tetraalkyl-1,3-cyclobutanediones undergo ring-opening reactions in the presence of base to yield β-keto esters[102]. The chlorotrialkyl-1,3-cyclobutanediones also undergo ring-opening reactions to yield β-keto esters (equation 42). Although two β-keto esters are possible, only the expected α-chloro-β-keto esters were found[103].



(42)

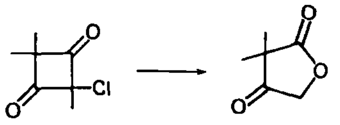
The chlorotrialkyl-1,3-cyclobutanediones react with tri-*n*-butyltin hydride to yield the corresponding trialkyl-1,3-cyclobutanediones which exist as the dione in the solid state; but the enol form is the predominant form in solution[103].

The peracid oxidation of tetramethyl-1,3-cyclobutanedione occurs smoothly and in good yield to the expected lactone, 2,4-furandione (equation 43)[104,105]. This



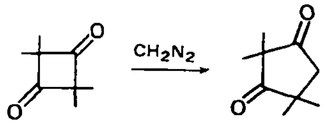
(43)

Baeyer–Villiger oxidation of chlorotrialkyl-1,3-cyclobutanedione gives the ring-expanded product as shown (equation 44). No other ring-expansion products were detected[103].



(44)

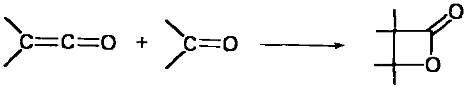
Diazomethane reacts with tetramethyl-1,3-cyclobutanedione to give the ring-expanded product in quantitative yield (equation 45)[106].



(45)

H. 2-Oxetanones

The preparation of 2-oxetanones (β-lactones) by the cycloaddition of ketenes and carbonyl compounds (equation 46) dates back to the early investigations of Staudinger[107]. The addition of simple carbonyl compounds to diphenylketene did not normally proceed unless elevated temperatures were employed. Since the high temperature required for cycloaddition-polymerized aldoketenes (monosubstituted

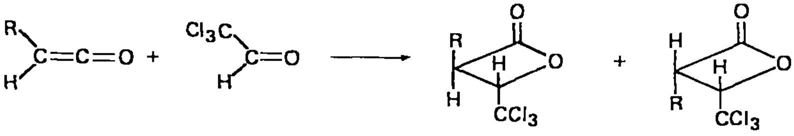

(46)

ketenes) and lower molecular weight ketoketenes (disubstituted ketenes), early investigations were mostly limited to diphenylketene[108].

Later the cycloaddition of ketene to aldehydes was found to proceed smoothly in ether in the presence of mild Friedel–Crafts-type catalysts[109]. Ketones, however, required much stronger catalysts and more vigorous conditions to react with ketene[110].

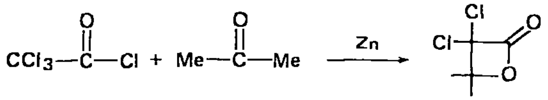
It has been more recently reported that the cycloaddition of simple ketoketenes and carbonyl compounds is possible when the carbonyl compound is activated by electronegative substituents on the α-carbon atom[111]. Thus, the cycloadditions of several ketenes to chloral to yield the corresponding 2-oxetanones were accomplished. The 2-oxetanone derived from dichloroketene and chloral was prepared by the *in situ* preparation of dichloroketene and subsequent trapping of this ketene with chloral[112]. However, under these conditions it was found that dichloroketene would not react with simple ketones such as acetone, cyclohexanone and acetophenone when the ketene was prepared by the dehydrohalogenation method.

The reaction of methyl-, chloro-, isopropyl- and phenoxy-ketenes with chloral yields both *cis*- and *trans*-2-oxetanones in approximately equal amounts (equation 47)[113,114].


(47)

R = Me, Cl, *i*-Pr, PhO

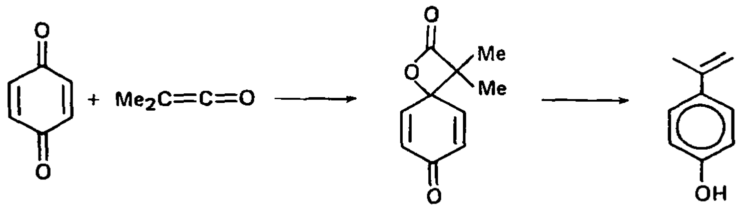
The generation of dichloroketene by the zinc dehalogenation of trichloroacetyl chloride in the presence of acetone and cyclohexanone afforded these 2-oxetanones (equation 48). The zinc halide ethenate apparently activates the carbonyl group, thus increasing the reactivity of these simple ketones with dichloroketene[114].


(48)

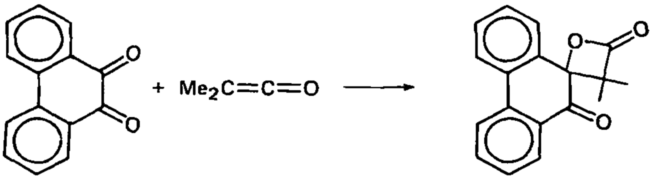
The cycloaddition of methylchloro- and methylbromo-ketenes with chloral, *o*-chlorobenzaldehyde and *sym*-dichlorotetrafluoroacetone reveals that activation of the carbonyl group is necessary for cycloaddition[115].

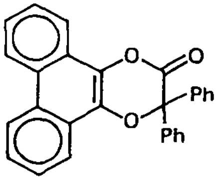
The formation of the 2-oxetanone from hexafluoroacetone and diphenylketene in the presence of potassium fluoride has been reported[116].

The cycloaddition of dimethylketene and *p*-benzoquinone at room temperature yields 3,3-dimethyl-1-oxaspiro[3,5]nona-5,8-diene-2,7-dione (equation 49)[117]. This reaction appears to be general for monoalkyl-, dialkyl- and trimethyl-*p*-benzoquinones. Thermolysis or ultraviolet irradiation of the spirolactones results in decarboxylation. The spirolactones have also been found to undergo acid-catalysed rearrangements, and addition reactions such as halogenation, hydrogenation and Diels–Alder addition[117].

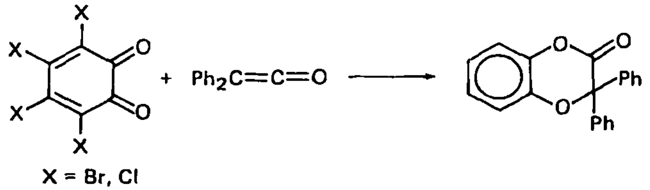

(49)

The reaction of dimethylketene with phenanthrenequinone in the presence of zinc chloride gave the mono-β-lactone (equation 50)[118]. However, diphenylketene undergoes a 1,4-addition with this quinone to give 2[119].

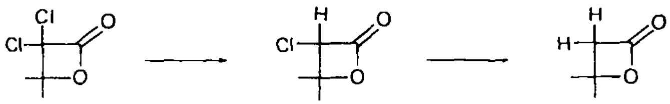

(50)


(2)

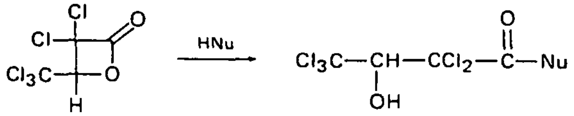
Dimethyl- and diphenyl-ketenes undergo a 1,4-addition with halogenated *o*-quinones (equation 51)[120–123].


(51)

The 3,3-dichloro-2-oxetanones may be selectively reduced with tri-*n*-butyltin hydride to the corresponding monochloro-2-oxetanones. The reduction may also be effected to produce the nonhalogenated 2-oxetanones (equation 52)[124].


(52)

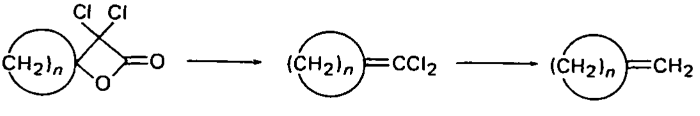
Halogenated 2-oxetanones are much more reactive towards nucleophiles such as water, methanol, dimethylamine, etc. than nonhalogenated 2-oxetanones. Nucleophilic addition to halogenated 2-oxetanones yields only acyl-oxygen cleavage products (equation 53)[125].



(53)

1. Exocyclic olefins

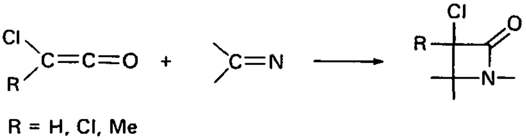
Exocyclic olefins are generally prepared by the Wittig reaction but aside from this well-known reaction, little information on other methods is available in the literature. The cycloadducts resulting from the cycloaddition of dichloroketene and cyclic ketones, 3,3-dichloro-2-oxetanones, are easily decarboxylated upon heating, yielding dichloromethylenecycloalkanes (equation 54). The dechlorination of this exocyclic olefin with sodium in liquid ammonia affords the methylenecycloalkanes in near quantitative yield[124].



(54)

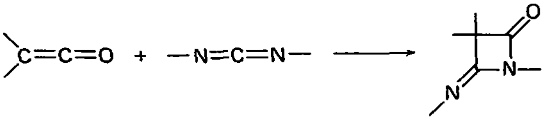
I. 2-Azetidinones

There are many examples in the literature of the formation of 2-azetidiones (β-lactams) by the cycloaddition of a ketene and an imino compound. The synthesis of 3-chloro-2-azetidinones, 3,3-dichloro-2-azetidinones and 3-chloro-3-methyl-2-azetidinones, which are potential precursors of various functionally substituted 2-azetidinones, is possible by the cycloaddition of chloro-, dichloro- and methylchloro-ketenes with imines (equation 55)[126–128].



(55)

4-Imino-2-azetidinones are available through ketenes by cycloaddition with carbodiimides (equation 56). Various types of ketenes have been shown to undergo cycloaddition with the aliphatic carbodiimides, dicyclohexyl- and diisopropylcarbodiimides[129–131]. The aliphatic carbodiimides are more reactive than the aromatic carbodiimides, therefore in mixed aliphatic–aromatic substituted carbodiimides one of the C=N bonds preferentially cycloadds[132].



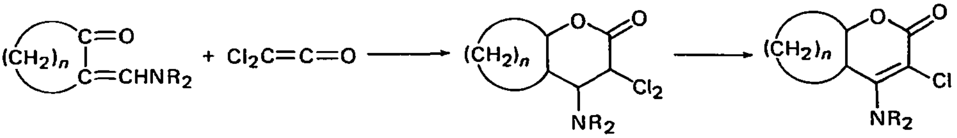
(56)

The cycloaddition of chiral carbodiimides to prochiral ketenes yields diastereoisomeric, nonracemic mixtures of 4-imino-2-azetidinones, the formation of one of the diastereoisomers being preferred[133].

Chlorocyanoketene has recently been prepared and allowed to undergo cycloaddition with dicyclohexylcarbodiimide to yield the α-chloro-α-cyano-β-imino-β-lactam[134]. It appears that a variety of functionally substituted β-lactams are available by this new method.

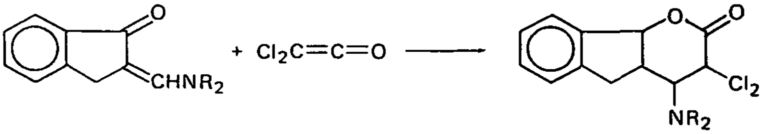
J. Miscellaneous Heterocyclic Compounds

Dichloroketene reacts with *N,N*-disubstituted 2-aminomethylenecyclopentanones, cyclohexanones, cycloheptanones and cyclooctanones to yield the 1,4-cycloaddition products, namely *N,N*-disubstituted 3,3-dichloro-4-amino-5,6-polymethylene-3,4-dihydro-α-pyrones (equation 57)[135,136]. This represents the same type of 1,4-cycloaddition involving a ketene as described at the end of Section II.F.



(57)

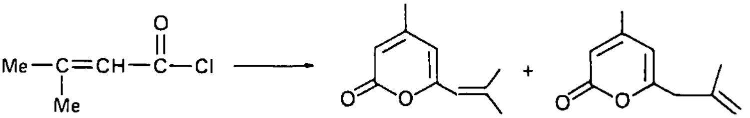
Diphenylketene and ketene also undergo this 1,4-cycloaddition reaction[137,138]. *N,N*-Disubstituted 2-aminomethylene-1-indanones react with dichloroketene in an analogous fashion (equation 58)[139].



(58)

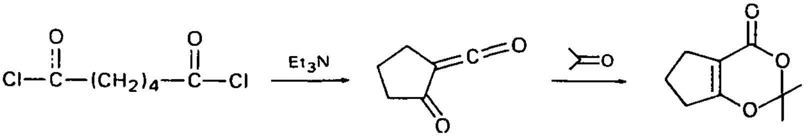
Cycloaddition of some *N,N*-disubstituted 2-aminomethylenecycloalkanones with some new dithioalkylketenes, 2-carbonyl-1,3-dithiane and dithioethylketene, yielded the expected thio-α-pyrones[140,141].

Another new method for the synthesis of α-pyrones has been reported which probably involves the cycloaddition of a vinylketene to an acid chloride. The triethylamine dehydrochlorination of α,β-unsaturated acid chlorides yields two isomeric α-pyrones (equation 59)[63].

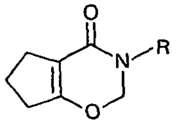


(59)

The triethylamine dehydrochlorination of adipoyl chloride in the presence of aldehydes and ketones affords 1,3-dioxin-4-ones (equation 60)[142]. This reaction apparently occurs via the acylketene. In an analogous manner the acylketene cycloadducts 3—5 were obtained employing an imine, diphenylketene and isocyanates[143] respectively.



(60)



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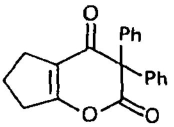

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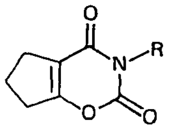
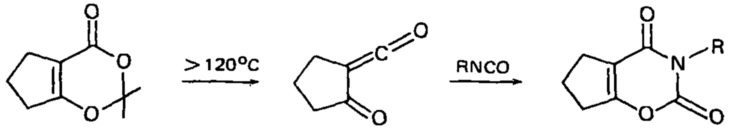
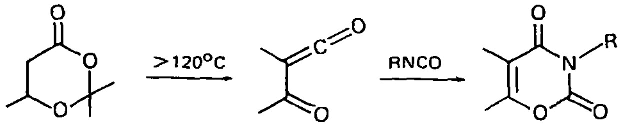


(5)

The *in situ* generation of acylketenes by the thermolysis of 1,3-dioxin-4-ones in the presence of isocyanates yields 1,3-oxazine-2,4-diones (equation 61)[144]. Analogous reaction with phenyl isothiocyanate, carbodiimides, aryl cyanides, aryl cyanates and cyanamides also affords the 1:1 cycloadducts (equation 62). Some of the cycloadducts are very interesting starting materials for the synthesis of new heterocyclic compounds with herbicidal activity.

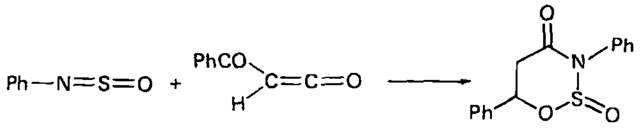


(61)



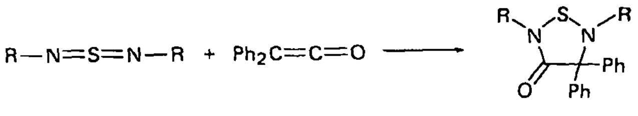
(62)

N-Sulphinylamines are useful reagents for the synthesis of heterocyclic compounds containing adjacent nitrogen and sulphur atoms. *N*-Sulphinylaniline undergoes cycloaddition with benzoylketene, generated *in situ* by pyrolysis of 5-phenylfuran-2,3-dione, to give a [2 + 4] cycloadduct, 3,6-diphenyl-1,2,3-oxathiazin-4(3*H*)-one 2-oxide (equation 63)[145].



(63)

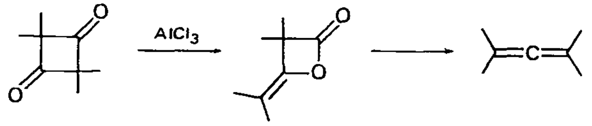
The cyloaddition of sulphur diimides with diphenylketene affords the 1,3-cycloadducts, 4,4-diphenyl-1,2,5-thiadiazolidin-3-one in good yield (equation 64). This reaction is temperature dependent as in some cases at lower temperatures the 1,2-cycloadduct is formed but can be isomerized into the 1,3-cycloadduct by refluxing in hexane[146-149].



(64)

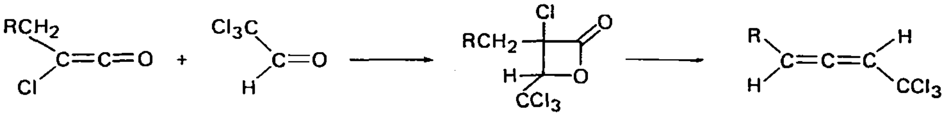
K. Allenes via Ketenes

A characteristic reaction of 2-oxetanones is a thermal decarboxylation with the resultant formation of an olefin. If an alkylidene substituent is at the 4-position, decarboxylation leads to an allene. Tetramethylallene is prepared from the dimer of dimethylketene, 2,2,4,4-tetramethyl-1,3-cyclobutanedione. Isomerization of this dimer by heating with aluminium chloride affords the 2-oxetanone dimer which when pyrolysed near 500°C yields the allene in near quantitative yield (equation 65)[150,151].



(65)

Halogenated 2-oxetanones, the cycloadducts of halogenated ketenes and carbonyl compounds, are less susceptible to decarboxylation than other 2-oxetanones. However, the decarboxylation of 2-oxetanones derived from halogenated ketenes and chloral over an electrically heated wire produces halogen-containing allenes (equation 66). It is likely that dehydrochlorination precedes decarboxylation. Perchloroallene has been observed by the pyrolysis of the cycloaddult of dichloroketene and chloral[152,153].



(66)

Tetraphenylallene has been obtained directly from diphenylketene when the ketene is treated with a large excess of hexamethylphosphoric triamide[154]. Apparently the allene is derived from the trimer as all efforts to prepare the allene from the dimer were unsuccessful.

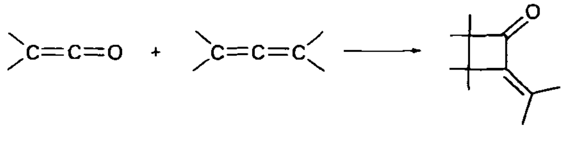
Ketenes may be converted directly to allenes via the Wittig reaction[155–159]. However, the above described method for the preparation of tetraphenylallene is reportedly superior to the Wittig reaction for this particular ketene.

III. SYNTHETIC USES OF ALLENES

Most of the recent advances utilizing allenes as intermediates in syntheses have generally involved: (1) cycloaddition reactions with ketenes to yield 2-alkylidenecyclobutanones, (2) the oxidation of α- and β-allenic alcohols and allyl allenes, (3) the cycloaddition of allenes to various unsaturated compounds to yield a variety of heterocyclic compounds, (4) organometallic additions to allenic systems as well as the addition of some organometallic allenes to unsaturated systems.

A. Alkylidenecyclobutanones

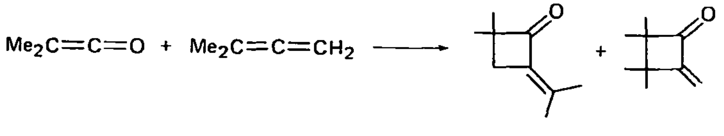
2-Alkylidenecyclobutanones are obtained by the regiospecific cycloaddition of ketenes and allenes (equation 67). The reaction of variously substituted ketenes



(67)

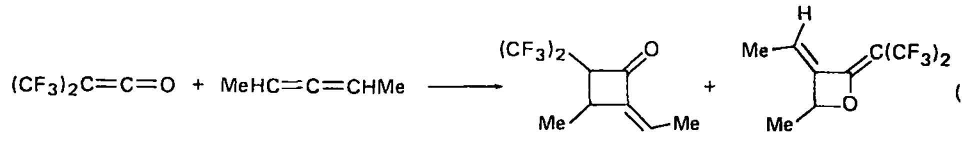
and allenes has been investigated and it has been found that tetramethylallene and 1,2-cyclononadiene give much better yields of the 2-alkylidenecyclobutanones than other allenes investigated[160]. Tetramethylallene exhibits a particularly unusual reactivity in cycloaddition reactions with ketenes[161].

The cycloaddition of dimethylketene with *unsym*-dimethylallene resulted in a regiospecific cycloaddition of the central carbons to give conjugated alkylidenecyclobutanones (equation 68)[162].



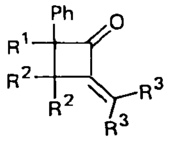
(68)

The cycloaddition of ketenes to acyclic 1,3-disubstituted allenes yields mainly 2-*Z*-alkylidenecyclobutanones with lesser amounts of the 2-*E*-alkylidene isomers[163,164]. Optically-enriched allenes give *Z*-isomers, which, in contrast to *E* isomers, have little or no optical activity[165,166]. However, 1,3-diphenylallene behaves differently with *t*-butylcyanoketene giving exclusively 2-*E*-benzylidenecyclobutanones[167]. *sym*-Dimethylallene reacts with bis(trifluoromethyl)ketene to form both oxetane and 2-alkylidenecyclobutanone (equation 69), but tetramethylallene forms only products of an ene reaction, apparently because of steric hindrance to ring-closure[168].



(69)

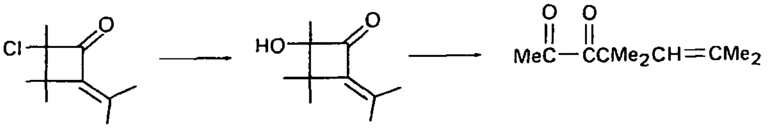
The reaction of excess *unsym*-dimethylallene with diphenylketene gave the two isomeric 2-alkylidenecyclobutanones in a ratio of **6a**:**6b** = 3. The *in situ* reaction of phenylchloroketene with an excess of *unsym*-dimethylallene gave a ratio of **7a**:**7b** = 5.[169].



(6a) R^1 = Ph, R^2 = H, R^3 = Me
(6b) R^1 = Ph, R^2 = Me, R^3 = H
(7a) R^1 = Cl, R^2 = H, R^3 = Me
(7b) R^1 = Cl, R^2 = Me, R^3 = H

t-Butylcyanoketene reacts with tetramethylallene to give a good yield of the expected 2-alkylidenecyclobutanone. The reaction of this ketene with *unsym*-dimethylallene produces about a 2:1 mixture of the expected products[170].

The reaction of the cycloadduct of methylchloroketene and tetramethylallene with base resulted in the formation of an α-hydroxy compound which underwent an unusual ring-opening reaction to yield an α,β-dione (equation 70)[171].



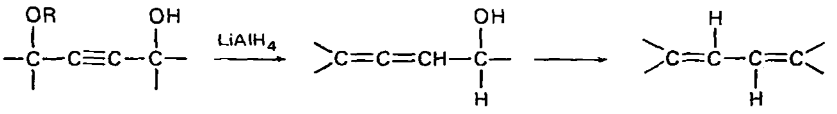
(70)

The synthesis of (+)-isocaryophyllene has been reported utilizing the cycloaddition of dimethylketene with the allene, bicyclo[7,1,0]deca-4,5-diene, as a key step in the synthetic sequence[172].

Another method for the preparation of ethylidenecyclobutanones was described in Section II.D.

B. Conjugated Dienes

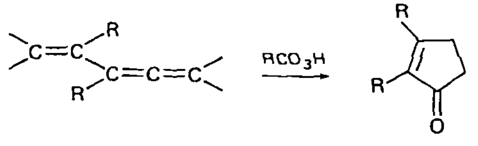
Conjugated dienes may be prepared in near quantitative yield from acetylenic compounds through α-allenic alcohols[173,174]. The easily assessible 4-alkoxy- and 4-(tetrahydro-2-pyranyloxy)-1-hydroxy-2-butynes can be conveniently converted into the conjugated dienes by treatment with an excess of lithium aluminium hydride in refluxing THF (equation 71). The reaction proceeds via the α-allenic alcohol, as indicated, formed *in situ* as the corresponding alkoxides. The dienes are generally free from positional isomers. Due to the facile preparation of the starting acetylenic compounds[174-179], many conjugated dienes of the above type are thus easily accessible in three steps from readily available starting materials.



$$-\overset{OR}{\underset{|}{\overset{|}{C}}}-C\equiv C-\overset{OH}{\underset{|}{\overset{|}{C}}}- \xrightarrow{LiAlH_4} >C=C=CH-\overset{OH}{\underset{H}{C}}- \longrightarrow >C=\overset{H}{C}-\underset{H}{C}=C< \qquad (71)$$

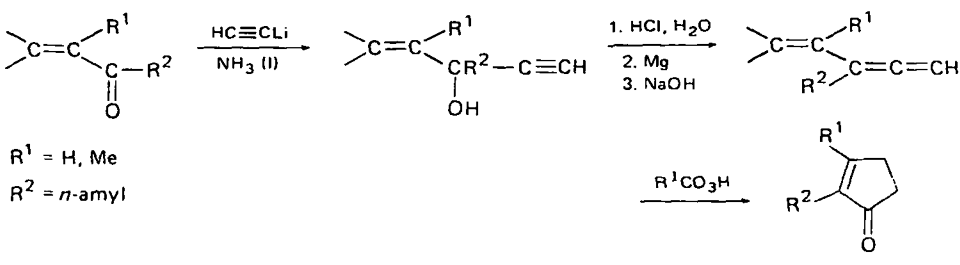
C. Cyclopentenones

A new preparation of cyclopentenones has been reported which involves the epoxidation of vinylallenes (equation 72). The cyclization process probably occurs via the transposition of an intermediate vinylcyclopropane[180-182].



(72)

The utilization of this method of synthesis of cyclopentenones has provided a new alternative route to several natural products[182]. The synthesis of dihydrojasmone and 2-pentyl-2-cyclopentenone, from which methyl dihydrojasmonate can be easily obtained, is shown in equation (73) involving a vinylallenic Grignard reagent from readily available starting materials.

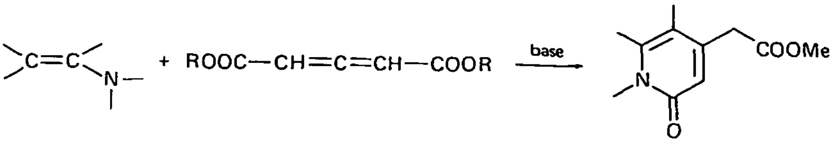


(73)

D. Heterocyclic Compounds

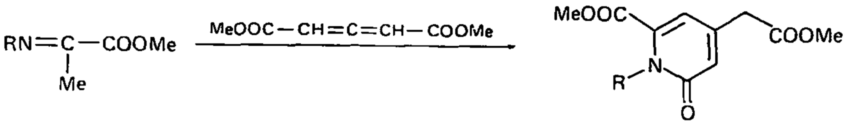
1. *2-Pyridones*

The nucleophilic addition of enamines to a dicarboxyallene has provided the basis for an extremely valuable method of preparing highly substituted 2-pyridones (equation 74)[183]. This method has been applied to the total synthesis of camptothecin, an antitumour alkaloid[184].



(74)

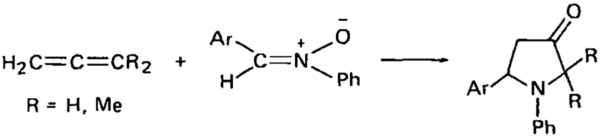
An extension of this method has led to the development of a new route to pyridones via imines of pyruvic esters[185]. The imines, prepared by the condensation of amines and ethyl pyruvate, were cycloadded to a dicarboxy allene to yield a pyridone unsubstituted at $C_{(5)}$ (equation 75).



(75)

2. *3-Pyrrolidinones*

The cycloaddition of azomethine oxides with allene and 1,1-dimethylallene provides a new synthesis of 3-pyrrolidinones (equation 76)[186]. Apparently, a 1,3-dipolar cycloaddition occurs followed by intramolecular rearrangement. It is clear that the reaction between allenes and azomethine oxides differs from the cycloaddition reactions of the same dipolarophile with nitrile oxides[187], azides[188] and diazoalkanes[189]. In these cases stable spiro compounds and/or exocyclic alkylidene adducts are formed as primary reaction products.

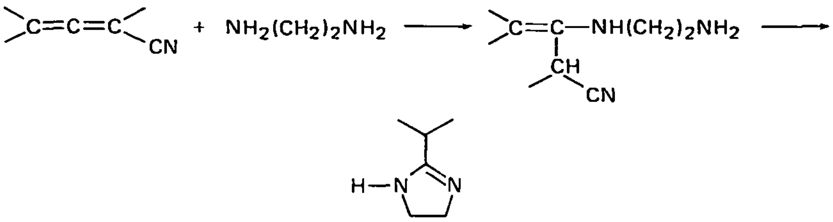


(76)

More recently it has been reported that the reactions of *C*-aryl-*N*-alkylazomethine oxides with 1,1-dimethylallene proceed through an initial 1,3-dipolar cycloaddition followed by two competing processes: formation of a substituted 4-piperidinone by a further addition reaction of the intermediate with the azomethine oxide *and* intramolecular rearrangement of the alkylideneisoxazolidine monoadduct leading to a 3-pyrrolidinone. This novel reaction pathway to the 4-piperidinone provides clear evidence of the influence of the substituent groups of the dipole, azomethine oxide, in its reaction with allenes[190].

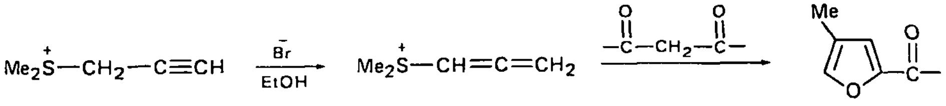
3. *Imidazolines*

A double Michael addition of ethylenediamine to allenic nitriles gives good yields of imidazolines (equation 77). Apparently, the diamine initially adds to the sp-hybridized carbon atom of the allene and then rearrangement occurs to the conjugated enaminic nitrile which readily cyclizes to the 2-alkylimidazoline. Similarly *o*-phenylenediamine yields 2-alkylimidazoles[191]. This is a novel synthesis of imidazolines and imidazoles by the Michael addition to allenic or acetylenic nitriles.


(77)

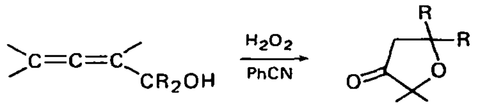
4. *Furans*

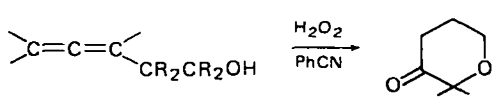
A simple new synthesis of furans has been described which involves the addition of enolate anions to allenic sulphonium salts. Dimethyl-2-propynylsulphonium bromide isomerizes rapidly to the allene in ethanol. The addition of an ethanolic solution of a β-keto ester, a β-keto sulphone, or a β-diketone and sodium ethoxide rapidly gives the furan in high yield (equation 78)[192].


(78)

5. *3-Oxacyclanones*

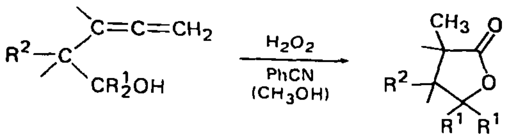
The oxidation of α- and β-allenic alcohols by hydrogen peroxide in benzonitrile represents a new method for the preparation of 3-oxacyclanones (equations 79 and 80)[193].


(79)


(80)

6. *γ-Lactones*

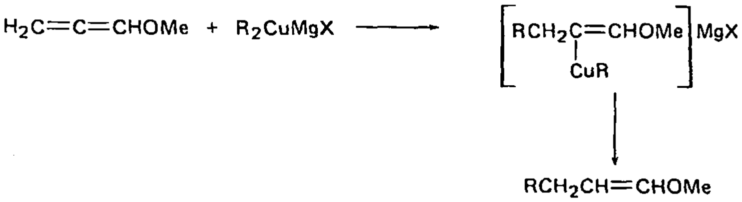
The selective oxidation of β-allenic alcohols represents a novel method for obtaining γ-lactones (equation 81)[194]. Epoxidation of the allene followed by rearrangement and a proton transfer from methyl alcohol results in the formation of the γ-lactone.



(81)

E. Miscellaneous

Methoxyallene undergoes a smooth reaction with preformed homocuprates and heterocuprates in THF leading to the vinylic ethers which after protonation are generally obtained as a mixture of *E* and *Z* isomers (equation 82)[195].

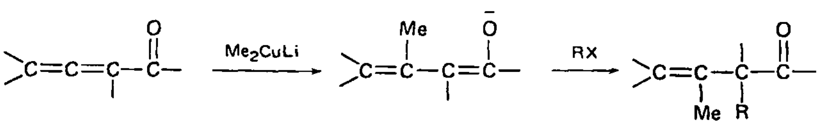


(82)

Grignard reagents add to propynal diethyl acetal in the presence of catalytic amounts of cuprous bromide in ether solution at the terminal carbon atom and not the β-carbon atom to afford the allene ethers in good to excellent yields (equation 83)[196]. When the reaction mixture is subjected to acid hydrolysis, the 3-substituted *trans*-propenals are obtained.

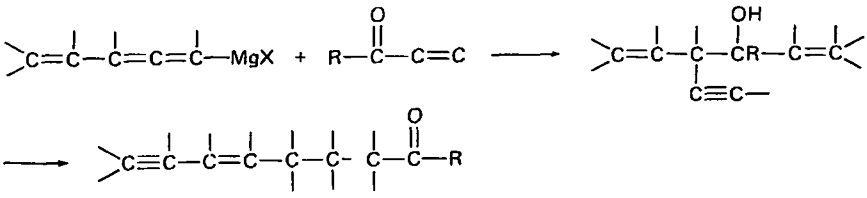
$$HC\equiv C-CH(OEt)_2 \xrightarrow[\substack{CuBr\\Et_2O}]{RMgX} R-CH=C=CH-OEt \xrightarrow{H_3O^+} R-CH=CH-CHO \qquad (83)$$

The 1,4-addition of lithium dialkylcuprates to conjugated allenic ketones and esters results in an enolate which can be alkylated yielding the unsaturated ketone or ester (equation 84). This 1,4-addition has been applied to the synthesis of the natural product, lavandulol[197].



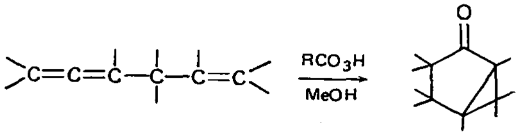
(84)

Vinylallenic Grignard reagents prepared from 5-halo-3-alken-1-ynes react with acyclic conjugated aldehydes and ketones to give exclusively 4-ethynyl-1,5-hexadiene-3-ols (equation 85). These alcohols are easily isomerized to δ-ethylenic ε-acetylenic aldehydes and ketones by heating[198].



(85)

The peracid oxidation of allylallenes yields bicyclo[3,1,0]hexan-2-ones (equation 86). This reaction is highly solvent-dependent and gives a quantitative yield[199].



(86)

Also, the peracid and osmium tetraoxide oxidation of some allene intermediates have been utilized in an important step in the total synthesis of steroids. The elaboration of the pregnane and the trioxygenated corticoid chains at position 17 has been accomplished by this oxidation of the allene intermediate[200].

1,3-Diethoxycarbonylallene has been found to be an active dienophile and ethoxycarbonylketene equivalent in the synthesis of antibiotic *C*-nucleosides[201,202].

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The Chemistry of Ketenes, Allenes and Related Compounds
Edited by Saul Patai

CHAPTER 9

Kinetics and mechanisms (excepting cycloadditions)

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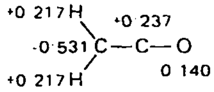
I. KETENES: INTRODUCTION

At the time of Lacey's review of the reactions of ketenes[1] little quantitative kinetic data had been published, although some general trends in reactivity were long known, and the general mechanistic outline was reasonably clear. Since 1964 there has been a considerable advance in our knowledge of both the kinetics and mechanism of many of the reactions undergone by ketenes. Two of the main areas of progress have been in cycloaddition reactions with unsaturated systems, and in additions to molecules containing reactive hydrogen atoms. The former are the concern of another chapter and will not be considered here, excepting when polymerization of ketenes is discussed. Understanding of the latter, for a wide range of reaction partners, has been much facilitated by the work of Satchell and his group, who have also usefully generalized matters by discussing the close kinetic and mechanistic similarities between ketenes and isocyanates[2], and fitted ketene acylations into the pattern of acylation in general.

The main reactive centre in ketenes is the electrophilic carbonyl carbon atom, positive charge appearing there in two of the canonical forms:

$$R_2C{=}C{=}O \longleftrightarrow R_2C{=}\overset{+}{C}{-}\overset{-}{O} \longleftrightarrow R_2\underset{..}{\overset{..}{C}}{-}\overset{+}{C}{=}O$$

Attempts have been made to calculate the ground-state charge distribution in ketene[3-5], and although the results vary considerably, all yield a fairly positive α-carbon. The most recent SCF values are shown below[4].



Whether oxygen or β-carbon carries the greater negative charge depends on the calculation. It would be interesting to relate charge distribution in the heterocumulene skeleton to reactivity for a series of ketenes. A Hückel calculation on dimethylketene[5] indicates that the only effect of methyl substitution is to *reduce* the negative charge at the β-carbon, but obviously more work is needed.

Additions to molecules with reactive hydrogen (HS) follow a fairly uniform pattern. All those studied are heterolytic in character, with the possible exception of addition to thiols, ketenes usually acting as electrophiles. Addition is normally to the carbon–carbon double bond and probably proceeds through cyclic transition states in most cases. In these, attack of the nucleophilic portion of the substrate on the ketene α-carbon is concerted with proton attachment to the β-carbon. Sizeable deuterium isotope effects indicate that S–H bond-breaking is kinetically important. With water and alcohols single molecules are unable to form viable transition states and dimers or trimers are involved, whereas carboxylic acid monomers are able to function successfully. Carboxylic acid-catalysed additions of water, alcohols and amines pass through cyclic transition states involving one molecule of ketene, HS and acid, the last transferring a proton from HS to the ketene β-carbon. Amides, through their tautomerism, play a similar catalytic role in the acylation of alcohols.

Many of these additions are kinetically third order and presumably proceed through fast preequilibrium steps, giving hydrogen-bonded complexes between substrate molecules, or substrate and catalyst, which then react with ketenes in rate-determining steps. Solution kinetics are often complicated, especially at low temperatures, by uncertainty concerning which associated species are taking part; the order in ketenes, however, remains stubbornly at unity.

Results using different ketenes generally conform to the known trends that electron withdrawal accelerates the rate of addition to nucleophiles. Steric factors come into play when bulky substrates are adding, although the favoured formation of transition states at right angles to the plane of the ketene molecule helps to minimize these. Change of solvent tends to decrease the rate in the direction of increasing solvent polarity, which suggests some decrease in charge separation in forming transition states. In ketene dimerization, however, the solvent effect, although weak, is in the reverse direction.

With strong electrophiles such as hydrogen halides ketenes appear to take up a nucleophilic role. Nominally, protonation may occur at either oxygen or β-carbon; theoretical calculations[4] and results in superacid solution[6] show the acetyl ion to be more stable than the hydroxyvinyl cation.

Kinetic and mechanistic aspects of the polymerization, oxidation and thermal decomposition of ketenes have received recent attention and are reviewed here, as is relevant work on ketene derivatives. In general, material reviewed by Lacey[1] is not included.

II. KETENE ADDITION REACTIONS

A. Reactions with Water

As might be expected the first relevant observations were made by Hermann Staudinger[7] who noted that the rate of hydrolysis to carboxylic acids increased substantially in the order dimethylketene < diethylketene < diphenylketene <

biphenyleneketene. However, only within the last ten years have there been any quantitative kinetic studies and three of widely-differing types are discussed here.

1. Kinetics

Direct measurements in aqueous solution have recently been made by Meier and his coworkers[8], who generated *p*-substituted phenylketenes *in situ* by flash photolysis of diazoacetophenones and measured the rate of production of carboxylic acid by a fast conductometric technique (equation 1). Hydrolysis of the ketene ($t_{1/2} \sim 15-200\ \mu s$) is believed to be the rate-determining step in the sequence and reaction is first order in ketene. The effect of substituents is shown in Table 1, and the accelerating effect of electron-withdrawing groups is clearly seen; $\rho = +1.19$. Activation parameters measured for R = Cl, are $E_a = 39$ kJ/mol and $A = 10^{10.72}\ s^{-1}$, based on the pseudo first-order rate constant. Rates were independent of pH in the range 4.0–10.8 and rates measured in D_2O for R = H or Cl were slower by factors of 2.0 and 1.8 respectively. The main kinetic complications of autocatalysis by the acid product and concurrent dimerization of the ketene are circumvented by working in aqueous solution.

$$RC_6H_4COCHN_2 \xrightarrow[-N_2]{h\nu} RC_6H_4COCH{:} \longrightarrow RC_6H_4CH{=}C{=}O \xrightarrow{H_2O}$$

$$RC_6H_4CH_2CO_2H \longrightarrow RC_6H_4CH_2CO_2^- + H^+ \qquad (1)$$

Lillford and Satchell[9] used dimethylketene in ether, employing a tenfold excess of water and allowing for autocatalysis by adding varying amounts of isobutyric acid and extrapolating back to zero acid concentration. Both spontaneous and isobutyric acid-catalysed reactions are first order in ketene, uncatalysed hydrolysis is second order in water up to 0.3 M, thereafter increasing more rapidly with increasing water concentration, and the acid-catalysed addition is first order in all three reactants.

The third study concerned the gas-phase reaction reaction of water with ketene itself, alone and catalysed by acetic acid in the range 224–324°C[10]. The uncatalysed reaction is heterogeneous, with an order of 0.4 in water and unity in ketene and an apparent activation energy of 10 kJ/mol. The surface reaction is self-inhibited by the acetic acid product, which presumably blocks the active surface sites, and the effect of added acetic acid is shown in Figure 1. Heterogeneous reaction is soon fully inhibited, and is replaced above acetic acid pressures of 10 Torr by a homogeneous reaction of the third order, first in ketene, water and acid, for which $k = 10^{4.34} (\exp -20{,}500\ J/RT)\ l^2/mol^2 s$.

TABLE 1. Effect of *p*-aryl substituents on the rate of hydrolysis of phenylketenes, *p*-RC_6H_4CHCO at 26°C

R	$10^{-3}k(s^{-1})$
NO_2	49.5
CN	25.6
Cl	9.6
F	5.9
H	4.9
OMe	4.5
Me	3.8

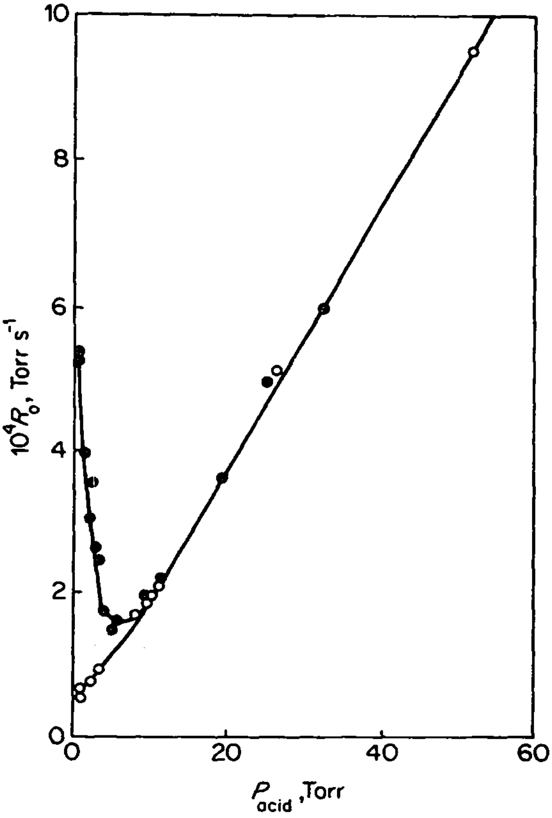
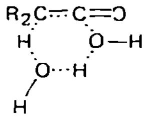


FIGURE 1. Initial rate versus acetic acid pressure in the gas-phase acetic acid-catalysed addition of water to ketene. R_0 = initial rate with both ketene and water initial pressures at 10 Torr; temperature = 254°C
○: Unpacked vessel of surface-to-volume ratio 0.88 cm^{-1};
●: packed vessel of surface-to-volume ratio 9.7 cm^{-1}. Reproduced from P. G. Blake and H. H. Davies, *J. Chem. Soc., Perkin II*, 322 (1972) by permission of The Chemical Society.

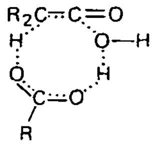
2. *Mechanism*

The three studies are conveniently discussed together. In all cases one molecule of a ketene is involved in the rate-determining step. It is also clear from the gas-phase and ethereal solution work that reaction does not occur with a single water molecule, a surface, a molecule of acid or a second molecule of water being necessary. Such a bimolecular addition would be the back-reaction of the unimolecular decomposition of acetic acid[11] for which the activation energy is 272 kJ/mol; combination with ΔH gives a high activation energy of 144 kJ/mol for the homogeneous addition of one water molecule to ketene, which is thus supplanted by lower energy paths.

Cyclic transition states seem probable, especially since change in pH has no effect, and the ether solvent is unable to adopt a catalytic role. These involve a ketene and two molecules of water (or a water dimer) in the uncatalysed solution reaction (1), the second water molecule being replaced by the more effective acid catalyst in the catalysed process (2). It is unlikely that the transition states are produced in a termolecular step: water dimer and hydrated carboxylic acid molecules probably react with the ketene in the uncatalysed and catalysed reactions respectively. In the catalysed process the relative rates of reaction rule out a mechanism involving the initial formation of anhydride followed by hydrolysis. The transition states shown are compatible with the deuterium isotope effect.



(1)



(2)

Substituent effects in phenylketene hydrolysis support the concept of an electrophilic attack of the ketene carbonyl carbon on the water oxygen, which is promoted by electron withdrawal. The studies are too different in type to usefully compare the rate constants for phenylketene, dimethylketene and ketene hydrolysis: for example, work in ethereal solution indicates that water polymers would be kinetically important in aqueous solution. However, the lowering in activation energy from 39 to 20 kJ between uncatalysed phenylketene and catalysed ketene hydrolysis, when structural and solvent factors would tend to increase it, emphasises the efficiency of carboxylic acid catalysis in this case.

B. Reactions with Alcohols

This important reaction has attracted a number of quantitative studies which are divided here into uncatalysed and catalysed reactions.

1. *Uncatalysed addition*

a. Kinetics. Lillford and Satchell[9] investigated the kinetics of acylation of several alcohols by dimethylketene in ether at 25°C. The reaction is clean and complete in dry, air-free systems (alcohols generally react more slowly than water) and unlike the reaction with water is unaffected by autocatalysis. The order in the ketene is one in all cases, but as in all the work with alcohols, the order in alcohol is complicated by association in solution. Results here show a power in total alcohol of between two and three; when the degree of association of the alcohol is taken into account the results are best fitted by

$$-\mathrm{d}[\text{ketene}]/\mathrm{d}t = k[\text{ketene}][(\mathrm{ROH})_3]$$

that is, reaction of the ketene with an alcohol trimer. Participation by alcohol dimers is not however ruled out, and cyclic transition states involving either two or three alcohol molecules may be written.

Brady, Vaughn and Hoff[12] on the other hand found a first-order dependence on alcohol when pentan-2-ol reacted with a variety of ketenes in hexane. They employed only a slight excess of alcohol over ketene and worked at lower alcohol concentrations than Lillford and Satchell, obtaining good second-order plots, first in each reactant. Different behaviour again was reported by Tille and Pracejus[13] for phenylmethylketene with methanol in toluene between +1°C and −95°C. Here the order in alcohol was two in the range +1°C to −50°C but fell to one at −95°C. The latter was interpreted as being effectively second order in methanol monomer, the concentration of which was suggested as having an unusual proportionality to $[\mathrm{MeOH}_{\mathrm{total}}]^{1/2}$ at this temperature due to the existence of higher oligomers. It was also found that the order in methanol rose above two at higher alcohol concentrations. However with ketene at 20°C in toluene, Samtleben and Pracejus again obtained orders of two in alcohol and one in ketene[14].

Finally, on the question of alcohol order, the gas-phase results of Baghal-Vayjooee[15] on ketene itself with alcohols are of interest. Even at 200°C there was no homogeneous reaction with the lower alcohols studied, except possibly a very slow one with *n*-butanol. The surface reaction on glass or sodium chloride was first order in ketene and that in methanol fell with increasing pressure in the range 0.9–0.3. These results support Satchell's conclusion that one alcohol molecule alone cannot form an attainable transition state with ketenes, and that an alcohol dimer or trimer, a surface, or a catalyst is essential. In view of the uncertainties concerning the degree of association at low temperatures the results of Tille and Pracejus may be accommodated within this framework; there remains the clear first-order result of Brady, who suggested that steric hindrance might prevent the involvement of pentan-3-ol dimers in the transition state. However, the rate constants do not seem to be particularly low, as might have been expected, and the problem cannot be said to have been resolved.

Apparent activation energies are very low, 14 kJ for ethanol and dimethylketene in ether, and almost zero for the heterogeneous gas reaction, both values incorporating negative ΔH values for alcohol association and adsorption respectively. In the former case $\Delta S^{\neq}$ at −240 J/K mol is very negative.

b. Structural and solvent effects. Staudinger[7] showed that ketene structure affected the rate of ester formation and that $(C_6H_4)_2 > Ph_2 > PhMe > Me_2$. Brady's work[12] also shows that aryl ketenes react faster than the alkyl and that dihaloketenes are similar to the latter (Table 2). The bulky nature of the alcohol used diminishes the rate differences. Tille and Pracejus[13] similarly observed that diphenylketene reacted approximately three times faster with methanol than did phenylmethylketene; electron-withdrawing substituents again increase the electrophilic nature of the carbonyl carbon.

Structural and substituent effects in the alcohol partner are less easily understood. In solution, association occurs to different extents and it is not entirely clear which species is involved. Even in the gas phase the extents of adsorption of alcohol on surface will vary. However the general trends are that primary > secondary > tertiary, and rate increases slightly with chain length for the lower primary

TABLE 2. Effect of ketene structure on rate of reaction with pentan-3-ol in hexane at 25°C

Ketene	$10^4 k$(l/mol s)
Ph_2CCO	74
Me_2CCO	36
Cl_2CCO	24
Et_2CCO	17.6
Br_2CCO	9.7
BuEtCCO	4.3

TABLE 3. Relative rates of reaction of ketenes with various alcohols

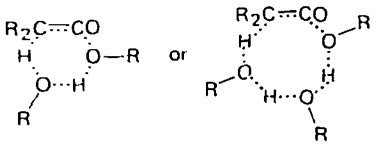
	Relative Rate		
Alcohol	Ketene (gas phase)[a]	Dimethylketene (solution)[b]	Ketene (solution)[c]
MeOH	1.0	1.0	1.0
EtOH	0.78	0.78	0.40
n-PrOH	4.0	2.6	0.45
n-BuOH	3.8	2.4	0.46
i-PrOH	0.26		0.23
t-BuOH	0.13	0.22	
CH_2ClCH_2OH	0.72	0.04	
Me_3CCH_2OH			0.27
Me_3SiCH_2OH			1.3
Me_3GeCH_2OH			1.0
$Me_3C(CH_2)_4OH$			0.44
$Me_3Si(CH_2)_4OH$			0.46
$Me_3Ge(CH_2)_4OH$			0.43

[a] Reference 15.
[b] Reference 9.
[c] Reference 16.

alcohols, although the latter trend was not found by Samtleben and Pracejus. The only significant discrepancy in Table 3 is for chloroethanol. Steric factors are important, even with ketene itself, as is electron donation to the oxygen. Table 3 also gives the relative rates of addition of various silyl and germyl alcohols of formula $Me_3Si(CH_2)_nOH$ and $Me_3Ge(CH_2)_nOH$[16]. The larger +*I* effect of Me_3Si and Me_3Ge groups as against Me_3C increases the rate but, as expected, the effect is soon attenuated by CH_2 groups.

Rates decrease with increasing polarity of the solvent. With diphenylketene and pentan-3-ol, for example, rates in hexane are some twenty times those in ether, which in turn are twice those in acetonitrile[12]. The possible effect of change of medium on alcohol association must be borne in mind.

c. Mechanism. The kinetic results, including the entropy of activation, suggest a cyclic transition state (3), involving one molecule of the ketene and one of alcohol dimer or trimer, formed by electrophilic attack by the carbonyl carbon on an alcohol oxygen and attachment of hydroxyl hydrogen of the second or third alcohol unit on the second carbon, the transition state being rather less polar than the reactants.



(3)

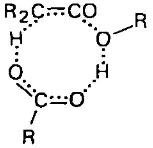
2. *Catalysed addition*

A variety of catalysts have been employed. The general kinetic picture is of a reaction first order in ketene, alcohol and catalyst, the latter proving more effective than further alcohol molecules in forming cyclic transition states.

a. Catalysis by acids. Satchell's work[9] with dimethylketene in ether catalysed by various carboxylic acids answers one important question in showing that this formally termolecular reaction does not occur through acylation of the alcohol by an anhydride intermediate, the formation of the latter being usually too slow. A fast preequilibrium step in which alcohol and acid form a hydrogen-bonded cyclic complex is proposed. The rate of the catalysed reaction is given by

$$\text{Rate} = k[\text{Me}_2\text{CCO}][\text{ROH}][\text{RCO}_2\text{H}]$$

and as shown in Table 4 the rate constant decreases with increasing acid strength. The latter result in the authors' view emphasizes the dual function of the acid catalyst in forming the cyclic transition state (4), involving nucleophilic attachment to the alcohol hydrogen as well as proton donation to the ketene.



(4)

b. Catalysis by amines. A series of studies by Pracejus and his associates provides our quantitative knowledge of these systems[13,17]. Several phenylketenes were studied with various alcohols and tertiary nitrogen bases, mainly in toluene solution and at temperatures down to −95°C. The main kinetic features of the reactions are that marked catalysis occurs and rates are first order in the ketene, alcohol and amine at ordinary temperatures. With strongly basic amines the order in alcohol falls to zero below −50°C, but even in this region alcohol structure and isotopic substitution have a marked effect on the rate. Rates increase with base strength and Figure 2 shows that a linear Brönsted relation exists between log k_3 and pK_a in the case of heterocyclic bases with sp^2-hybridized nitrogen atoms, although amines with sterically hindered sp^3 nitrogen atoms deviate markedly. Rates are lower in more polar solvents[18]. Amine catalysis of the ketene–methanol reaction was measured in toluene, dibutyl ether and methylcyclohexane solvents[19], in the temperature range −90°C to +50°C. Results in general resemble those obtained with phenylketenes, with third-order kinetics, deuterium isotope effects giving k_H/k_D of 2–3 and rates reducing tenfold on changing from toluene to dibutyl ether.

The results support a mechanism of rapid preequilibrium between alcohol and amine to form a hydrogen-bonded complex (equation 2) in which the oxygen atom

TABLE 4. Effect of acid strength on the third-order rate constant (k_3) for carboxylic acid-catalysed acylation of alcohols by dimethylketene[9]

Acid	pK_a	k_3 (l^2/mol^2 min)
Trichloroacetic	0.70	<0.5
Dichloroacetic	1.3	≤2.8
Chloroacetic	2.9	4.2
2-Chloropropanoic	4.1	5.5
Benzoic	4.2	8.6
Isobutyric	4.9	11.3
Pivalic	5.0	12.4

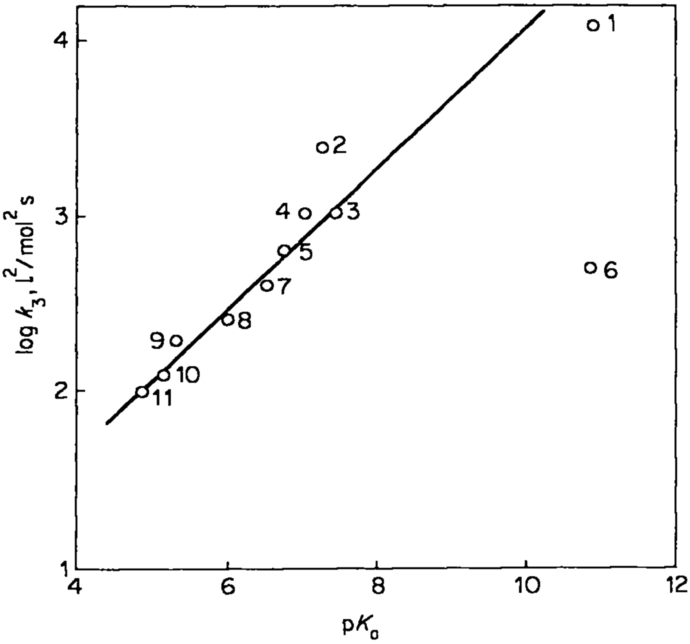
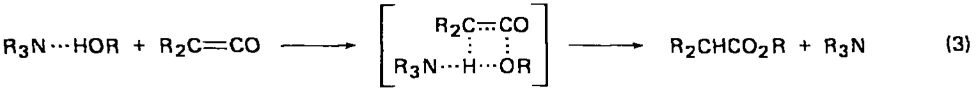


FIGURE 2. Plot of third-order rate constant (k_3) against base strength (expressed as pK_a of the conjugate acid) for the amine-catalysed addition of n-butanol to diphenylketene in toluene at 20°C[17]. (1) 1-Azobicyclo[2.2.1]heptane, (2) N-ethylimidazole, (3) 2,4,6-collidine, (4) 2,3-benzo-1-azobicyclo[2.2.1]heptane, (5) 2,4-lutidine, (6) triethylamine, (7) 2,6-lutidine, (8) α-picoline, (9) quinaldine, (10) pyridine, (11) quinoline.

is activated for attack on the ketene (equation 3). Thus Rate = k_3 [ketene] [com-

$$R_3N + ROH \rightleftharpoons R_3N\cdots HOR \qquad (2)$$



$$R_3N\cdots HOR + R_2C{=}CO \longrightarrow \left[\begin{matrix} R_2C{=}CO \\ \vdots \quad \vdots \\ R_3N\cdots H\cdots OR \end{matrix}\right] \longrightarrow R_2CHCO_2R + R_3N \qquad (3)$$

plex]. The dependence of complex concentration on alcohol is given approximately by

$$[\text{complex}] = \frac{K_{ass}[\text{amine}][\text{alcohol}]}{1 + K_{ass}[\text{alcohol}]}$$

where K_{ass} is the equilibrium constant for complex formation.

Thus at the lowest temperature, when $K_{ass} \gg 1$, the order in alcohol is effectively zero, although the nature of the alcohol continues to affect the rate through its effect on the reactivity of the complex.

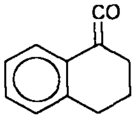
Rates for different ketenes follow the usual increase phenylmethyl < diphenyl < phenyl-α-naphthyl, but steric effects begin to counter this trend in the case of

TABLE 5. Effect of alcohol structure on the dependence of the rate of amine-catalysed addition to ketenes on the ketene used. Measurements were made in toluene at 20°C. *R* is the ratio of the third-order rate constant with diphenylketene to that with phenylmethylketene[17]

Alcohol	Ratio(*R*)
MeOH	4.6
n-BuOH	3.9
i-PrOH	1.5
t-BuOH	1.5
neo-$C_5H_{11}OH$	1.2

more bulky alcohols as is shown by Table 5[17]. The much more marked effect of alcohol structure than ketene structure on the rate, for example k (MeOH) = 4500 k (*t*-BuOH), provides support for the view that preequilibrium involves amine and alcohol, rather than amine and ketene, as had been proposed. Additional evidence comes from the quinoline-catalysed addition of diphenylketene to methanol where the rate of esterification far exceeds that of reaction between the ketene and base[18].

Finally, the stereospecific effect of alkaloids on the reaction has been measured[20]. For example at low temperatures the diastereomers quinine and quinidine produced oppositely enriched yields of chiral esters from phenylmethyl- and phenyl-α,*o*-trimethyleneketenes (5). Temperature and small structural changes have a marked effect on the result.



(5)

c. Catalysis by amides. This has been kinetically investigated by Pracejus and Samtleben[14] using ketene itself and methanol in toluene. Unlike amines, amides have the advantage of not catalysing concurrent polymerization. Third-order kinetics are again shown:

$$\text{Rate} = k_3\,[\text{ketene}]\,[\text{alcohol}]\,[\text{amide}]$$

A deuterium kinetic isotope effect on the alcohol hydroxyl of around two exists, rates are again lower in ethers as against toluene (by a factor of about four), and activation parameters are 28 kJ/mol for $\Delta H^{\neq}$ and -85 J/K mol for $\Delta S^{\neq}$. Ketene substituent effects are in the usual direction:

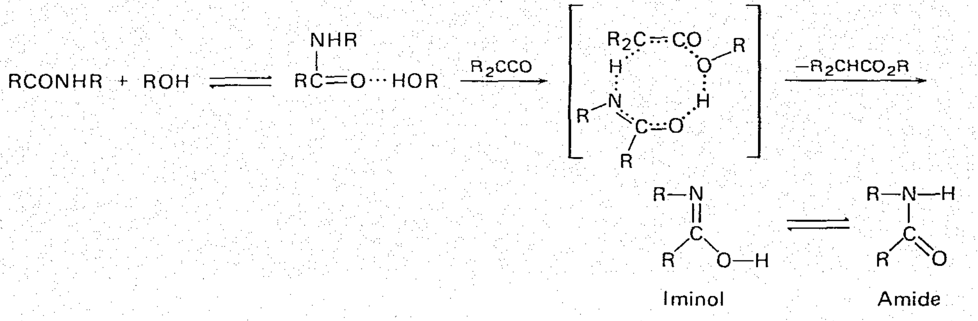
ketene $\simeq$ dimethylketene $<$ diphenylketene.

The catalytic power of different acid amides varies considerably (Table 6).

TABLE 6. Effect of amide catalysis on the third-order rate constant (k_3) for the reaction with methanol in toluene at 20°C

Catalyst	k_3 (l^2/mol^2 s)
N,*N*-Dimethylacetamide	<0.15
N-Methylacetamide	1.0
Acetamide	20.4
Chloroacetamide	4.0
Acetanilide	3.8
4-Hydroxyquinoline	0.15
2-Hydroxyquinoline	114
2-Piperidone	116
2-Thiopiperidone	<0.15
Azocyclooctanone-2	87.3
Azocyclotridecanone-2	0.4

The proposed mechanism incorporates a cyclic transition state preceded by a fast preequilibrium step as shown in equation (4). The resemblance to carboxylic acid catalysis is clear. The relative activity of the amides supports this mechanism in that the higher reactivity of *cis* over *trans* forms (compare e.g. 2- and 4-hydroxyquinoline) indicates a cyclic transition state and that facile iminol ⇋ amide transitions are required.

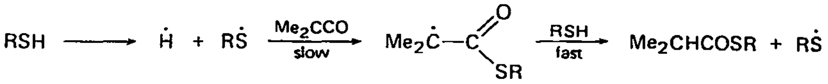


(4)

d. Other catalysts. Samtleben and Pracejus[21] reported that, in a study of the effect of transition metal chelates on the ketene/methanol reaction in toluene, only copper acetonylacetonate showed marked activity. Alkyl chlorostannanes were totally inactive. The catalytic effect of alkali metal acetates on the kinetics of acetylation by ketene of hydroxyl end-groups in polyformaldehyde has been studied[22]; orders of reaction were complex but activation energies measured around 35 kJ in each case.

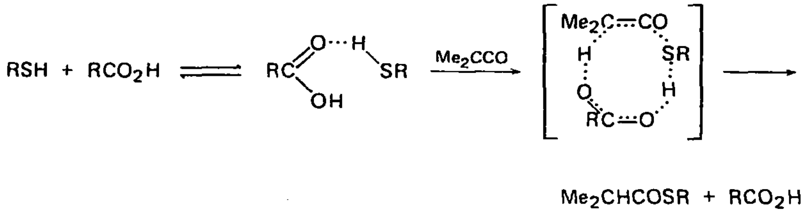
C. Reactions with Thiols

The reactions of dimethylketene with ethanethiol and 1,1-dimethylethanethiol in ether have been studied, both alone and catalysed by isobutyric acid[23]. Rates were in general similar to those with alcohols but there were notable kinetic differences. The spontaneous thiolysis was first order in ketene but gave erratic results, and the order in thiol was not determined. Involvement of free radicals, at least in part, was suspected; added free radicals did accelerate the reaction, and the mechanism shown in equation (5) was proposed. The acid-catalysed reaction showed no



$$\mathrm{RSH} \longrightarrow \dot{\mathrm{H}} + \mathrm{R\dot{S}} \xrightarrow[\text{slow}]{\mathrm{Me_2CCO}} \mathrm{Me_2\dot{C}{-}C({=}O)SR} \xrightarrow[\text{fast}]{\mathrm{RSH}} \mathrm{Me_2CHCOSR} + \mathrm{R\dot{S}} \qquad (5)$$

sign of free-radical processes and was first order in all three reactants. An acid/thiol preequilibrium was suggested as preceding a cyclic transition state (equation 6).



(6)

However, acid catalysis was undetectable with the branched-chain thiol, presumably because of steric difficulties in the transition state.

D. Reactions with Carboxylic Acids

Here either symmetrical or unsymmetrical anhydrides are formed, although the latter commonly disproportionate into a mixture of the former. Most kinetic results have been obtained in two series of studies, one in solution the other in the gas phase.

1. *In solution*

Briody, Lillford and Satchell[24] studied the addition of carboxylic acids to dimethylketene in ether and to diphenyl- and mesitylphenylketenes in *o*-dichlorobenzene. In ether reaction is first order in both dimethylketene and carboxylic acid; in dichlorobenzene the ketene order is again unity, that in acid more variable but usually near one. However, since carboxylic acids exist mainly as dimers in the latter solvent, the rate equation is expressed as

$$\text{Rate} = k_{\text{dimer}}[\text{ketene}]\,[\text{acid dimer}].$$

In both solvents plots of rate versus acid pK_a in aqueous solution show a minimum at chloroacetic acid. The results in ether are given in Figure 3. An acidic deuterium isotope effect of 3.0 was observed for dichloroacetic acid.

The results are interpreted on the basis of two mechanisms. The weaker acids form a cyclic transition state (6) involving one acid molecule (a monomer in ether, an open dimer in dichlorobenzene). It is considered that the inverse relation between rate and acid strength in this region stems from the decrease in nucleophilicity of the acid's oxygens as strength increases and consequently attack on the ketene weakens. The strongest acids are presumed to react by protonation of the ketene followed by rapid rearrangement of the ion pair, ketene now playing a

$$\mathrm{R_2C{=}C{=}O} + \mathrm{RCO_2H} \xrightarrow{\text{slow}} [\mathrm{R_2CH{-}C{=}O}]^+\,[\mathrm{RCO_2}]^- \xrightarrow{\text{fast}} \mathrm{R_2CHCOOCOR} \qquad (7)$$

nucleophilic role (equation 7). The evidence is that an acetyl ion is more stable than a hydroxyvinyl cation when ketenes are protonated[4].

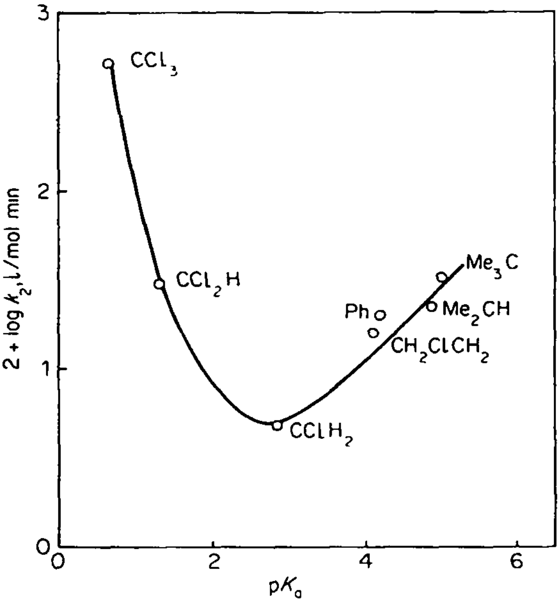
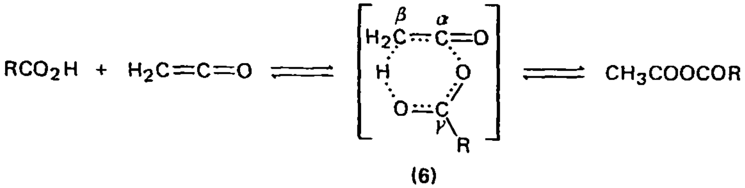


FIGURE 3. Plot of log k_2 (the second-order rate constant) against acid strength for the addition of carboxylic acids RCO_2H to dimethylketene in ether at 25°C. Reproduced from J. M. Briody, P. J. Lillford and D. P. N. Satchell, *J. Chem. Soc. (B)*, 887 (1968) by permission of The Chemical Society.

2. *In the gas phase*

The gas-phase kinetics of homogeneous reaction of ketene itself with carboxylic acids has been studied[25] and in some cases that of the back-reaction (the unimolecular decomposition of anhydride)[26] and the thermodynamics of the equilibrium[27]. All forward reactions are first order in ketene. Carboxylic acids are partly dimerized in the gas phase at the lower end of the temperature range studied (100°C). When the known extents of dimerization[28] are allowed for, the fractional dependence of rate on total acid pressure gives first order in acid monomer, as found at higher temperatures where dissociation of dimer is complete.

There is a broad increase in rate with acid strength (as measured in water), but the detailed correlation with pK_a is poor. This is not surprising since the important hydration terms are now absent. Measurements of intrinsic (gas-phase) acidities have been made by Yamdagni and Kebarle[29] and expressed as O—H bond dissociation energy minus electron affinity ($D - EA$). The electron affinity is that of A in the acid HA. A plot of log k against ($D - EA$) is shown in Figure 4 and is linear except for the very strongest acids which react more rapidly. Arrhenius constants are shown in Table 7. When the results are compared with those obtained from the kinetics of the back-reaction and the equilibrium data (obtained from both directions) it seems clear that these additions are simple reactions, probably proceeding through cyclic transition states (6). k_H/k_D is 3.7 on the acid proton in acetic acid



(6)

(about 62% of the maximum), which implies that the O–H bond is substantially broken in the transition state. The *A* factors are consistent with a six-centre transition state and the increases in rate brought about by electron-withdrawing groups at the γ position parallel the effects in ester decompositions, which pass through similar transition states. Methyl substitution at the β carbon, that is, using dimethylketene, reduces the rate of acid addition by a factor of 2.5.

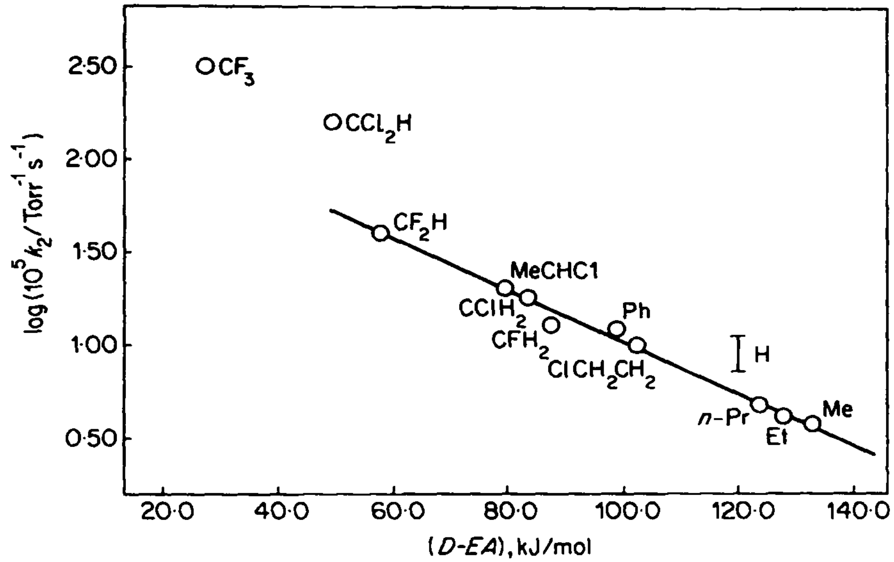


FIGURE 4. Plot of log k_2 (the second-order rate constant) against intrinsic acid strength ($D - EA$) for the gas-phase addition of carboxylic acids (RCO_2H) to ketene at 155°C. ($D - EA$) is the O–H bond dissociation energy minus the electron affinity of A for the carboxylic acid HA. Reproduced from P. G. Blake and M. H. Baghal-Vayjooee, *J. Chem. Soc., Perkin II*, 1535 (1976) by permission of The Chemical Society.

TABLE 7. Arrhenius constants for the gas-phase additions of ketene to carboxylic acids[25]

Acid	*A*(l/mol s)	E_a(kJ/mol)
CH_3COOH	$10^{6.1}$	49.9
CH_3COOD	$10^{6.2}$	55.8
Propenoic	$10^{6.3}$	49.6
2-Chloropropanoic	$10^{5.7}$	41.4

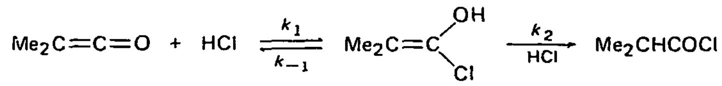
The solution and gas-phase studies generally support one another but one discrepancy is the effect of acid strength on rate in that a minimum occurs in solution. The weaker acid results in solution point to the importance of the nucleophilicity of the acids' carbonyl oxygen; with stronger acids and in the gas phase the heterolytic strength of the O–H bond is more important. Clearly the solvent may have a differential effect. The effects of substituents on ΔG^0 for acid ionization are attenuated some three to five times in solution as compared with the gas phase. In the latter, therefore, acidity may be dominant throughout, but becomes less important in solution.

E. Reactions with Other Acids

Lilliford and Satchell[30] have studied the kinetics of addition of hydrogen halides to dimethylketene in ether to give isobutyryl halides (equation 8). The reactions are fast, HBr being 25 times faster than HCl, and first order in the ketene. Order in HCl is one at higher concentrations but rises with decreasing concentrations, and the overall rate equation is

$$\text{Rate} = k_1\,[\text{HCl}]^2\,[\text{ketene}]/(k_{-1}/k_2 + [\text{HCl}])$$

where the rate constants relate to a mechanism of addition to the carbonyl group followed by catalysed rearrangement to product. The overall rate is governed by k_1 except at low concentrations. Note that in equation (8) *O*- rather than *C*-protonation is proposed. Measurements using DCl gave $k_H/k_D = 2.3$. The reactions of dimethylketene with HCN and with H_2S are extremely slow.



$$\text{Me}_2\text{C}{=}\text{C}{=}\text{O} + \text{HCl} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{Me}_2\text{C}{=}\text{C}(\text{OH})\text{Cl} \xrightarrow[\text{HCl}]{k_2} \text{Me}_2\text{CHCOCl} \qquad (8)$$

In the gas phase rates and equilibria in the system $CH_2CO + HCl = CH_3COCl$ have been studied[31]. Reaction of ketene with hydrogen bromide is slow at room temperature but rapid and quantitative at 492°C yielding methyl bromide and carbon monoxide via decomposition of acetyl bromide[32]. Ketene and hydrogen iodide gases react rapidly at 500 K, giving initially acetyl iodide which decomposes by radical processes yielding methane, carbon monoxide, acetaldehyde and iodine[33].

Thio- and selenophosphoric acids of the formula $(EtO)_2P(S\text{ or }Se)OH$ react with ketene in benzene forming mixed anhydrides[34]. The mechanism is thought to involve rapid protonation of ketene, followed by electrophilic attack of the acetyl cation on the acid anion.

F. Reactions with Amines

Several papers by Satchell and his group[5,35] provide the main kinetic information on these reactions. They employed diphenylketene, dimethylketene and ketene with substituted anilines in ethereal or benzene solution. Uncatalysed rate equations contained both first- and second-order terms in amine, the rate equation being

$$\text{Rate} = (k_1[\text{amine}] + k_2[\text{amine}]^2)[\text{ketene}].$$

Both rate constants increase linearly with the basicity of the aniline but k_2 much more than k_1 (Table 8). This dependence of rate of acylation of amines on strength of base was first noted by Staudinger[7].

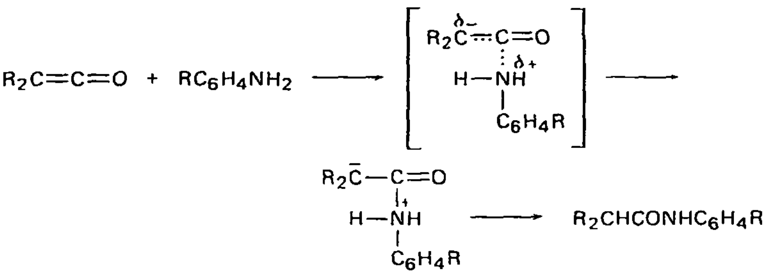
With *m*-chloroaniline, Arrhenius constants appropriate to k_1 are $E_a = 44$ kJ/mol and $\Delta S^{\neq} = -168$ J/K mol. For k_2 the apparent activation energy is almost zero,

TABLE 8. Effect of aniline structure on the second- and third-order rate constants (k_1 and k_2) in the additions to dimethylketene in ether and diphenylketene in benzene at 25°C

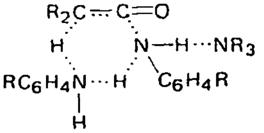
Aniline derivative	pK_a	k_1 (l/mol min)	k_2 (l^2/mol^2 min)
		With diphenylketene	
H-	4.6	13	2100
4-methyl-	5.1	21	15,000
4-chloro-	4.0	6.2	370
N,N-dideutero-4-chloro-	–	6.2	380
3-chloro-	3.5	2.3	150
3,4-dichloro-	3.0	1.9	29
		With dimethylketene	
4-chloro-	4.0	0.64	6.6
N,N-dideutero-4-chloro-	–	0.66	2.3
3-chloro-	3.5	0.42	2.26
3,4-dichloro-	3.0	0.12	0.46
2,4-dichloro	2.0	0.028	0.030

which is considered to result from the falling concentration of aniline dimers at higher temperatures balancing a true activation energy of 26 kJ/mol. Deuterium substitution on the nitrogen has no effect on k_1 but produces rather variable changes in k_2.

The results support a mechanism for the overall second-order route as shown in equation (9). The catalytic power of the second aniline molecule in the third-order mechanism might then stem either from making the nitrogen attacking the ketene more nucleophilic or by acting as a proton-transfer agent in a cyclic transition state. The latter seems more important since tertiary base catalysts, where this route is not possible, are less effective than *m*-chloroaniline itself. Even with triethylamine (10^7 times more strongly basic than the aniline) the rate is not much increased. However, both routes seem to operate so that the rate equation for ketenes plus anilines catalysed by tertiary amines will contain four terms involving either one or two aniline molecules, both alone and tertiary base-catalysed. 7 is the most complex of the four transition states.

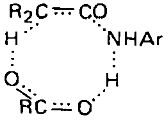


(9)



(7)

Carboxylic acids catalyse the reaction much more effectively and the kinetics simplify to first order in ketene, aniline and catalyst, at least in ether. As in the catalysed acylation of alcohols, carboxylic anhydrides are ruled out as intermediates on kinetic grounds. Chloroacetic acid appears to be less than half as effective as the weaker isobutyric acid. The acids' role again seems to be to transfer a proton from the amine to the β carbon of the ketene in a cyclic transition state (8) formed from the amine/acid complex and ketene.



(8)

It is interesting to note that anthranilic acid, which might have been expected to play both amine and acid roles in the one molecule, only appears in second-order terms in the kinetic equation for reaction with methylketene, one molecule acting as amine and the other as acid catalyst. Steric difficulties might be responsible.

There is also a little evidence for the effect of ketene structure on the uncatalysed reaction. Dimethylketene reacts some six (for k_1) and nine (for k_2) times more slowly than ketene in ether, which is more than expected on purely steric considerations. Rates with diphenylketene in benzene are substantially faster than with dimethylketene in ether (see Table 8), but both structural and solvent effects are involved and here operate in the same direction. Some attempt has been made to correlate charge distribution and reactivity in ketenes, and in this instance the rate lowering caused by the methyl groups is associated with a reduced negative charge at the β carbon, and consequent less efficient proton transfer to that site[5]. This is the reverse of the usual expectation that methyl groups release electrons, when rate-lowering would be attributed to a diminution of electrophilic activity at the α carbon. Although the role of larger alkyl substituents bonded to sp^2-hybridized carbon is ambiguous in that their polarizability aids stabilization of both positive and negative charges[36], methyl groups would be expected to give a net donation. A calculation of higher order than Hückel is needed to settle this point.

Possible mechanisms have been discussed for reactions of ketenes with other nitrogen compounds, including amine *N*-oxides[37], isoquinoline and acridine[38] and diarylnitrones[39]; but in view of their affinity with cycloadditions these are not considered here.

G. Addition of Hydrogen Atoms

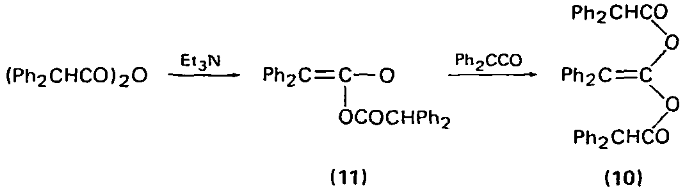
Several studies have been made. The rate equation for the reaction is $k = 6 \times 10^{-12} \exp(-9.8\ kJ/RT)$ cm^3/molecule s[40]. The activation energy is normal for addition of hydrogen atoms to double bonds but the low preexponential factor is taken to result from stricter than usual configurational needs. Methane and carbon monoxide are the main products, plus a little ethane. Glyoxal has been detected at −196°C[41]. The formation of extensive amounts of methyl radical and the absence of any significant sign of CH_2 or CHO suggest that the acetyl radical is the primary intermediate, rather than CH_2CHO. Matrix trapping at 77 K gives interesting results which are rather difficult to explain. Using e.s.r. methods Bennett and Mile[42] showed that the matrix used appeared to affect the site of both H and D addition to ketene. In water acetyl radicals were formed, in benzene hydrogen added to the α carbon, and using adamantane, addition to both carbons occurred. Acetyl radicals decompose extensively to methyl and carbon monoxide even at 77 K, and a chain-reaction occurs under normal conditions[43].

H. Other Additions

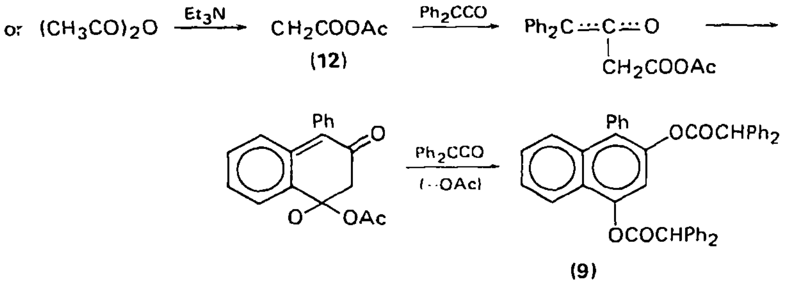
Little quantitative work has been published and the relevant reactions are summarized fairly briefly. In the reaction of ketenes with acid halides to give β-keto acid halides (equation 10), rates increase with the strength of the parent acid (of

$$R^1_2C{=}C{=}O + R^2COX \longrightarrow R^2COCR^1_2COX \qquad (10)$$

the acid chloride). Also, unusually, dimethylketene is apparently more reactive than ketene, diphenylketene or phenylethylketene[44]; however the work was semi-quantitative only. In the base-catalysed acylation of carboxylic anhydrides by diphenylketene either *C*- or *O*-acylation is possible[45] giving naphthalene-1,3-diol esters (**9**) and ketene acylals (**10**) respectively. The former is preferred unless sterically hindered. The mechanism (equation 11) involves initial deprotonation of the anhydride by tertiary amine followed by electrophilic attack by the ketene's α carbon on the resulting anions **11** and **12**.

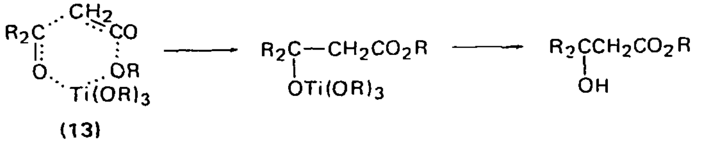


(11a)



(11b)

The mechanism (equation 12) of reaction of ketene with ketones in the presence of alkyl orthotitanates to give β-hydroxy esters[46] is believed to involve cyclic transition state **13**.

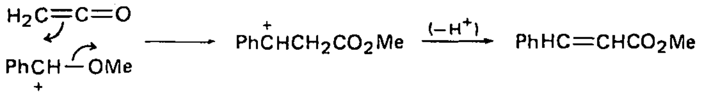


(12)

Reaction of ketene with acetals catalysed by zinc chloride involves the formation of a carbonium ion which attacks the nucleophilic β carbon of ketene (equation 13)[47].

$$\mathrm{RCH(OMe)_2 \xrightarrow{ZnCl_2} R\overset{+}{C}HOMe \xrightarrow{CH_2CO} RCH(OMe)CH_2\overset{+}{C}O \xrightarrow{OMe^-} RCH(OMe)CH_2CO_2Me} \quad (13)$$

The rate constant for formation of the (1:1) adduct of ketene with BH_3 in the gas phase at low pressures has been measured[48], and a low-temperature study of the addition of the α-methoxybenzyl carbonium ion to ketene made[49]. This appears to proceed as shown in equation (14).

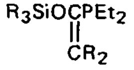


(14)

Germyl and silyl phosphines (**14**) add to the carbonyl double bond of ketenes giving **15**[50].

R_3SiPEt_2

(14)



$$\mathrm{R_3SiO\underset{\underset{\displaystyle CR_2}{\|}}{C}PEt_2}$$

(15)

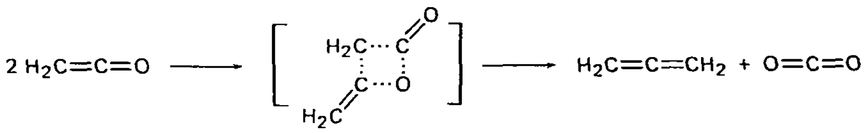
With octacarbonyl dicobalt in aromatic solvents diphenylketene is converted into tetraphenylethylene[51]. Diphenylcarbene is proposed as the intermediate. The mechanism of the thermal isomerization of 1-propenylketene to 2,4-pentadienaldehyde has been discussed[52]. Ulrich[53] has reviewed the addition reactions of mercury alkoxides and similar metal—electronegative atom singly-bonded molecules to ketenes. These may in some cases be electrophilic.

III. THERMAL DECOMPOSITION OF KETENES

The more recent kinetic studies of ketene itself fall into two classes, those at around 500°C in conventional static systems, and those in the range 1000–2000°C including shock-tube work. At lower temperatures both Young[54] and Guenther and Walters[55] found a second-order dependence of rate on ketene pressure, the Arrhenius equation being

$$k = 10^{10.0} \exp(-150\ kJ/RT)\ 1/\text{mol s}.$$

At lower temperatures and small extents of decomposition allene and carbon dioxide were the main products, but at higher temperatures or more extensive reaction, carbon monoxide, ethylene and methane predominated. Addition of allene increased the rate of formation of carbon monoxide. It seems clear that allene and carbon dioxide form in a bimolecular process through a transition state having some resemblance to the diketene structure (equation 15). Carbon monoxide is probably produced in a chain reaction which is accelerated by radicals produced in the decomposition of allene.



(15)

In high-temperature work the initial step is unimolecular decomposition to carbene and carbon monoxide. Wagner and Zabel[56] in shock-tube experiments obtained fall-off curves for this step and obtained a high-pressure value at 1650 K of $k_\infty = 3 \times 10^{14} \exp(-298\ kJ/RT)\ s^{-1}$. Tsuda and Kuratani[57] obtained an order of 1.5 and $k = 10^{14.2} \exp(-274\ kJ/RT)\ l^{1/2}/mol^{1/2}\ s$. The initially-formed carbene reacts readily in steps as shown in equation (16). The carbene yield rises to a maximum at around 2000°C and the pyrolysis of ketene at this temperature has been used to produce carbene molecular beams[58].

$$CH_2 + CH_2CO \longrightarrow C_2H_4 + CO \tag{16a}$$

$$CH_2 + CH_2CO \longrightarrow CH_3 + CHCO \tag{16b}$$

followed by

$$CH_3 + CH_2CO \longrightarrow CH_4 + CHCO \tag{16c}$$

$$CHCO \longrightarrow CH + CO \text{ etc.} \tag{16d}$$

The products of the thermal decomposition of methylketene suggest that the reaction is similar in nature to that of ketene[59]. Carbon dioxide and penta-2,3-diene in equal amounts are the main initial products at 360°C, but carbon monoxide and but-2-ene, and additionally buta-1,3-diene and methane, increase with increasing temperature and extent of reaction. However, both carbon dioxide and carbon monoxide production are inhibited by added isobutene and affected by vessel surface, so that a clear distinction between the mechanisms producing the two oxides cannot be made in this complex free-radical system.

IV. OXIDATION OF KETENES

In addition to general combustion studies, the oxidation of ketenes has attracted some recent attention because of interest in α-lactone intermediates and the possible existence of ketene in smog due to oxidation of olefins by ozone. Kinetic studies of the slow combustion of ketene have been made by Barnard and Kirschner[60] and Michaud and Ouellet[61]. The reaction is autocatalytic and major products are carbon monoxide, carbon dioxide, water and formaldehyde. Cool flames and explosive regions are observed. A distinction is drawn between low-(280–350°C) and high-(380–500°C)temperature stages of reaction. In the former the activation energy is approximately 170 kJ/mol, falling to about 40 kJ at higher temperatures. In both regions a mainly free-radical chain mechanism is indicated, hydroxyl and hydroperoxyl radicals being the main chain-carrying species. At higher temperatures chain-branching is due to the oxidation of formaldehyde as shown in equation (17).

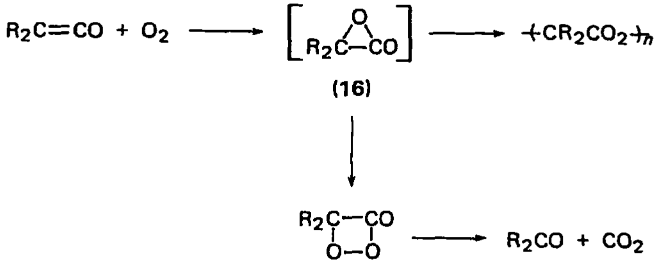
$$CH_2O + O_2 \longrightarrow HCO_2H + O: \tag{17a}$$

$$O: + CH_2O \longrightarrow CHO^{\cdot} + OH^{\cdot} \tag{17b}$$

At low temperatures hydroperoxides are present and contribute to branching (equation 18).

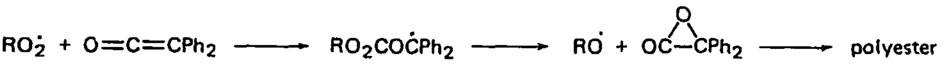
$$CH_3OOH \longrightarrow CH_3O^{\cdot} + OH^{\cdot} \tag{18}$$

Rate constants for reaction of $O(^3P)$ atoms with ketene have been measured by several groups[43,62]. A mean value of around 3×10^{-8} l/mol s results, which is substantially smaller than values for most other organic molecules implicated in smog formation, for example terpenes. Products of reaction of oxygen atoms with ketene are many, including oxides of carbon, water, hydrogen and formaldehyde. The hot molecule $CH_2CO_2^*$, possibly excited glyoxal[62] or a biradical, is proposed as the initial product. This leads on to the work of α-lactone interest. Staudinger proposed the structure **16** as the first intermediate in oxidation with molecular oxygen, equation (19) showing the subsequent steps to polyester or to ketone plus carbon dioxide.


(16)

(19)

Bartlett and Gortler[63] proposed the mechanism shown in equation (20) for the reaction of diphenylketene with peroxy radicals. Wheland and Bartlett[64] also found


(20)

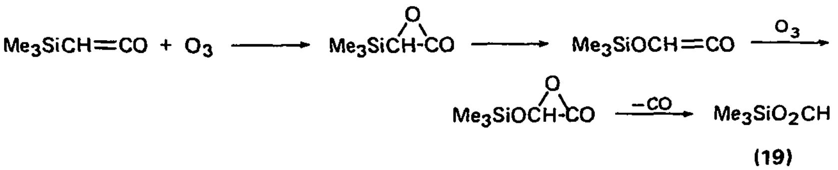
(17)

evidence for **17** when reacting diphenylketene with ozone at –78°C in chlorotrifluoromethane. **17** was thought to have a short lifetime at –100°C but could be trapped with methanol to give **18**. Crandall and his coworkers[65] used the hindered

$$Ph_2C(OMe)CO_2H$$

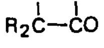
(18)

di-*t*-butylketene. With ozone at –78°C in methylene chloride the presence of an α-lactone was indicated by infrared absorption at 1889 cm^{-1}. With peracetic acid, products were again plausibly obtained through the α-lactone intermediate. Depending on the ketene used, either an α-lactone route or a 1,3-addition across the carbon–carbon double bond is suggested. The former has also been proposed in the perbenzoic acid oxidation of diphenylketene[66]. With trimethylsilylketene, the formate **19** is produced[67], and the suggested mechanism involves a twofold α-lactone formation (equation 21).


(21)

(19)

Chemiluminescence occurs when ketene or diphenylketene (or their acetals) are treated with a singlet oxygen precursor and a fluorescer at –70°C and warmed to room temperature[68]. Dioxetane decomposition is the key step in a number of chemiluminescent reactions and the dioxetanone **20** was therefore proposed as an intermediate in this case.


(20)

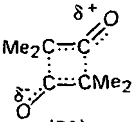
V. POLYMERIZATION OF KETENES

The fairly involved field of the dimerization, oligomerization and polymerization of ketenes was extensively reviewed by Lacey[1] in 1964 and more recently by Ulrich[53]. Since that time there have been some kinetic results and some clarifying generalizations. Woodward and Hoffmann[69] considered the concerted cycloaddition to ketene dimers to involve one molecule in the $_{\pi}2_s$ and the other in the $_{\pi}2_a$ mode. However, the theoretical calculations of Jug and Chickos[70] imply, in opposition to this, that supra—antara routes are essentially forbidden and that the supra—supra pathway is allowed.

A. Dimers and Trimers

Kinetic studies of the dimerization of lower ketenes give rather similar results. In the gas phase, with vessel walls carbon-coated to minimize heterogeneous polymerization, dimerization of ketene is second order with an activation energy of 74 kJ/mol and an entropy of activation of −166 J/K mol[71]. The activation energy resembles the early solution value of 46 kJ obtained by Rice and Greenberg[72], and that of 57 kJ obtained for the second-order dimerization of ketene in solution in diketene[73]. The gas-phase work was restricted to small percentage reactions, since further polymerization occurred at higher conversions. Methylketene gas showed second-order kinetics in a heterogeneous dimerization[74], but results were erratic. Huisgen and Otto studied the dimerization of dimethylketene in a range of solvents[75]. All showed second-order kinetics and change in solvent polarity had but a modest effect on the rate (Table 9). Activation constants in benzonitrile were $\Delta H^{\neq} = 46$ kJ/mol and $\Delta S^{\neq} = -176$ J/K mol.

The above results suggest an ordered, not very polar transition state such as 21 rather than a route involving a zwitterion intermediate.



(21)

The rate of spontaneous dimerization of ketenes decreases with increasing size of substituent(s). For example, see Table 10 for alkyl substituents[76] and the sequence of *i*-Pr > *t*-Bu > neopentyl in alkylbromoketenes[77].

Samtleben and Pracejus[19] have studied the kinetics of base-catalysed dimerization of ketene in toluene. Reaction was second order in ketene and first in catalyst.

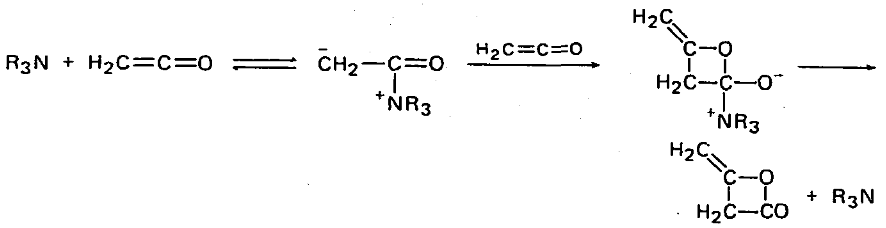
TABLE 9. Effect of solvent polarity on dimerization rate constants (k_2) of dimethylketene at 35°C

Solvent	$10^5 k_2$ (l/mol s)
CCl_4	2.3
C_6H_6	4.6
PhCl	6.5
$CDCl_3$	23.8
CH_2Cl_2	26.1
PhCN	34.9
MeCN	67.5

TABLE 10. Effect of ketene structure on rate constants (k_2) for dimerization at 20°C

Ketene	$10^6 k_2$
Me_2CCO	70
MeEtCCO	10
Et_2CCO	0.17
EtBuCCO	0.04
Et(*i*-Bu)CCO	0.006

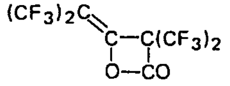
Powerful catalysis was shown, the effect increasing with relative nucleophilicity rather than pK_a of the base (Table 11). Attachment of base to one ketene molecule renders it open to electrophilic attack by a second (equation 22).



(22)

Bis(trifluoromethyl)ketene does not dimerize thermally[78] but with triethylamine catalyst forms linear dimer 22 apparently through isomerization to the acid fluoride 23. However, with diethylnitrosamine the β-lactone dimer 24 is formed.

$$(CF_3)_2C{=}CO \xrightarrow{Et_3N} \underset{(23)}{F_2C{=}C(CF_3)COF} \xrightarrow{(CF_3)_2C=CO} \underset{(22)}{FOCC(CF_3)_2CF{=}C(CF_3)COF} \qquad (23)$$



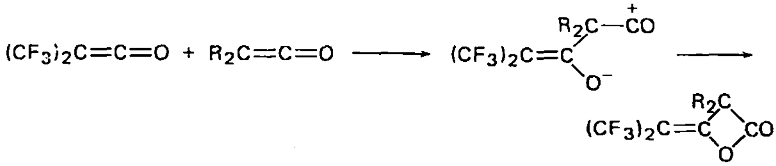
(24)

Although bis(trifluoromethyl)ketene does not dimerize thermally it efficiently forms mixed dimers with other ketenes. Both 1,3-diones and β-lactones are formed,

TABLE 11. Third-order rate constants (k_3) for the base-catalysed dimerization of ketene in toluene at 20°C

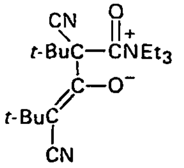
Catalyst	k_3 (l^2/mol^2 s)	Relative nucleophilicity	pK_a
Pyridine *N*-oxide	0.22	–	0.8
Pyridine	0.53	0.1	5.3
Ph_3P	2.5	0.23	2.7
Et_3N	21	1.0	10.3
Acetylquinine	95	–	7.2
$(n\text{-Bu})_3P$	1100	10	8.4
Quinuclidine	37,000	300	10.8
1-Azobicyclo[2,2,1]heptane	120,000	–	10.65

but in all cases cycloaddition is to the carbon–carbon double bond of the nonfluorinated ketene. The pattern of behaviour has been rationalized in terms of a dipolar intermediate by England and Krespan[79]. Methylketene gives only β-lactone, whereas dimethylketene yields mainly 1,3-dione in cyclohexane but a mixture of both products in ethyl acetate. Fluoride ion converts the 1,3-dione to β-lactone. It is suggested that only the β-lactone derived from the most stabilized dipolar intermediate is normally formed (equation 24). With dimethylketene this route is sterically hindered to some extent and allows addition across the carbon–carbon double bond of the fluorinated ketene to give the 1,3-dione.



(24)

The mechanism of dimerization of *t*-butylcyanoketene catalysed by triethylamine has been discussed by Moore and Duncan[80] in terms of a zwitterionic intermediate, produced by base attachment at the carbonyl carbon, which is then attacked at the β-carbon by the electrophilic carbon of a second molecule of the ketene to give 25. The β-lactone dimer produced is unstable under the conditions of formation, decomposing to give carbon dioxide and the allene 26 (compare the pyrolysis of ketene).



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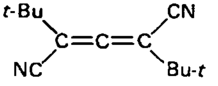
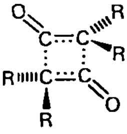


(26)

Depending on circumstances, dimerization of ketenes may yield β-lactones, 1,3-cyclobutanediones, the enolic 3-hydroxycyclobutenones and trimers formed by acylation of the last. In addition to the work reported above attempts have been made to rationalize the product distribution[81]. It is suggested that with the exception of ketene itself, spontaneous dimerization affords mainly 1,3-diones, which in the case of aldoketenes may appear in the enol form. β-Lactone formation is facilitated by catalysts, triethylamine or its hydrochloride for aldoketenes and aluminium chloride or other strong Lewis acid for ketoketenes. The explanation advanced is that, in the most suitable dispositions for π-orbital overlap in concerted transition states, there is less crowding in forming 1,3-diones (27) than with β-lactones (28);



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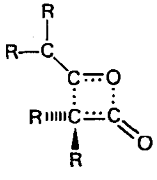

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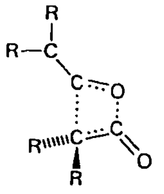
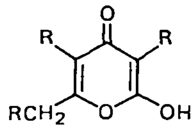


(29)

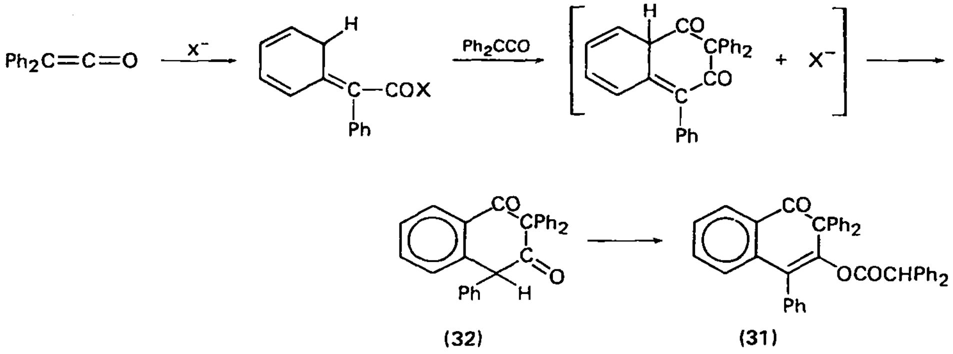
by increasing the electrophilicity of the carbonyl carbon, the acid catalyst assists carbon–oxygen bond formation in the β-lactone route. A stronger, shorter bond here may distort the transition state **29**, and help to reduce steric crowding.

In addition to the ester trimers mentioned above, pyranone trimers (**30**) may form on triethylamine catalysis of aromatic aldoketenes.



(30)

Diphenylketene also forms ester trimer **31** in the presence of base[82], through acylation of the enol of dimer **32** formed as shown in Scheme 1.



SCHEME 1.

The mechanism of formation of the symmetrical trimers, cyclohexane-1,3,5-triones, has been reviewed previously[1].

B. Higher Polymers

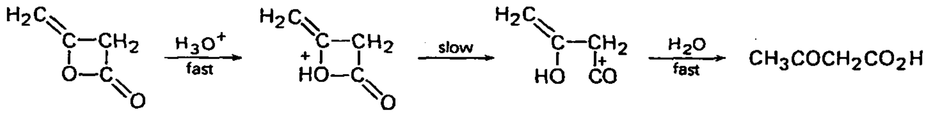
The kinetics of catalytic dimerization of diketene to dehydroacetic acid have been followed[83]. Tertiary amines are effective catalysts and in order of decreasing efficiency $Me_2NBu > Me_2NEt > Et_3N > EtONa >$ pyridine. The reaction is second order in diketene and first in catalyst and the activation energy is low. The routes to the variety of self-condensation products obtained from diketene in the presence of a little water have been discussed[84]. Higher polymers of ketenes, which may be polyesters, polyketones, or polyacetals are obtainable with anionic catalysts[85].

C. Reactions of Ketene Dimers

The reactions of ketene dimers have been reviewed[1,86]: kinetic work deals mainly with the hydrolysis of diketene.

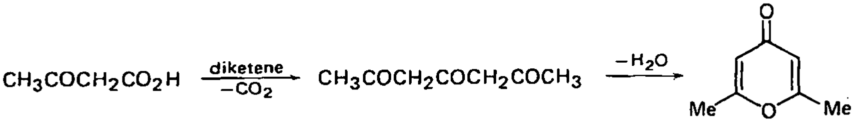
1. *Hydrolysis*

The spontaneous reaction of diketene with water appears to be very slow, mainly because diketene is not very soluble. In aqueous dioxane reaction is first order in diketene and independent of pH in the range 1–8 units[87]. The activation energy is 50–55 kJ/mol. Both acids and bases catalyse the reaction – acids below pH 1 when a straight line plot of log k_{H^+} against H_0 (the Hammett acidity function) of slope 0.91 is obtained. The mechanism proposed is shown in equation (25).



(25)

Pyridine gives strong nucleophilic catalysis, rates being proportional to pyridine concentration, whereas acetate and chloroacetate give rise to a weaker general base catalysis. Catalysis by hydroxide ions is very rapid. In all cases ring-opening occurs at the acyl-oxygen bond. In the presence of tertiary amine catalysts, the initial product, acetoacetic acid, will react with further diketene[88] as in equation (26) to give ultimately the pyranone derivative 33.



(26)

(33)

The reactions of higher alkylketene dimers with methanol and ethanol are strongly catalysed by acid and are kinetically first order in acid and in dimer[89]. Rates decrease with increasing size of alkyl group on both dimer and alcohol. Samtleben and Pracejus[19] have shown that the base-catalysed reaction of diketene with methanol in toluene is first order in all three components. Table 12 shows the catalytic efficiency.

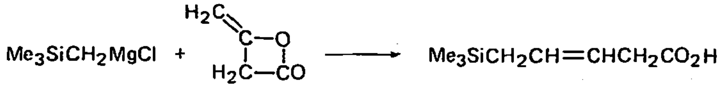
TABLE 12. Third-order rate constants (k_3) in the base-catalysed reaction of diketene with methanol in toluene at 20°C

Catalyst	k_3 (l^2/mol^2 s)
None	2×10^{-4}
Et_3N	5.5×10^{-3}
$(n\text{-}Bu)_3P$	2.3
1,4-Diazobicyclo[2,2,2]octane	6.8

2. *Other reactions*

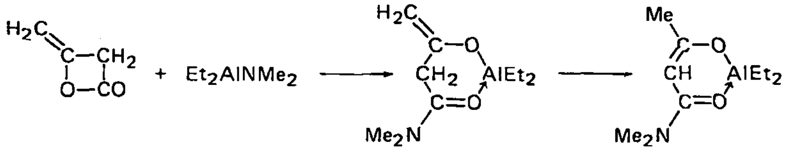
The flow pyrolyses of diketene and perdeuterodiketene at 410–510°C give the monomers only[90], although β-lactone dimers may often split in the opposite sense. The fact that k_H/k_D is different in high-pressure and fall-off regions indicates that decomposition is homogeneous. The high-pressure ratio of 1.06 for k_H/k_D is consistent with a secondary isotope effect for hydrogen attached to a carbon undergoing an $sp^3 \rightarrow sp^2$ rehybridization in the rate-determining step, suggesting that C—C bond-breaking is involved.

The reaction of diketene with the Grignard reagent **34** to give the corresponding 3-butenoic acid **35** is said to be the first example of vinyl-oxygen bond cleavage in diketene[91]. With diethylaluminium derivatives on the other hand[92] diketene reacts



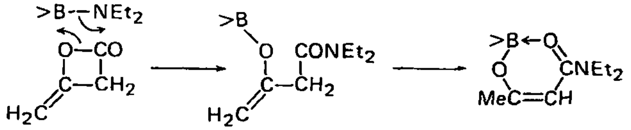
(34) (35) (27)

by acyl-oxygen cleavage followed by a rapid 1,3-hydrogen shift to yield chelates of acetoacetic acid derivatives (equation 28). Similarly[93] organic derivatives of boron,



(28)

aluminium and tin, such as o-$C_6H_4O_2BNEt_2$, react with diketene through a concerted opening of the acyl-oxygen bond (**36**) to give β-ketoenolates (**37**).



(36) (37) (29)

Mechanisms have also been discussed for the cleavage of the diketene ring with triethylamine[94], and the reaction with acridine *N*-oxide[95].

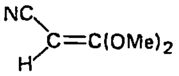
VI. REACTIONS OF KETENE DERIVATIVES

A. Ketene Acetals and Thioacetals

1. *Hydrolysis*

Converting ketenes into their acetals or thioacetals has the effect of suppressing electrophilic tendencies and strikingly increasing the nucleophilic ones[96]. An area of recent kinetic and mechanistic interest has been that of acid-catalysed hydrolysis. Kankaanpera and coworkers[97] studied the rate of hydrolysis of ketene diethyl acetal in water and in carbonate/bicarbonate buffer solutions. Rates were too fast to measure below pH 9, but general acid catalysis by weak Brönsted acids was demonstrated. The solvent deuterium isotope effect was $k_{D_2O}/k_{H_2O} = 0.16$. The rate-determining step is proton transfer to acetal and the high rates are attributed to the stabilizing effect of the alkoxy groups on the intermediate carbonium ion. The less reactive acetal $H_2C{=}C(OCH_2CH_2OMe)_2$ was used[98] in aqueous dioxane to widen the range of acid catalysts which could be used. The overall rate constant was $k_{obs} = k_{HA}[HA] + k_{H_3O^+}[H_3O^+] + k_{H_2O}[H_2O]$. A linear free-energy relation results from plotting log k (hydrolysis) against acid pK_a, giving a Brönsted α value of 0.54. The rate of proton transfer from water to acetal was about ten times slower for D_2O than H_2O. Activation constants are $E_a = 30–65$ kJ/mol and $\Delta S^{\neq} = -80$ to -125 J/K mol depending on the catalyst used.

Gold and Waterman[99] using **38** and **39** again showed the existence of general acid catalysis with $\alpha = 0.62$ and 0.49 respectively. Protons are much less effective catalysts than expected. The rate-controlling step is that of proton transfer from the catalysing acid to the acetal, and replacement of H by D in the acid lowers the rate by a factor of 5.3. Hydrolysis products are methyl cyanoacetate and methanol from **38** and 2-hydroxyethyl dichloroacetate from **39**.



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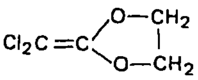
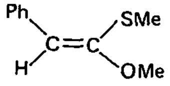


(39)

In rather similar studies[100] Schmir has examined the behaviour of *O,O*- and *O,S*-acetals **40**–**43**. In acidic solutions, catalysis by both protons and acetic acid occurred. The non-linear dependence of rate on buffer concentration at constant pH with **43** is considered to result from a mechanistic change, the rate-determining step at low buffer concentration being proton addition, and that at high concentration the decomposition of the carbonium ion intermediate. In Scheme 2 this means that step (1) increases with buffer concentration until its back-reaction becomes faster than step (2). Using **40** it was shown that rates and product ratios (thiol ester to oxygen ester) varied differently with changes in pH, low pH favouring the thiol ester. Thus the breakdown of tetrahedral intermediate **44** controls product distribution, although not the rate.



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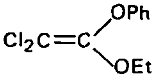

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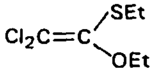

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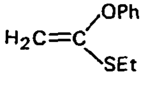

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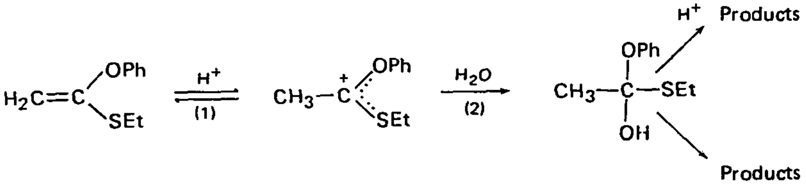


(44)

SCHEME 2.

Kankaanpera[101] has also examined the alcoholysis of **45** and **46**

$$\underset{(45)}{ClHC{=}C(OEt)_2} \qquad \underset{(46)}{Cl_2C{=}C(OEt)_2}$$

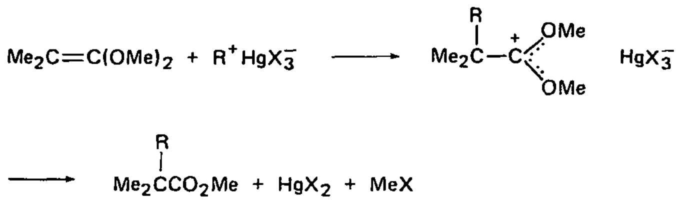
catalysed by oxonium ions, using perchloric acid. **46** reacts some 10^5 times more slowly than **45**. The activation parameters show that this is entirely due to a difference in the entropies of activation, which are +34 and −64 J/K for **45** and **46** respectively, both activation enthalpies being 60 kJ. Again, proton transfer to the acetals is rate-determining.

2. *Other reactions*

Ketene diethyl acetal undergoes rearrangement to ethyl *n*-butanoate in a thermal reaction initiated by *t*-butyl peroxide[102]. The short chain sequence shown in equation (30) is proposed. Under similar conditions ketene acetals react with ethers

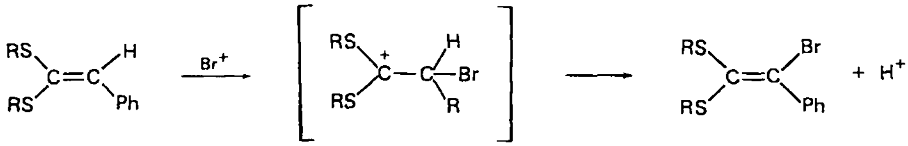
$$\dot{R} + H_2C{=}C(OR)_2 \longrightarrow RCH_2\dot{C}(OR)_2 \longrightarrow RCH_2CO_2R + \dot{R} \qquad (30)$$

to give α-substituted esters. Esters are also formed with carbonium ions as in equation (31).

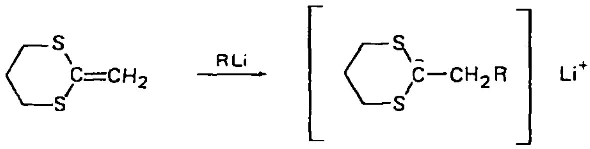


$$Me_2C{=}C(OMe)_2 + R^+HgX_3^- \longrightarrow Me_2C(R){-}\overset{+}{C}(OMe)_2\ HgX_3^- \longrightarrow Me_2C(R)CO_2Me + HgX_2 + MeX \qquad (31)$$

When a trityl cation is used however[103], steric hindrance prevents reaction at the central carbon and nucleophilic attack instead occurs at a ring *para* position. Ketene thioacetals react readily with electrophilic reagents such as bromine in carbon tetrachloride, presumably through their ability to stabilize carbonium ions


(32)

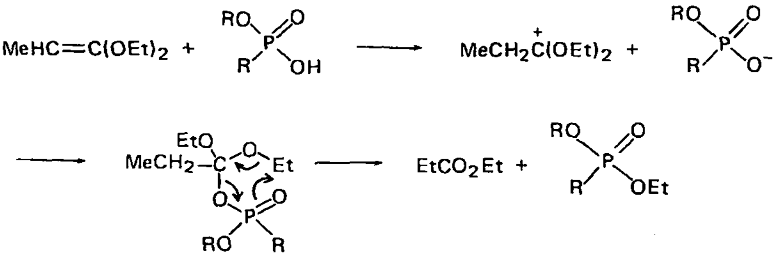
(equation 32)[104]. Conversely, their ability to stabilize carbanions is shown in the efficient addition of lithium alkyls (equation 33)[105].


(33)

Ketene acetals polymerize easily in acid solution and with cationic initiators which give $RCH_2\overset{+}{C}(OR)_2$. However, it is difficult to obtain high polymers because of the ease of chain-breaking reactions such as equation (34) (MX_3 is a metal halide)

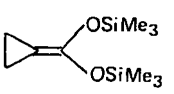
$$RCH_2\overset{+}{C}(OR)_2MX_4^- \longrightarrow RCH_2CO_2R + MX_3 + RX \qquad (34)$$

which have activation energies only slightly above those of the propagation steps[106]. The mechanism of reaction of methylketene diethyl acetal with alkyl hydrogen alkylphosphonates or phosphonothionates has been investigated[107], and that shown in Scheme 3 is considered to be the most likely.



SCHEME 3.

Dimethylketene trimethylsilylacetal (47) undergoes a 1,3-migration of a trimethylsilyl group from oxygen to carbon on heating, yielding (48). This contrasts with the behaviour of such acetals of ketene or dimethylketene which revert to the ketene[108].



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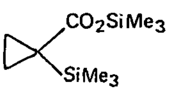


(48)

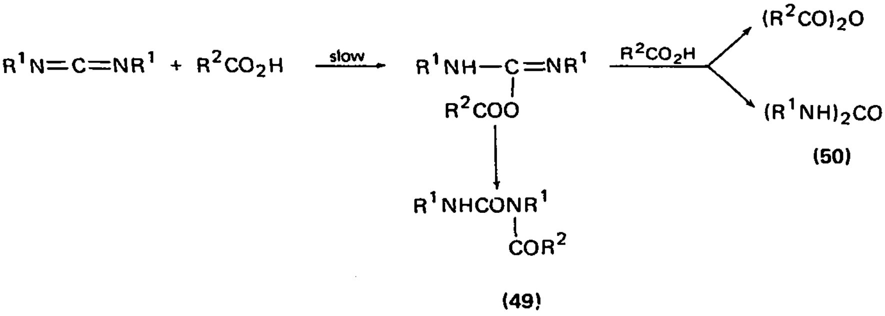
B. Carbodiimides

The chemistry of carbodiimides, including kinetics and mechanisms, was reviewed in 1967[109]. Since then there have been some further studies of kinetic and mechanistic interest. The kinetics of hydration of 1-cyclohexyl-3-(4-methylmorpholinoethyl)carbodiimide *p*-toluenesulphonate are pseudo first order in aqueous acid and thought[110] to involve attack of water on the protonated carbodiimide; in alkaline solution second-order kinetics were followed and attack of OH^- on the central carbon atom was proposed. Arrhenius equations for the two processes are $k = 2.2 \times 10^{10} \exp(-42\ kJ/RT)$ and $k = 6.05 \times 10^{7} \exp(-36\ kJ/RT)$ l/mol min respectively. De Tar, Silverstein and Rogers[111] studied the reactions of carbodiimides with carboxylic acids, alone and in the presence of amines and phenols, and also the reactions with peptide acids. The latter react about 50 times more rapidly than simple carboxylic acids. With acetic acid in acetonitrile, reaction is first order in carbodiimide and of an order above one in acetic acid. This fact and the thirtyfold increase in rate on changing to carbon tetrachloride solution suggests that acid dimer molecules react more rapidly than monomer. The main products are anhydrides, ureas and acylureas, and acylisoureas are postulated as intermediates. In the presence of amines ion-pair or hydrogen-bonded complexes with acetic acid now participate in reaction. Mironova and Dvorko[112] found that rates of reaction of mono- and dicarboxylic acids with dicyclohexylcarbodiimide to form anhydrides are first order in each component, and increase with acid strength and with dielectric constant of the solvent. The suggested mechanism comprises hydrogen

TABLE 13. Arrhenius parameters for the reaction of dicarboxylic acids with dicyclohexylcarbodiimide at 25°C in tetrahydrofuran

Acid	E_a (kJ/mol)	$\Delta S^{\neq}$ (J/K mol)
Glutaric	48	−131
Succinic	50	−121
Phthalic	48	−109
Malonic	42	−140
4-Nitrophthalic	47	−102
3-Nitrophthalic	61	−59
Maleic	50	−85

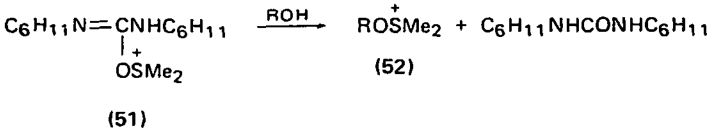
bonding of acid to nitrogen, followed by a rate-controlling ring-closure, and nucleophilic attack onto the central carbon of the carbodiimide. Activation constants are shown in Table 13. A more detailed product study[112] with monocarboxylic acids led to a pattern similar to that of De Tar and Silverstein[111] (Scheme 4) except that acid monomer and dimer were thought to be of similar reactivity. The product



SCHEME 4.

ratio 49:50 depends on temperature and solvent. When amines were added to the system the rate of formation of amide was independent of the nature or concentration of the amine, if chloroacetic acid was used, and was approximately equal to that of anhydride formation in the absence of amine.

Uridine and uridine 5′-phosphate react with carbodiimides showing second-order kinetics and an activation energy of 27 kJ/mol[113]. The effect of pH shows that the carbodiimide reacts as the anion. In the acid-catalysed reactions of alcohols and phenols with dicyclohexylcarbodiimide in dimethyl sulphoxide (equation 35)[114], the initial step is the formation of 51, which is then attacked by the nucleophilic alcohol oxygen. 52 then loses dimethyl sulphide to form aldehydes in the case of

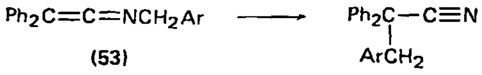


$$\underset{(51)}{C_6H_{11}N{=}\underset{\overset{|+}{OSMe_2}}{C}NHC_6H_{11}} \xrightarrow{ROH} \underset{(52)}{RO\overset{+}{S}Me_2} + C_6H_{11}NHCONHC_6H_{11} \qquad (35)$$

alcohols, and rearranges to give mainly *o*-thiomethoxymethyl phenols with phenols. However, a concerted mechanism has also been suggested[115]. Other reactions of carbodiimides which have received mechanistic study are those with phenols in the presence of 2-dialkylaminoethanol[116], the dehydration of asparagine and maleamic acid[117], the acylation of amines with amino acid esters in the presence of carbodiimides[118], and the tetrafluoroboric acid-catalysed reactions with alcohols, epoxides, amines and oximes[119].

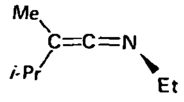
C. Ketene Imines

Reactions of ketene imines were reviewed by Krow[120] in 1971. As with carbodiimides, their use in peptide synthesis and in dimethyl sulphoxide oxidation of alcohols is of current interest. There have, however, been few quantitative studies. The kinetics of thermal rearrangement of diphenyl-*N*-(arylmethyl)ketene imines (53) to nitriles (54) at 60°C have been studied[121]. Weak solvent and substituent effects and free-radical scavenging experiments indicate that reaction occurs through homolytic decomposition to a caged radical pair which recombines to give nitrile. The effect of substituents on the free-energy barrier to racemization of various ketene imines has been studied by n.m.r. methods[122]. The highest barriers, around 60 kJ, are obtained with aliphatic substituents, for example 55. Substituents which can stabilize a negative charge on the carbon end of the heterocumulene lower the barrier. Pyrolysis of ketene *N*-*t*-butylimines (56) at 150°C in solution follows first-order kinetics[123] with an activation energy of 126 kJ and entropy of activation of −34 J/K. The cyclic transition state 57 is proposed.



$$Ph_2C{=}C{=}NCH_2Ar \longrightarrow Ph_2C(CH_2Ar){-}C{\equiv}N$$

(53) (54)



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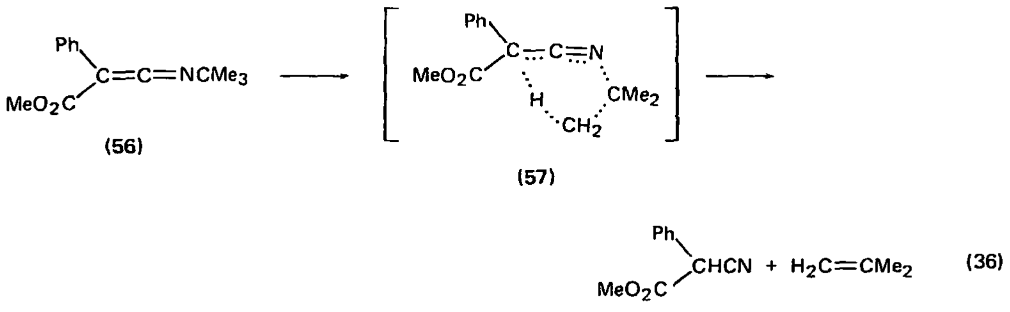
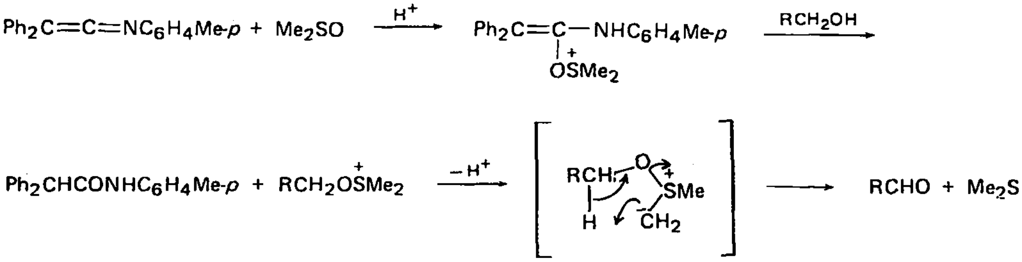


(56) (57) (36)

The mechanism of ketene imine/dimethylsulphoxide oxidation of alcohols has been studied[124] and Scheme 5, resembling the equivalent carbodiimide reactions, proposed.



SCHEME 5.

The reaction of 2-isoalkyloxazines with organolithium compounds has been shown to involve ketene imine intermediates[125], and the mechanism of their further conversion to α-substituted ketones considered. The mechanism of the reaction of ketene imines with peracids and ozone has also been discussed[126].

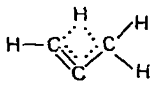
VII. ALLENES: INTRODUCTION

Differences between allenes and ketenes show up most clearly in polar additions. The vast majority of additions to ketenes are by nucleophiles, whereas studies of such reactions are rare in allenes unless strongly electron-withdrawing substituents are present[127], and electrophilic addition predominates. Also initial polar attack is normally at the central cumulene atom in ketenes, whereas both central and terminal sites may be the target in allenes. This gives greater mechanistic variety which is further increased in that central addition gives an ion which may be stabilized by allylic resonance only if a 90° rotation occurs. If a bridged complex results from primary addition this rotation may not be easy. Similar questions arise in radical additions to allenes, although in this case planar allylic configurations are readily achieved. Mechanistic understanding of allenes is assisted by the much more detailed knowledge of alkenes and the orthogonality of the two π systems in the former results in many similarities. A powerful means of following the mechanistic course of allene additions is provided by the use of dissymmetric allenes.

Oxymercuration and hydroboration of allenes have recently been studied in addition to the more usual electrophilic additions. Isomerization to alkynes under a variety of conditions continues to attract attention as does allene oxidation. Mechanisms of allene reactions in general were reviewed fairly extensively about ten years ago[128] and allene additions more recently[129]. Normally only later work is considered here.

VIII. ISOMERIZATION AND THERMAL DECOMPOSITION OF ALLENES

The isomerization of allenes to alkynes has received considerable study[128]. In recent work attention has been paid to the isomerization of gaseous allene itself, particularly in shock-tube studies. Under these conditions isomerization and thermal decomposition may coexist and both are therefore treated in this section. Lifshitz, Frenklach, and Burcat have studied both isomerization[130] and pyrolysis[131] of allene behind reflected shocks in a single-pulse shock tube. In the temperature range 1030–1220 K isomerization is very much faster than thermal decomposition; first-order kinetics are followed and $k = 10^{13.17}\exp(-253\ kJ/RT)\ s^{-1}$. Isomerization of mixtures of allene and fully deuterated allene gives no isotopically-mixed propyne. The results therefore support a unimolecular mechanism involving a sigmatropic 1,3-hydrogen shift. Bradley and West[132] obtained similar results in the higher temperature range 1440–1810 K, with $k = 10^{14.2}\exp(-388\ kJ/RT)\ s^{-1}$ and also favoured a molecular mechanism. Theoretical (RRKM) calculations using transition state 58 agreed with the experimental findings. Walsh[133] has suggested an alternative

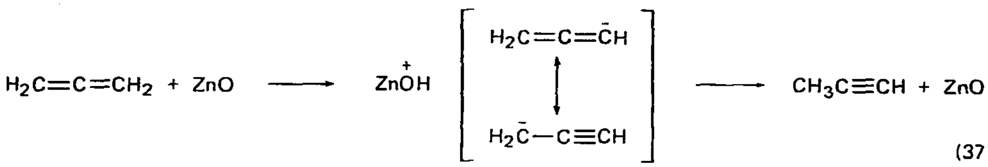


(58)

mechanism in which cyclopropene is an intermediate. This route would involve two 1,2-hydrogen shifts rather than a single 1,3-shift.

It is clear from the above that pyrolysis of allene at high enough temperatures is effectively that of an allene/propyne equilibrium mixture, although at low temperatures the product profiles from allene and propyne are different. The main products are acetylene, methane, ethylene, ethane and hydrogen, and it was shown[131] that methane arises from propyne and ethylene from allene. The mechanism is not a typical free-radical chain because of the unreactivity of some of the radicals formed. Similar product distributions were reported at 900–1150°C by Levush and coworkers[134].

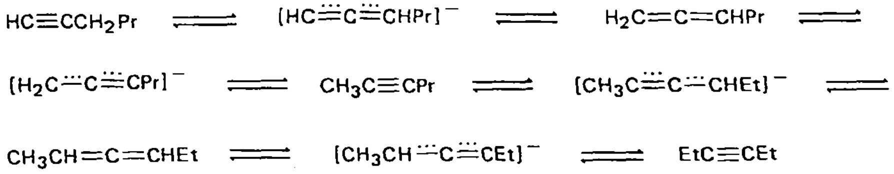
If solid catalysts are used the propadiene–propyne isomerization will take place at low temperatures[135], even at 320 K on rutile[136]; but it is then frequently accompanied by other reactions, such as self-hydrogenation of allene[137]. The solid surface, for example zinc oxide[138], appears to act as a base. Infrared studies of the adsorbed species show the presence of an O–H band; also the spectra of adsorbed species starting with either allene or propyne are identical and presumably due to the propargyl anion. The mechanism is therefore as shown in equation (37), and is further



(37)

supported by the easy exchange of hydrogen with deuterium oxide.

Base-catalysed isomerizations proper have recently been reviewed[139], and have received subsequent kinetic and mechanistic study using potassium *t*-butoxide in *t*-butanol and sodium amide in liquid ammonia[140]. Using hexa-1,2- and -2,3-dienes and hex-1-, -2- and -3-ynes, rates of isomerization were measured and found to support a stepwise mechanism involving carbanion intermediates (Scheme 6). Proton removal is rate-determining and no conjugated dienes are formed, so that



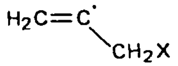
SCHEME 6.

the acidity (from a kinetic viewpoint) of protons attached directly to the allenic system is greater than those conjugated with it.

The kinetics of racemization of 1,3-dimethyl- and 1,3-di-*t*-butylallenes have been studied[141] in the gas phase at 260–320°C. Arrhenius equations are $k = 10^{13.6} \exp(-193\ kJ/RT)\ s^{-1}$ and $k = 10^{13.4} \exp(-196\ kJ/RT)\ s^{-1}$ respectively. Activation energies were equated with energy barriers for C=C bond rotation, and from them was also obtained an estimate of 58 kJ for the resonance energy of the allyl radical. Mechanistic proposals have also been made concerning the thermal rearrangement of allenes containing a second allenic group or a double bond in the molecule[142], and the sigmatropic rearrangement of α-allenic and α-allenic-α-ethylenic alcohols[143]

IX. RADICAL ADDITIONS TO ALLENES

Mechanistic studies have been concerned with the site of addition, the effects of allene substituents, the radical nature and reaction conditions on the reaction path, and the likely intermediates in view of the special nature of the allene structure[128]. In general, alkyl substitution favours central addition and there is no clear correlation between radical type and regioselectivity, except that CX_3 radicals prefer terminal addition, whatever their polarity. The latter orientation produces vinylic radicals (**59**), central attack gives initially radical **60** which must then undergo a 90° internal rotation before benefiting from full allylic stabilization (**61**). Heiba[144] has shown that the difference in activation energy in forming radicals **60** and **59** where X = PhS is only 4.5 kJ, the energy for central addition being the greater. In Scheme 7 the latter is irreversible since **62** undergoes rapid rotation to the allylic form with low activation energy, whereas terminal addition is reversible. The mechanism successfully accounts for concentration and temperature effects in this case and in HBr addition (see below). Furthermore, the results of Byrd and Caserio[145] on $CCl_3^{\bullet}$ terminal addition to (+)-2,3-pentadiene suggest that the α-alkylvinyl radicals formed may be configurationally unstable and equilibrate rapidly with their geometric isomers.



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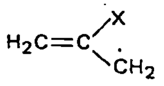

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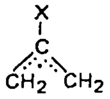

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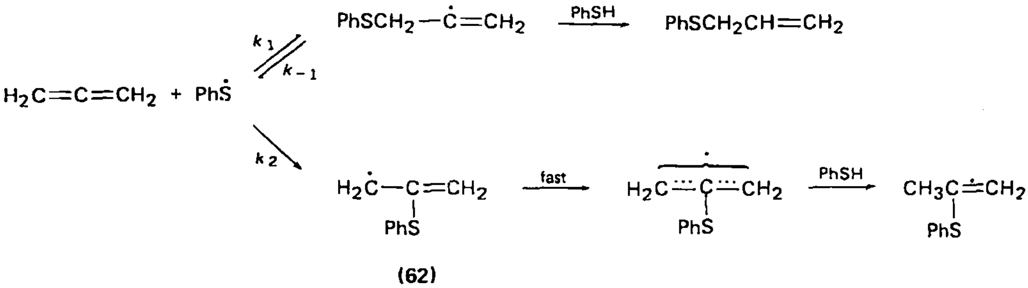


SCHEME 7.

A. Hydrogen Atoms

At 77 K in water or benzene matrices hydrogen atoms add exclusively to the terminal carbon of allene (equation 38)[42] and the terminal CH_2 carbon of 1-methylallene. No allyl radical is formed but some propargyl radical results, probably from the initially-formed methylvinyl radical. The absence of allyl radicals is related to

$$\mathrm{H^{\bullet} + H_2C{=}C{=}CH_2 \longrightarrow CH_3\dot{C}{=}CH_2 \xrightarrow{+H_2C{=}C{=}CH_2} CH_3CH{=}CH_2 + [CH_2{\overset{\cdots}{-}}C{\overset{\cdots}{\equiv}}CH]^{\bullet}} \qquad (38)$$

the difficulty of obtaining overlap between the orthogonal π orbitals. At higher temperatures (270–470 K) hydrogen atoms add to both terminal and central carbons[146] and the rate equations for reactions (39) and (40) are $k = 10^{9.9} \exp \times (-8.4\ kJ/RT)$ l/mol s and $k = 10^{9.6} \exp(-11.3\ kJ/RT)$ l/mol s respectively

$$\mathrm{H^{\bullet} + H_2C{=}C{=}CH_2 \longrightarrow CH_3{-}\dot{C}{=}CH_2} \qquad (39)$$

$$\mathrm{H^{\bullet} + H_2C{=}C{=}CH_2 \longrightarrow \dot{C}H_2{-}CH{=}CH_2} \qquad (40)$$

(compare Heiba's value for the activation energy difference, above). Hydrogen, propylene and methylacetylene are the main products in this case but other workers[147] find that acetylene is formed in large amounts, probably through isomerization and displacement (equation 41). Allene has been found to react rather slowly with deuterium atoms at 90 K compared with other alkenes[148]. Allene has also been reacted with active nitrogen producing mainly the propargyl radical[149].

$$\mathrm{H_2C{=}C{=}CH_2 + H^{\bullet} \longrightarrow CH_3C{\equiv}CH + H^{\bullet} \longrightarrow CH_3^{\bullet} + C_2H_2} \qquad (41)$$

B. Alkyl Radicals

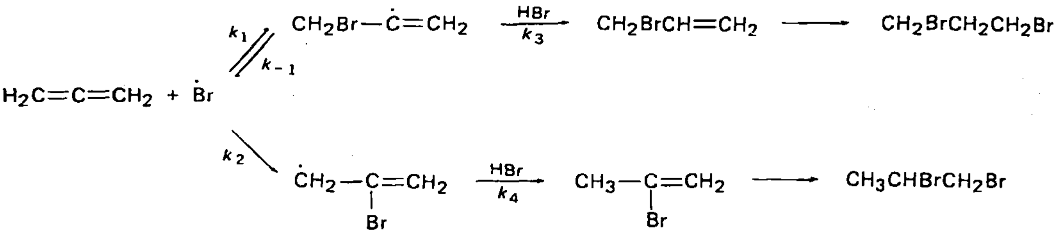
Several workers have investigated the kinetics of reaction of alkyl radicals with allenes. Finding that tetraphenylallene added methyl radicals at least as rapidly as allene itself, Rajbenbach and Szwarc[150] assumed that addition must be on the central carbon. However Getty, Kerr and Trotman-Dickenson[151] showed that methyl, ethyl and *i*-propyl radicals add exclusively to terminal carbons at 100–200°C. Their kinetic data are given in Table 14. Under their conditions there was no evidence of isomerization of the product alkenyl radicals. Meunier and Abell[152] confirmed terminal addition of methyl radicals and showed also that trifluoromethyl radicals add to the same position; thus the site of attack does not depend on the electrophilic or nucleophilic character of the radical as once argued[153]. Trichloromethyl radicals also add to the end-carbons.

TABLE 14. Rate data for the addition of alkyl radicals to allene

Radical	E_a(kJ/mol)	A(l/mol s)	$k_{142°C}$ (l/mol s)
Me$^{\bullet}$	34	$10^{8.3}$	10^4
Et$^{\bullet}$	38	$10^{8.5}$	5×10^3
i-Pr$^{\bullet}$	30	$10^{7.5}$	5×10^3

C. Halogens

In free-radical addition of hydrogen bromide[154], bromine atoms add to both carbons. Addition is statistical with excess hydrogen bromide in pentane at −78°C, and the ratio of terminal to central addition decreases with decreasing hydrogen bromide concentration (Figure 5) and with increasing temperature. The results are explained by the reversibility of terminal addition and the irreversibility of central addition as in Scheme 8. At high HBr concentration $k_3[\mathrm{HBr}] > k_{-1}$ and the ratio



SCHEME 8.

of terminal to central addition equals that of initial bromine attack. Increasing temperature favours k_{-1} as against k_1 and k_2, which have activation energies near to zero, and terminal addition becomes less favoured.

Radical chlorinations have been studied using dichloroiodobenzene[155] and *t*-butyl hypochlorite[156]. In the latter both addition and abstraction occurred. In addition with 2,3-pentadiene *t*-butoxy radicals add to the central carbon as in Scheme

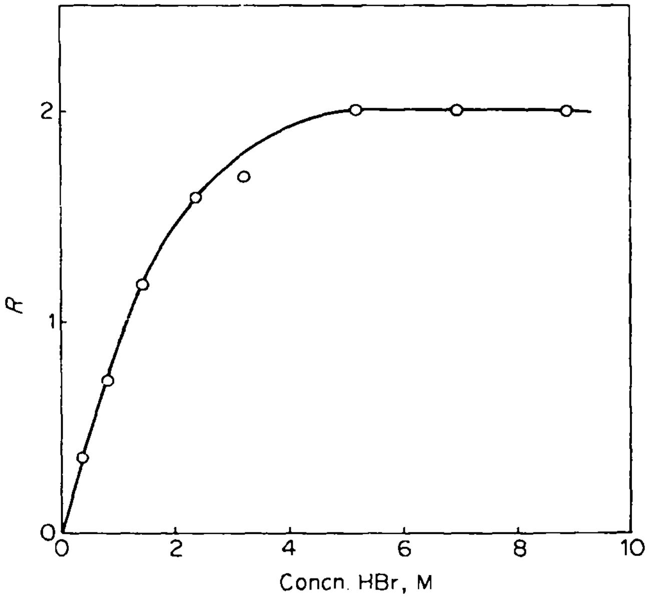
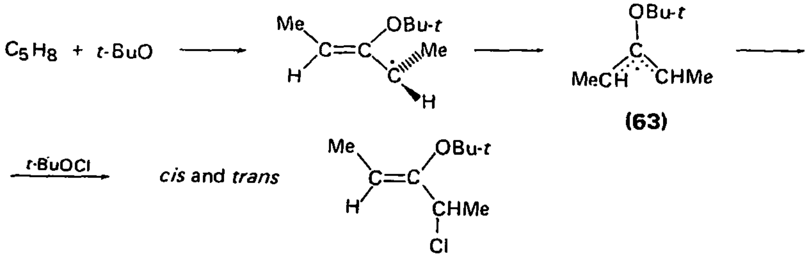
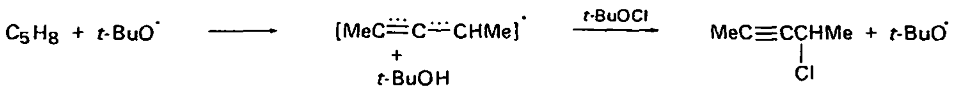


FIGURE 5. Ratio (R) of terminal to central Br$^\bullet$ addition as a function of HBr concentration in the addition to allene at −78°C in pentane[154]



SCHEME 9.

9. Symmetrical allylic intermediates 63 are also proposed by Lasne and Thuillier[155]. Abstraction is represented by Scheme 10.



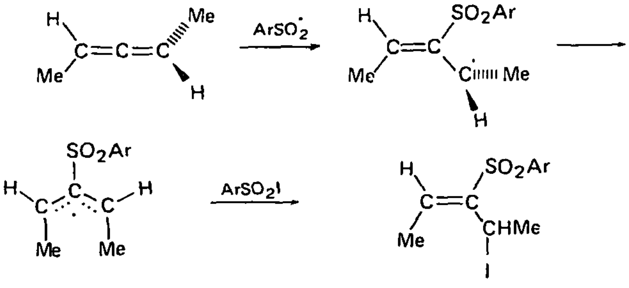
$$C_5H_8 + t\text{-BuO}^{\bullet} \longrightarrow \underset{t\text{-BuOH}}{[\text{MeC}\overset{...}{=}\text{C}\overset{...}{-}\text{CHMe}]^{\bullet} +} \xrightarrow{t\text{-BuOCl}} \text{MeC}{\equiv}\underset{\text{Cl}}{\text{C}\text{CHMe}} + t\text{-BuO}^{\bullet}$$

SCHEME 10.

D. Oxygen- and Sulphur-containing Radicals

The kinetics of addition of hydroxyl[157] and methoxy[158] radicals to allene have been studied. In both instances rates are faster than for addition to ethylene. Sulphur analogues of the above, the thiyl radicals, have been popular radical sources for allene additions, but there have been few developments since earlier reviews[128]. E.s.r. studies have thrown some light on the nature of the radical formed by addition of methylthiyl radicals to the central carbon of tetramethylallene[159]. The allyl radical formed is nonplanar, presumably in order to relieve the steric strain imposed by the substituent at the central carbon, and this gives rise to some loss of delocalization energy. Perner and Franken[160] have determined an absolute rate constant for the reaction of HS radicals with allene.

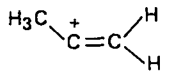
Free-radical additions of sulphonyl halides[145, 161] and thiocyanates[162] to allenes have been studied. With allene itself products include 1:1 adducts resulting from attack of the sulphonyl radical on both central and terminal carbons, the proportions varying markedly with the alkyl or aryl group of the radical used. Central attack is favoured as the electron-donating power of the group increases. Substituted allenes on the other hand give only allylic iodides, resulting from central attack by the sulphonyl radical. In addition a racemic adduct was obtained with (*S*)-(+)-2,3-pentadiene, indicating that symmetric delocalized allyl radicals are intermediates, as with *t*-butyl hypochlorite and as in Scheme 11.



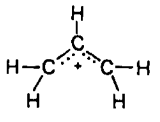
SCHEME 11.

X. ELECTROPHILIC ADDITIONS TO ALLENES

Electrophilic additions to allenes have attracted considerable attention[128,129] in respect of the direction of addition, the effect of electrophile character and allene structure, and the nature of the intermediates. The electrophile may add to the terminal carbon giving a vinyl cation, or to the central carbon. In the latter case the initially-formed cation is not fully allylic, since the empty p orbital is orthogonal to the π system, and rotation must occur before stabilization is possible. Aue, Davidson and Bowers[163] have studied this matter directly by the gas-phase protonation of allene with H_3S^+. The vinyl cation (**64**) is formed rather than the planar allyl one (**65**), despite the fact that the latter is more stable. This is because formation of the perpendicular allyl cation (**66**) is energetically unfavourable and because a concerted protonation and CH_2 rotation to yield **65** directly has an energy barrier. Also the vinyl cation was found to protonate methanol readily whereas separately-prepared allyl cations did not. However, 1,3-dimethylallene and 1,1,3,3-tetramethylallene in $FSO_3H{-}SbF_5$ solutions at −70°C yield allyl cations by direct protonation of the sp-hybridized central carbon[164] with no evidence for vinyl cations being either present or involved as intermediates. The stabilizing effect of the methyl groups is thus as expected.



(64)



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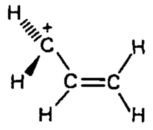

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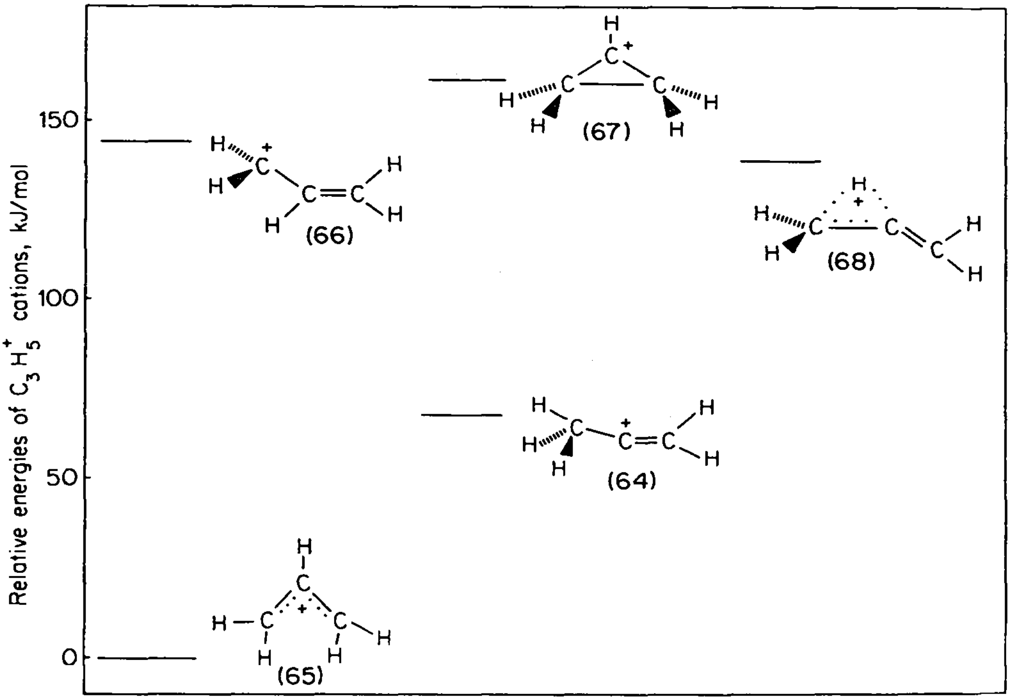
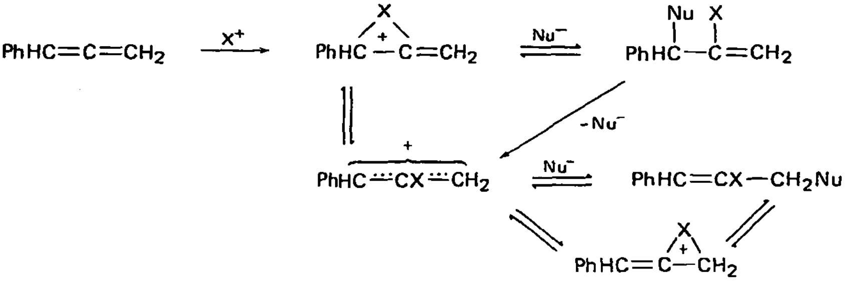


FIGURE 6. The calculated relative energies of $C_3H_5^+$ cations[165].

Ab initio molecular orbital calculations on the structures and stabilities of these cations are extremely illuminating[165], results being summarized in Figure 6. The planar allyl cation (**65**) is 147 kJ more stable than the perpendicular one (**66**), which is made up of 109 kJ resonance stabilization of **65** and 38 kJ destabilization of **66** by the double bond. However **65** is not directly accessible in allene protonation and the 2-propenyl cation (**64**) is preferred. The extent to which **66** converts to **65** is one of the major current questions in electrophilic additions to allenes. Progressive alkylation of allene favours the allyl route. The perpendicular allyl cation corresponds to a transition state for rotation of allyl cations, although the cyclopropyl cation **67** is a possible alternative. Bridged protonated allene **68** may similarly represent a transition state for a vinyl–allyl cation interconversion, the activation energy of which will be at least 70 kJ. Although these calculations are only for the simplest cations from allene and are for the gas phase they provide a useful reference point when considering the validity of the mechanisms in this section.

A. Halogens and Halogen Acids

Halogenation of phenylallene[166] gives 1,2- and/or 2,3-adducts depending upon conditions, higher temperatures favouring 2,3. In terms of the proportion of 1,2-adduct the effect of halogen is IBr > Br_2 > Cl_2; electron-donating substituents also decrease the proportion of 1,2-adduct (Table 15). These and other results are compatible with the initial formation and subsequent reactions of a 1,2-cyclic halonium ion as in Scheme 12. The more stable the cyclic halonium ion (I > Br > Cl) the greater the chance of 1,2-adduct being formed. Electron donation diffuses the positive charge on the α carbon and thus lowers the rotational barrier to formation of the open allylic cation. Increasing temperatures also reduce the stability of the cyclic ion.

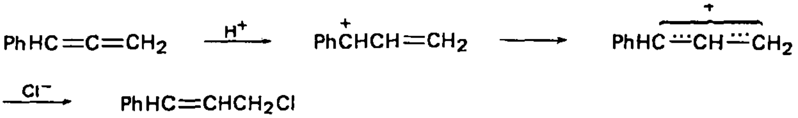


SCHEME 12.

TABLE 15. The effect of substituents on the percentage of 1,2-adduct in the products of halogenation of phenylallenes

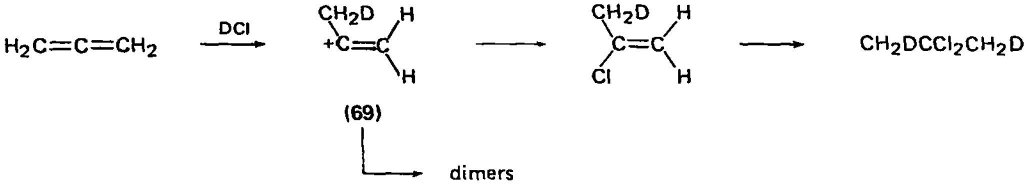
	1,2-adduct (%)		
Substituent	Cl_2	Br_2	IBr
m-Cl	–	89	100
H	70	84	100
p-Me	–	78	100
α-Me	–	58	100

Recent work on hydrohalogenation of allenes has thrown further light on the mechanism. Okuyama and his associates[167] studied the kinetics of hydrochlorination of phenylallenes in glacial acetic acid. Reaction is first order in allene, first order in acid at lower concentrations and second order in acid at higher concentrations. Rates with ring substituents obey a Hammett relationship with $\rho^+ = -4.2$. α- and γ-methyl substituents on the cumulene chain increase the rate by factors of 4000 and 200 respectively. These results and the fact that the sole product is a cinnamyl chloride strongly suggest that reaction proceeds through the formation of an α-vinylbenzyl cation (Scheme 13). The high negative ρ^+ value, which shows that the positive centre is conjugated with the ring in the transition state, and the large effect of α-methyl substitution both support the Scheme. Similar studies[168] on 1-phenyl-1,2-butadiene also yielded activation parameters of 75 kJ ($\Delta H^{\neq}$) and −69 J/K ($\Delta S^{\neq}$). The gas-phase addition of hydrogen chloride to allene has also been studied[169]. The activation energy is reported to be close to zero, and the product distribution leads to the suggestion that some charge separation, in the direction of forming a vinyl cation, occurs in the transition state. Addition of DCl to allene[170] gave monodeuterated methyl groups only, with no deuteration of unreacted allene, and tends to support Scheme 14, involving vinyl cation **69**.



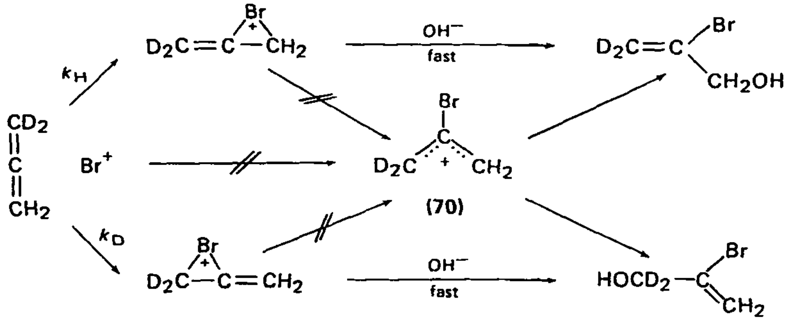
$$PhHC{=}C{=}CH_2 \xrightarrow{H^+} Ph\overset{+}{C}HCH{=}CH_2 \longrightarrow \overset{+}{\overline{PhHC{\cdots}CH{\cdots}CH_2}} \xrightarrow{Cl^-} PhHC{=}CHCH_2Cl$$

SCHEME 13.



SCHEME 14.

Further clarification of the parts played by halonium and allylic cations in halogenation is provided by secondary deuterium isotope effects in the addition of hypobromous acid to allene[171]. In Scheme 15 kinetic isotope effects will appear if **70** is not involved, either directly or after formation of bromonium ions. The observed ratio k_H/k_D of 0.83 agreed with that predicted. Results with hypochlorous acid also confirm that haloallyl cations do not participate in these cases.

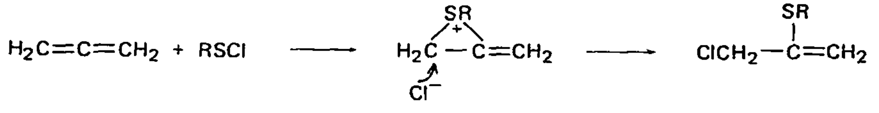


SCHEME 15.

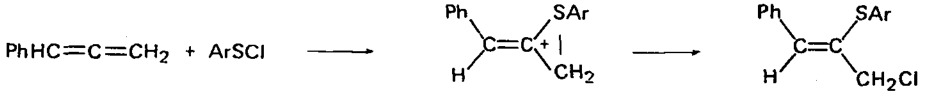
Bianchini and Cocordano[172] added hypochlorous acid to a range of alkyl allenes. In all cases chlorine is attached to the central carbon and hydroxyl to the more substituted terminal carbon; Hückel calculations were used to rationalize the findings.

B. Sulphenyl Halides

With allene itself[173] the primary monoadduct is 71, formed by nucleophilic chloride ion attack on the episulphonium ring in 72 (equation 42). With phenylallene and 2,4-dinitrobenzenesulphenyl chloride[174] a 2,3-adduct is formed with the SAr group *cis* to the phenyl (equation 43). Secondary deuterium isotope effects are much larger at the 3- than the 1-position and support the mechanism shown. Alkyl-substituted allenes give monoadducts principally of type 73[175]. With 3-methyl-1,2-butadiene addition occurs at the 1,2 double bond[176] although methyl substitution might be expected to favour electrophilic attack at the 2,3-bond. Steric factors probably operate but further electronic effects may also be involved.



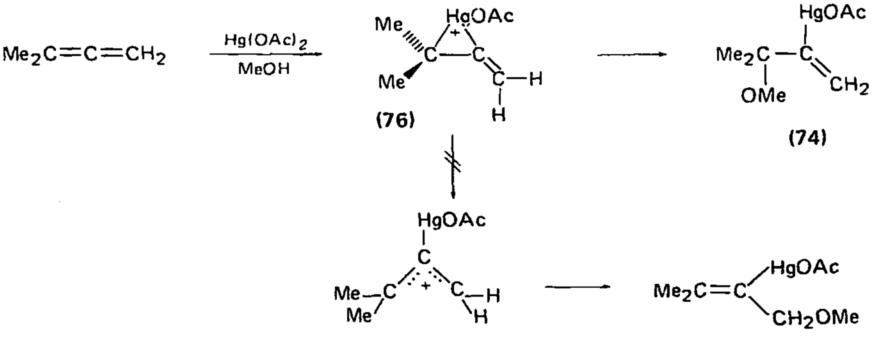
(72) (71) (42)



(73) (43)

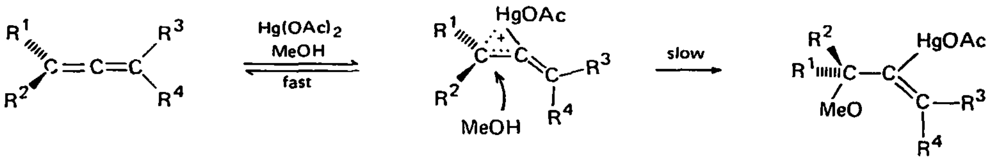
C. Oxymercuration

Oxymercuration of allenes has only been studied within the last decade or so[177]. With 1,2-cyclononadiene and ethanolic mercuric chloride, HgCl adds to the central carbon when forming the ethoxymercurial and a similar result obtains with 2,3-pentadiene. Waters and Kiefer also found central attack with a series of methyl-substituted allenes[178]; allene itself giving terminal attack before adding a second molecule of mercury acetate. Rates of reaction increase with methyl substitution (allene:methylallene:dimethylallene = 1:4:16) and tetramethylallene reacts at least 10^4 times more rapidly than tetramethylethene. 1,1-Dimethylallene gives solely 74 rather than the more stable 75, which provides good evidence for bridged mercurinium ions as intermediates with allenes as well as alkenes (equation 44). Bonding



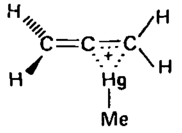
(76) (74) (77) (75) (44)

between mercury and terminal carbon must be strong enough in **76** to prevent rotation to the allylic intermediate **77**. Additional evidence is provided by the use of optically-active allenes. Bach[179] showed that optically-active 1,2-cyclononadiene yielded active 3-ethoxy-*cis*-cyclononene, that is with HgX^+ attack from outside the ring, but he considered that stereospecificity was not complete and that allyl intermediates did provide an alternative pathway. The type of mercury salt used had some effect and with chloride an almost racemic product was obtained. Theoretical calculations suggested that chloro ligands were better able to stabilize the allyl cation than mercurinium ion. Pirkle and Boeder obtained 6:1 and 19:1 *trans*:*cis* products from (*R*)-(−)-2,3-pentadiene and (*S*)-(+)-3,4-heptadiene respectively[180], the stereospecificity in the former case being unaffected by temperature change. The results are consistent with essentially complete stereospecificity. The precise nature of the mercurinium intermediate is not known, but σ rather than π bonding has been suggested and it has been represented[181] as an unsymmetrical bridged structure with σ bonding to the central carbon (**78**). Solvent attack on the complex is both rate-limiting and stereospecifically *trans*. Bach[182] has studied the gas-phase complexes between $HgMe^+$ ions and allene. Ions **79** and **80** are formed in the ratio



(78)

(45)



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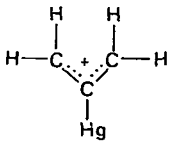
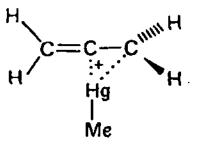


(80)

of 97:3. Also it was calculated theoretically that the energies of the unsymmetrical complexes (**81**) and (**82**) were 54 and 80 kJ respectively higher than that of (**79**). In contrast to the views above it is concluded that (**79**) is essentially a π rather than a σ complex. In addition mercurinium ions (**79**) are calculated to be considerably more stable than planar allylic ions (**83**) in the gas phase.



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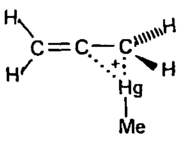
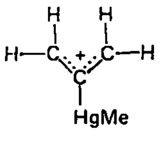


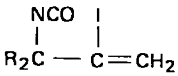
(82)



(83)

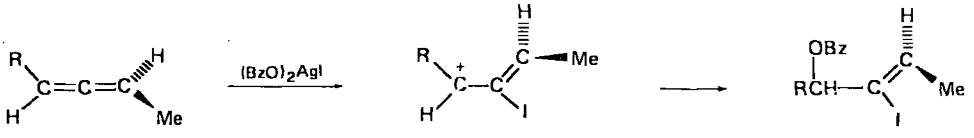
D. Other Additions

Additions of iodine isocyanate to alkyl- and aryl-allenes have been studied[183]. At −78°C addition occurs mainly at the substituted double bond with alkylallenes (**84**) but there is little preference at 0°C, or with phenylallene. With iodosilver dibenzoate[184] addition occurs through the nonallylic cation (**85**) (equation 46).



$$R_2\overset{NCO}{\overset{|}{C}}-\overset{I}{\overset{|}{C}}=CH_2$$

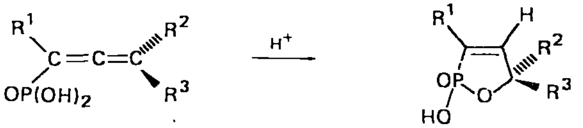
(84)



(85)

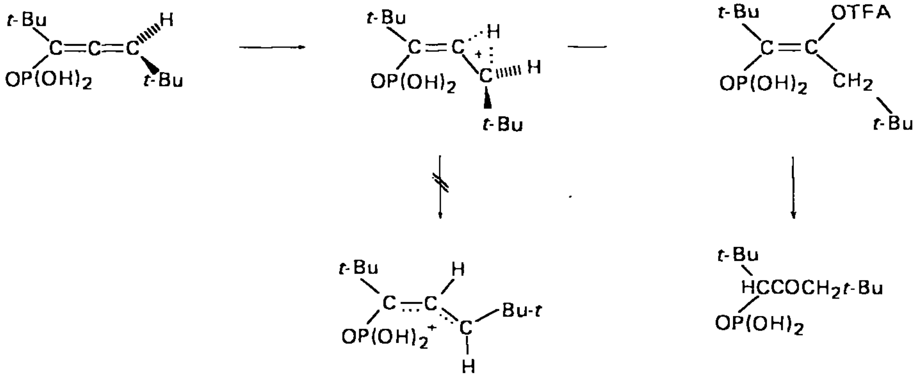
(46)

Electrophilic reactions of allene phosphonic acids (86) throw some light on the mechanism of allene additions[185]. When R^2 and R^3 are alkyl groups cyclization to oxaphospholenes takes place with Brönsted acids (equation 47). This may be visualized as protonation of the central carbon followed by attack with the internal nucleophile. If either R^2 or R^3 is hydrogen then no cyclization occurs. Thus alkyl groups are needed to stabilize the positive charge on the terminal carbon. With one hydrogen, and using trifluoroacetic acid, proton addition will occur but only at the terminal carbon as in Scheme 16. Rotation of the protonated allene to an allylic ion seems energetically less favoured than addition of trifluoroacetate (see also above).



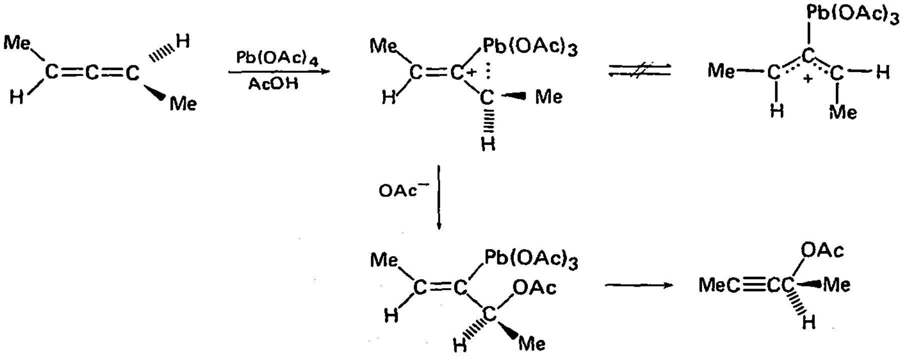
(86)

(47)



SCHEME 16.

Under suitable conditions lead tetraacetate reacts with allene in an electrophilic addition resembling oxymercuration, excepting that the carbon–lead bond is too labile for intermediates such as 87 to be detected, the final product being an alkyne. Using allenes such as (+)-1,3-dimethylallene Bach[186] has shown that addition is fairly stereospecific and proposes a suprafacial addition of solvent onto the complex (Scheme 17). This is supported by the more definite evidence of suprafacial attack with (–)-1,2-cyclononadiene[187], where the stereospecificity again



(87)

SCHEME 17.

shows that planar allyl cations do not participate to any degree. Addition to the metal–allene complex here is thus in the opposite sense to the antarafacial solvent attack in oxymercuration and oxythallation[188].

In hydroboration the regiospecificity of addition again depends on the allene used (Table 16), but only slightly on the hydroborating agent. Boron addition to the terminal carbon predominates when the latter is unsubstituted whereas 2,4-dimethyl-2,3-pentadiene gives 100% central attack[189]. It is assumed that a four-membered cyclic transition state is involved, and steric as well as electronic factors are important[190]. Terminally-unsubstituted positions are sterically most favoured for boron attack; when central attack occurs steric factors control the isomer produced. Partial hydroboration of racemic allenes with (+)-tetra-3-pinanyldiborane[191] led to optically-enriched recovered allenes. The results are discussed in terms of a skewed four-centre transition state. Kinetic and mechanistic work on the solvolysis of allenic substrates has been recently reviewed[129]; later publications are listed[192].

XI. OXIDATION OF ALLENES

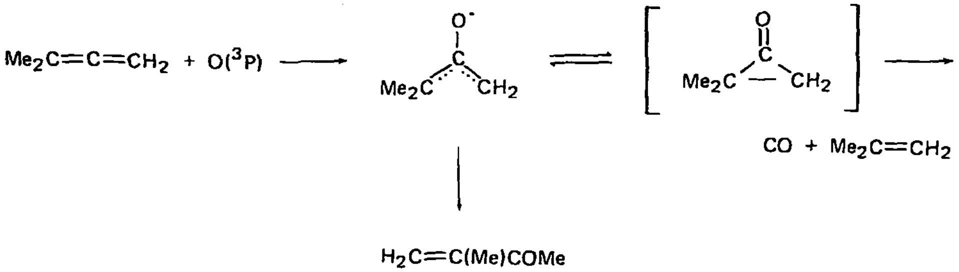
Oxidation of allenes is of interest both in the gas phase, from the standpoint of atmospheric chemistry, and in solution, where cyclopropanones and allene oxides are likely intermediates. Reactions with lead tetraacetate were considered in Section X.D.

TABLE 16. Effect of allene structure on site of hydroboration[189]

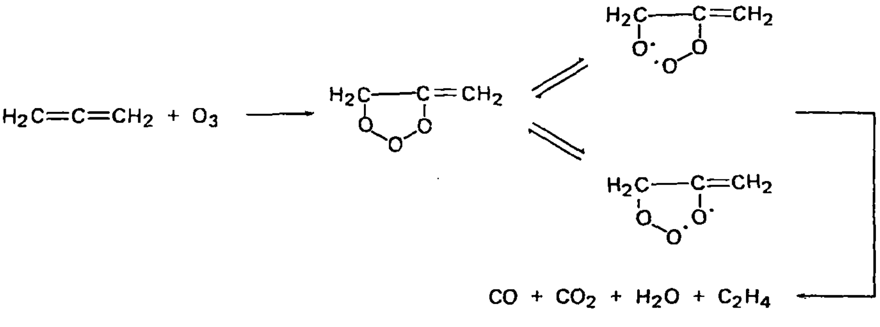
Allene	Central addition (%)	Terminal addition (%)
$H_2C{=}C{=}CH_2$	13	87
$Me_2C{=}C{=}CH_2$	22	78
MeHC=C=CHMe	81	19
$Me_2C{=}C{=}CMe_2$	100	~0
1,2-Cyclononadiene	100	0

A. Gas Phase

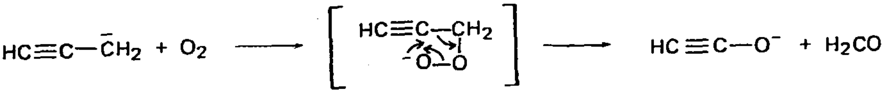
Reaction of oxygen (^3P) atoms with allene yields ethene and carbon monoxide as products[193]. The Arrhenius equation is $k = 10^{9.9} \exp(-6.7\ kT/RT)$ l/mol s, and the products are vibrationally excited[194]. Addition of $O(^3P)$ to a variety of allenes has been studied[195], products being carbon monoxide, an alkene and an α,β-unsaturated carbonyl compound. Oxygen adds to the central carbon of the allene and an excited cyclopropanone is produced (Scheme 18). Rate constants for reaction of allenes with oxygen atoms increase with alkyl substitution, allene reacting some 15 times more slowly than 2-methyl-2,3-pentadiene. With ozone, reaction is chemiluminescent, light emission being due to excited CH, OH and formaldehyde intermediates[196]. Toby and Toby[197] studied the kinetics of the allene/ozone reaction in the range 226–325 K. Oxygen was a major product followed by oxides of carbon, water and ethylene. The activation energy for the primary addition was 23 kJ and the *A* factor 10^6 l/mol s. Scheme 19 shows the mechanism proposed. The gas-phase reaction of oxide radical ions with allene gives principally proton abstraction[198] leaving a carbanion, plus some hydrogen atom abstraction yielding a radical. Similarly, hydroxide ions abstract a proton, leaving a carbanion. Carbanions formed in this way react with molecular oxygen as in equation (48).



SCHEME 18.



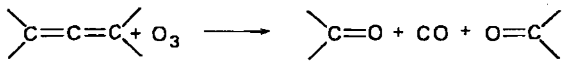
SCHEME 19.

 (48)

$$HC{\equiv}C{-}\bar{C}H_2 + O_2 \longrightarrow [\,\cdots\,] \longrightarrow HC{\equiv}C{-}O^- + H_2CO \qquad (48)$$

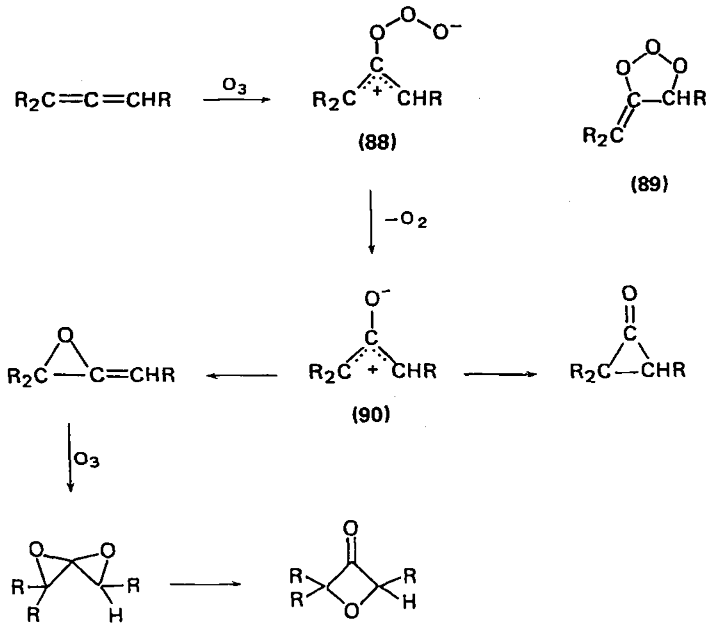
B. Solution

Crandall and coworkers[199] have reacted allenes with peracids or ozone in solution in an interesting series of studies. Unhindered allenes are cleaved by ozone as in equation (49). However with 1,1-di-*t*-butylallene at −78°C, cyclopropanone and



(49)

di-*t*-butylketone are obtained. Tri-*t*-butylallene gives a spiro dioxide and a small amount of allene oxide. Peracid acid oxidation again gives allene oxides and spiro dioxides, and with 1,1-di-*t*-butylallene the former spontaneously isomerizes to a cyclopropanone. The overall sequence with ozone is given in Scheme 20. The

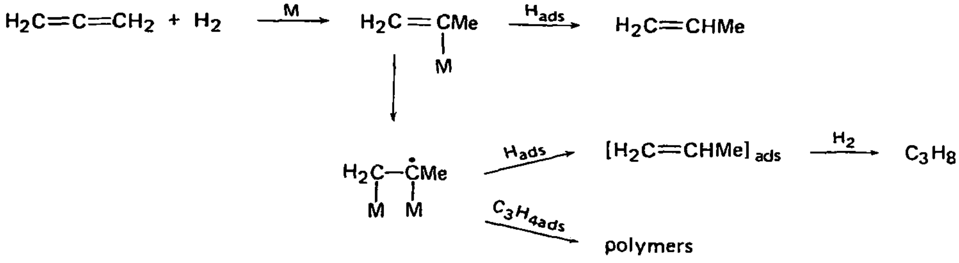


SCHEME 20.

balance between possible routes depends on the number and nature of the substituents. **88** is the result of electrophilic attack of ozone on the central carbon. Ozonide **89** is the intermediate for normal oxidative rupture, but here oxygen is lost to give the stabilized zwitterion **90**. The products shown may undergo further reactions.

XII. OTHER REACTIONS OF ALLENES

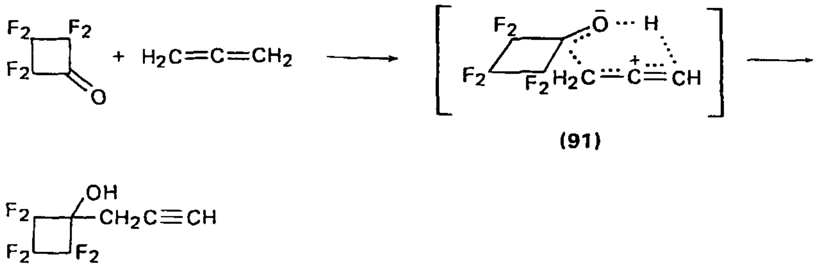
The hydrogenation of allene over a range of transition-metal catalysts is first order in hydrogen and zero order in allene[200]. Over the temperature range 20–200°C apparent activation energies are from 12–75 kJ depending on catalyst. Products are propene, propane and allene polymer, and the propene/propane ratio varies with conditions and catalyst used, nickel for example giving very little propane. Scheme 21 is proposed. σ-Allyl intermediates are postulated when molybdenum sulphide is



SCHEME 21.

the catalyst[201]. The kinetics of reduction of allene in deuterium oxide catalysed by the enzyme azotobacter nitrogenease have been studied[202].

Using primary and secondary deuterium isotope effects Dolbier and Dai[203] have shown that the Ene reaction between allene and perfluorocyclobutanone probably proceeds by a concerted mechanism involving the dipolar intermediate **91** (equation 50).



(91)

(50)

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The Chemistry of Ketenes, Allenes and Related Compounds
Edited by Saul Patai

CHAPTER 10

Organometallic derivatives of allenes and ketenes

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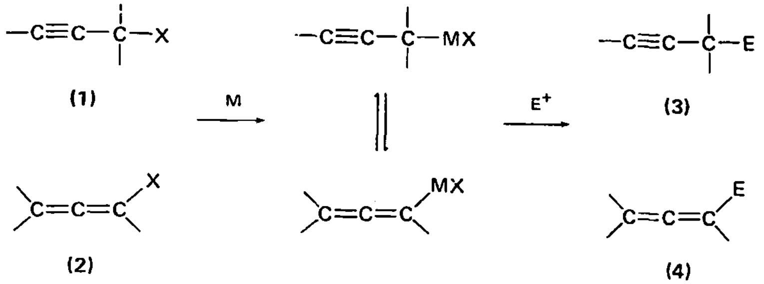
I. INTRODUCTION

In this chapter we shall limit our treatment to organometallics in which the metal is directly attached to the allenic or ketenic carbon atom. Organometallics derived from ketenes, which are rare and mainly restricted to elements of Group IVb, will be discussed at the end of this review. On the other hand, we also shall include in this chapter some reactions of functionalized allenic organometallics like ethers and thio ethers.

Organometallics of allenic structure are principally prepared either by the reaction of metals with propargylic or allenic halides, or by metalation with alkyllithiums of the corresponding hydrocarbons. These organometallics can exist in two



SCHEME 1.

mesomeric forms in equilibrium; they generally show great reactivity towards electrophiles and the resulting products are frequently mixtures of allenic and propargylic compounds (Scheme 1). Thus, the conversion of bromides 1 or 2 into compounds 3 or 4 can be made without any propargylic transposition or by one or two propargylic transpositions. To explain these phenomena, the term 'propargylic transposition' or rearrangement has been introduced simultaneously by Prévost and coworkers[1] and by Wotiz[2], in 1950.

II. ALLENIC AND PROPARGYLIC DERIVATIVES OF MAGNESIUM, ZINC AND ALUMINIUM

A. Preparation

1. Organomagnesium compounds

The preparation of Grignard derivatives from propargylic halides was at first very difficult and dimerization was often observed[8,9]. Only tertiary halides which had no hydrogen atoms on the α carbons, e.g. t-BuC≡CR^{1}R^{2}Br, were easily converted into organomagnesium compounds[6,7].

The first preparation of a Grignard reagent from a primary propargylic bromide was reported in 1949[10]. The preparation used a *cyclic reactor*[2,11] which achieved high dilution without the need for large volumes of ether, owing to the recycling of the latter. Using this method, primary bromides were converted in good yields[2,12], propargyl bromide and secondary bromides in ordinary yields[13,14] and tertiary bromides in poor yields[14].

Simultaneously, some more conventional techniques were developed for the preparation of these organometallics:

(i) The preparation of a Grignard reagent from γ-phenylpropargyl bromide was described for the first time by Lappin[15]. The procedure used a large dilution (350 ml of ether per 0.12 mole of bromide) and slow addition of the halide (4 h); the yield in magnesium derivative is about 92%.

(ii) The first preparation of allenylmagnesium bromide was realized by Prévost and coworkers[1]. This Grignard reagent was obtained by dropwise addition of diluted propargyl bromide (600 ml of ether per mole of bromide) to magnesium amalgamated by mercury chloride; the presence of the latter is important but its role is not well understood.

This last procedure has been extended to substituted primary and secondary bromides[3,16,17], but in these preparations the yields decrease and sometimes it is more advantageous to replace magnesium by zinc.

The influence of the solvent has been studied. Substitution of ether by THF gives mixtures of dimeric hydrocarbons[18,19]; to obtain the allenylmagnesium bromide in THF, one must add the propargyl bromide very slowly at −22 to −25°C to magnesium amalgamated by mercury chloride; in these conditions, the yield reaches up to 67%[20]. The allenylmagnesium bromide can also be obtained in THF from bromoallene[5].

Tertiary propargylic bromides (5) and their allenic isomers (6) yield, under reflux in ether, the same organometallics of mainly allenic structure 7 as shown by infrared spectrography[21,22].

$$\begin{array}{c} R^1R^2CBrC{\equiv}CH \\ (5) \\ R^1R^2C{=}C{=}CHBr \\ (6) \end{array} \xrightarrow[\text{ether, reflux}]{\text{Mg}} \begin{array}{c} R^1R^2C{=}C{=}CHMgBr \\ (7) \end{array} \qquad (1)$$

THF is necessary if tertiary propargylic chlorides are used[23]. Vinylogous propargylic halides give vinylallenic organomagnesium compounds[24,25].

Finally, by analogy with the preparation of allenic lithiums (see Section III.A), the 1,4-addition of Grignard reagents to conjugated enynes affords a mixture of hydrocarbons through the intermediate of an organomagnesium derivative (equation 2)[26]. This method has been applied to different types of enynes but gives poor yields[27,28].

$$EtC{\equiv}CCH{=}CH_2 \xrightarrow[\text{2. } H_2O]{\text{1. RMgX}} EtC{\equiv}CCH_2CH_2R + EtCH{=}C{=}CHCH_2R \qquad (2)$$

2. Organo-zinc and -aluminium compounds

Gaudemar was the first to prepare from propargyl bromide some solvated organozinc and organoaluminium compounds with allenic structures[17,29,30]. These reagents have been frequently used in many syntheses.

Allenylzinc bromide is prepared in good yields by addition of propargyl bromide in THF to very fine turnings of zinc; the temperature must be maintained at about −10°C during the preparation. Allenylaluminium bromide is prepared in ether or THF by addition of a solution of propargyl bromide to aluminium chips amalgamated with mercury chloride, under reflux of the solvent.

3. Stability

Allenyl-magnesium, -zinc and, to a lesser degree, -aluminium bromides cannot be stored. They must be used as soon as they have been prepared, since they undergo complicated and irreversible reactions at room temperature[17,31].

The organomagnesium reagent is a simple case. It yields at room temperature a mixture of propynylmagnesium bromide (8) and of organodimagnesium bromide (9)[17].

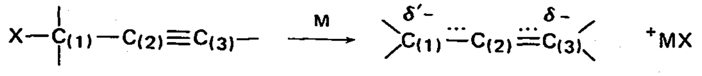
$$\begin{array}{cc} CH_3C{\equiv}CMgBr & BrMgCH_2C{\equiv}CMgBr \\ (8) & (9) \end{array}$$

Infrared spectrography confirmed this interpretation. The absorption at 2076 cm^{-1} is characteristic of 8 and the absorption at 1936 cm^{-1} is characteristic of 9. The wave number (1936 cm^{-1}) justified the structure 9, the presence of two magnesium atoms lowering this wavenumber considerably; this structure has also been proposed by Jacobs[46].

B. Structure

1. *Infrared studies*

Prévost, Gaudemar and coworkers[3,4] have contributed significantly to the structural analysis of organometallics obtained from α-acetylenic bromides, by means of infrared spectroscopy. These authors postulate the formation of a carbanionic intermediate when the halide gives the organometallic compound (equation 3). The charge density on carbons $C_{(1)}$ and $C_{(3)}$ and the steric hindrance in the neighbourhood of these poles determine the place where the ^{+}MX moiety will be attached. Thus in the case of propargyl bromide $\delta \gg \delta'$ and the steric hindrance is negligible at both poles, so that ^{+}MX will settle mainly the carbon atom $C_{(1)}$ and organometallics obtained will have essentially, but not exclusively, an allenic structure.



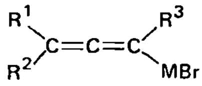
(3)

In the same way it can be explained that allenic organometallics RHC=C=CHMBr and R^1R^2C=C=CHMBr are obtained from bromides RCHBrC≡CH and R^1R^2 CBrC≡CH, while the mesitylpropargylzinc bromide ($\nu_{C\equiv C} = 2175$ cm^{-1} [32]) is obtained from mesitylpropargyl bromide, and an equilibrium between allenic and acetylenic forms results when the starting bromide is RC≡CCH$_2$Br or ArC≡CCH$_2$Br.

Moreover, this theory is bolstered by the fact that the organomagnesium derivative prepared from bromoallene has the same structure and reactivity as the organomagnesium compound prepared from propargyl bromide[5]; it fits also the results with substituted bromoallenes 6[22,33].

Some infrared data are assembled in Tables 1 and 2. Grignard derivatives of

TABLE 1. Wave number [ν_{as}(>C=C=C<), cm^{-1}] of some allenic organometallics:



				Solvent			
R¹	R²	R³	M	Ether	THF	THF + HMPA	Reference
H	H	H	Mg	1885[a]			34
H	Me	H	Mg	1892			37
H	*n*-Pr	H	Mg	1891			34
Me	Me	H	Mg	1905			21
H	Me	Ph	Mg	1891			34
H	H	H	Zn		1909	1900	35
H	Me	H	Zn		1913	1906	35
H	*n*-Pr	H	Zn		1915	1908	37
H	*i*-Pr	H	Zn		1904		36
H	Me	Ph	Zn		1908		36
H	H	H	Al	1920	1918	1912	20

[a] In THF, from BrCH$_2$C≡CH: ν_{as}(>C=C=C<) = 1874 cm^{-1} [20];
in THF, from H$_2$C=C=CHBr: ν_{as}(>C=C=C<) = 1865 cm^{-1} [5].

TABLE 2. Wave numbers (cm^{-1}) of allenic and propargylic organometallics from bromides of type $RC{\equiv}CCH_2Br$

R	M	Solvent	$\nu_{as}(>C=C=C<)$	$\nu(-C{\equiv}C-)$	Reference
Me	Mg	Ether	1891	2187	37
Et	Mg	Ether	1888	2183	34
n-Pr	Mg	Ether	1891	2189	34
n-Bu	Mg	Ether	1890	2179	37
n-Pe	Mg	Ether	1889	2183	34
Ph	Mg	Ether	1887	2159	34
Me	Zn	THF	1912	2206	37
Et	Zn	THF	1911	2199	37
n-Pr	Zn	THF	1911	2205	36
n-Pe	Zn	THF	1911	2201	37
Ph	Zn	THF	1900	2180	31

conjugated halogeno enynes in ether are also in the allenic form[25]

$$\left[\nu_{as}\left(>C=C=C<\right) = 1875\text{–}1880\ \text{cm}^{-1}\right].$$

The organocadmium compound prepared from propargyl bromide in HMPA[38] also has an allenic structure

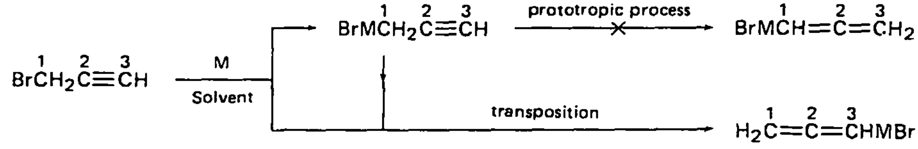
$$\left[\nu_{as}\left(>C=C=C<\right) = 1902\ \text{cm}^{-1}\,{}^{20}\right].$$

In the preparation of this reagent there is strong competition by Wurtz's reaction; its reactivity is low and it has not been widely studied for this reason[20].

2. *Nuclear magnetic resonance studies*

The n.m.r. spectra of the organometallics formed from propargyl bromide (magnesium, zinc, aluminium) are of type A_2B and confirm their allenic structures[39,40]; Table 3 shows various n.m.r. parameters.

Couffignal has studied the formation of these organometallics[40]; the process can be represented by Scheme 2. The use of deuterated propargyl bromide $BrCH_2C{\equiv}CD$



SCHEME 2.

has eliminated the possible prototropic process; indeed n.m.r. spectra of organometallics (M = Mg, Zn, $Al_{2/3}$) which derive from this deuterated bromide present an A_2 system (see Table 3) in agreement with the structure $H_2C{=}C{=}CDMBr$. Therefore, these result from a propargylic transposition either during or after the attack

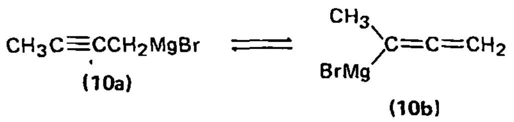
TABLE 3. ^{1}H-n.m.r. parameters of allenic organometallics (solution about 1.7 M)[40], values in Hz; external reference: TMS in CCl_4

Organometallic	Solvent	System	$\nu_A = \delta_{=CH_2}$	$\nu_B = \delta_{-CH=}$	$\Delta\nu = \nu_A - \nu_B$	J
$H_2C{=}C{=}CHMgBr$	Ether	A_2B	174.3	257.5	83	7.2
$H_2C{=}C{=}CHZnBr$	THF	A_2B	270.7	273	2.3	1.1
$H_2C{=}C{=}CHAl_{2/3}Br$	Ether	A_2B^a	219.4 227.6	268.4 269.6	48 42	7.5
$H_2C{=}C{=}CDMgBr$	Ether	A_2	177			
$H_2C{=}C{=}CDZnBr$	THF	A_2	272			
$H_2C{=}C{=}CDAl_{2/3}Br$	Ether	$A_2{}^a$	218 226			

[a] Two A_2B systems are superposed.

of the metal. Such a mechanism was also demonstrated for propargylic tin derivatives[41].

We believe that allenic organometallics are in fact a fast equilibrium mixture of allenic and acetylenic forms. The fact that the n.m.r. spectrum of the Grignard reagent from 1-bromo-2-butyne presents only one form[39] corroborates this hypothesis. This form would be the resultant of a rapid equilibrium between the propargylic organometallic **10a** and the allenic organometallic **10b** both observed in



$$\mathrm{CH_3C{\equiv}CCH_2MgBr} \rightleftharpoons \mathrm{(CH_3)(BrMg)C{=}C{=}CH_2} \qquad (4)$$

(10a) (10b)

infrared spectroscopy. Such an equilibrium has been unambiguously demonstrated in allylic series[42–44].

3. *Existence of propargylmagnesium bromide*

We have seen that organometallics from propargyl bromide are essentially in the allenic form. However, from the evidence of infrared and n.m.r. analyses, one cannot exclude the presence of a minor proportion of the acetylenic form. In a recent work[45], we have demonstrated the existence of propargylmagnesium bromide **11a** in a rapid equilibrium with the allenylmagnesium bromide **11b**, the latter being preponderant.

$$\underset{(11a)}{\mathrm{HC{\equiv}CCH_2MgBr}} \rightleftharpoons \underset{(11b)}{\mathrm{BrMgCH{=}C{=}CH_2}} \qquad (5)$$

It is known that organomagnesium derivative from propargyl bromide isomerize, (i) partly to give the organomagnesium from propyne when standing at room temperature, and (ii) chiefly to yield propynylmagnesium bromide in the presence of a primary or secondary amine (see Section II.C). According to the latter result the isomerization seems to be governed by the presence in the mixture of a compound having a slightly acid hydrogen atom, leading to the equilibrium shown by equation (5). The overall process, when starting from propargyl bromide is explained by Scheme (3).

$$\text{(a)}\quad \mathbf{11a} \rightleftharpoons \mathbf{(11b)}$$

$$\text{(b)}\quad H_2C{=}C{=}CHMgBr + HC{\equiv}CCH_2MgBr \longrightarrow BrMgC{\equiv}CCH_2MgBr + \begin{cases} CH_3C{\equiv}CH \\ H_2C{=}C{=}CH_2 \end{cases}$$

$$\text{(c)}\quad CH_3C{\equiv}CH + H_2C{=}C{=}CHMgBr \longrightarrow CH_3C{\equiv}CMgBr + \begin{cases} CH_3C{\equiv}CH \\ H_2C{=}C{=}CH_2 \end{cases}$$

SCHEME 3.

Moreover, if we start from deuterated propargyl bromide, we have to expect the equilibrium as shown in equation (6) and the reaction with an alkylmagnesium

$$H_2C{=}C{=}CDMgBr \rightleftharpoons BrMgCH_2C{\equiv}CD \qquad (6)$$

bromide must eliminate the deuterium atom. Indeed, the subsequent condensation with propanone gives only the diol $(CH_3)_2C(OH)C{\equiv}CCH_2C(OH)(CH_3)_2$ which contains no deuterium[45].

C. Reactivity

1. *Hydrolysis*

This generally leads to mixtures of hydrocarbons in variable proportions[1,12,15,16,23,33]; for instance, the allenylmagnesium bromide gives a 4/1 mixture of allenic/acetylenic products[47]. In the case of organomagnesium from tertiary α-

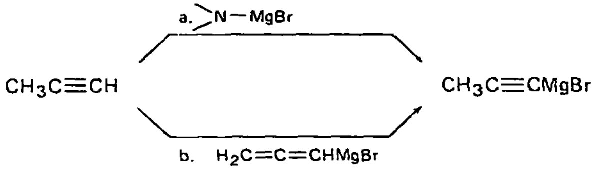
$$R^1HC{=}CR^2CR^3{=}C{=}CHMgX \xrightarrow{H_2O} R^1HC{=}CR^2CR^3{=}C{=}CH_2 \qquad (7)$$

acetylenic bromides, the hydrolysis yields only the allenic hydrocarbons[49]; the same is true for vinylallenic organomagnesium halides which give uniquely vinylallenes in moderate yields[25] (equation 7).

2. *Action of primary and secondary amines*

In the presence of about 10% of primary or secondary amines (aniline, diethylamine, piperidine, etc.) allenylmagnesium bromide isomerizes quickly according to equations (8) and (9)[45].

(8)



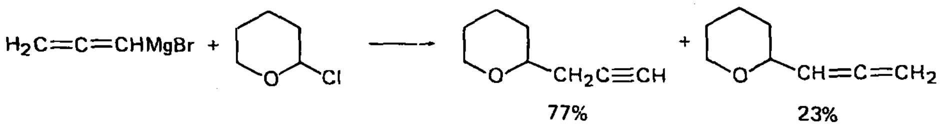
(9)

The propynylmagnesium bromide (equation 9) has been characterized by infrared spectroscopy and by the 1-phenyl-2-butyn-1-ol obtained after condensation with benzaldehyde (yield = 54%). We also found that the addition of 10% 1-hexyne to allenylmagnesium bromide was responsible for a less rapid but analogous isomeric change[48]. This method is an original route to organomagnesiums from terminal alkynes. Thus $BrMgC\equiv CEt$ and $BrMgC\equiv CBu$ are prepared from allenic organomagnesiums $MeHC{=}C{=}CHMgBr$ and $PrHC{=}C{=}CHMgBr$.

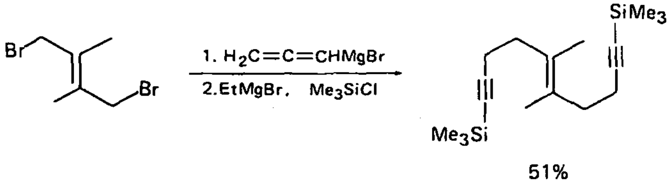
Under the action of primary and secondary amines, allenyl-zinc and -aluminium bromide undergo very complex transformations, still unexplained[45,86].

3. *Alkylation, substitution of halogens*

Simple alkyl halides do not react; however, butyl sulphate reacted with allenylmagnesium bromide to yield a 1-heptyne and butylallene mixture[50]; with allyl halides, mixtures were also isolated[18,19] which were richer in allenic constituents in presence of Cu_2Cl_2[51], while in the two next examples the acetylenic ones predominated (equations 10 and 11).



(Ref. 52) (10)

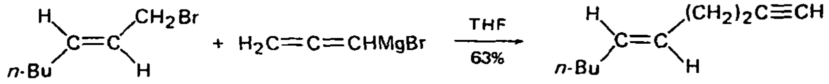


(Ref. 53) (11)

Likewise, the introduction of the propargyl form is important in reactions between allenylmagnesium bromide and *trans*-1-bromo-2-hexene[54] or geranyl bromide[55].

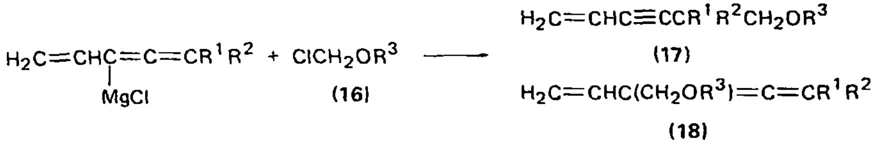
A synthesis of the pink bollworm sex pheromone has been described recently in detail, employing the coupling of allenylmagnesium bromide with halides **12** and **13** as the key reaction[56]. The adducts **14** and **15** contain a small amount of allenic impurities.

$$\underset{(12)}{n\text{-BuC}\equiv\text{CCH}_2\text{Br}} + \text{H}_2\text{C}{=}\text{C}{=}\text{CHMgBr} \xrightarrow[79\%]{\text{THF}} \underset{(14)}{n\text{-BuC}\equiv\text{C(CH}_2)_2\text{C}\equiv\text{CH}} \qquad (12)$$



(13) (15) (13)

With chloro ethers (**16**) vinylallenic magnesium compounds give a mixture of ethers **17** and **18** (equation 14)[57]; 17:18 = 3.

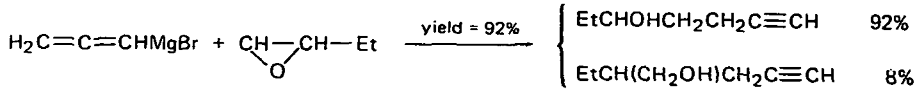


$$\underset{(16)}{\text{H}_2\text{C}{=}\text{CH}\underset{\substack{|\\ \text{MgCl}}}{\text{C}}{=}\text{C}{=}\text{CR}^1\text{R}^2 + \text{ClCH}_2\text{OR}^3} \longrightarrow \begin{array}{c}\text{H}_2\text{C}{=}\text{CHC}\equiv\text{CCR}^1\text{R}^2\text{CH}_2\text{OR}^3\\ (17)\\ \text{H}_2\text{C}{=}\text{CHC(CH}_2\text{OR}^3){=}\text{C}{=}\text{CR}^1\text{R}^2\\ (18)\end{array} \qquad (14)$$

Finally, acetylenic bromoethers $RCHBrCH(OEt)CH_2C{\equiv}CH$ are principally obtained from $EtOCHBrCRBr$[18,58].

4. Action of epoxides

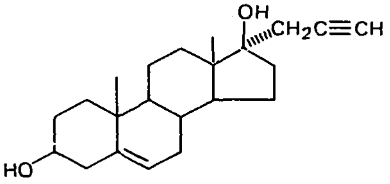
The treatment of allenylaluminium with ethylene oxide gives 2-bromoethanol (yield = 32–50%)[18], while the organomagnesium bromide reacts with 1,2-epoxybutane according to equation (15)[48].



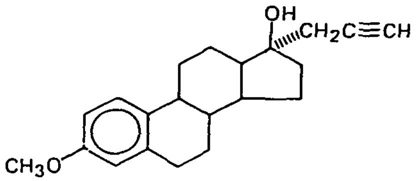
(15)

5. Action of carbonyl compounds

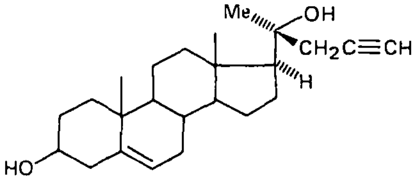
The reaction with carbonyl compounds has been extensively studied; the Reformatsky reaction with zinc has been very much used. It often gives mixtures of β-acetylenic and α-allenic alcohols[59–71], sometimes contaminated with by-products. The stereospecific syntheses in the steroid series of 17-α-propargyl-5-androstene-3β,17β-diol (**19**), 3-methoxy-17α-propargyl-1,3,5(10)-oestratrien-17β-ol (**20**)[67] and (20*S*)-propargyl-5-pregnene-3β,20-diol (**21**)[71] should also be mentioned. Carrying out the reaction in two separate steps (preparation of the intermediary organometallic, then condensation with the carbonyl compound), results in a substantial increase in yield, and also permits a more elaborate study.



(19)

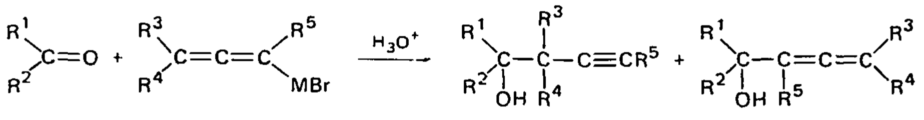


(20)



(21)

a. Organometallics of mainly allenic structure. These organometallics give mainly the transposed β-acetylenic alcohol 22 with good yields[1,3–5,17,20,21,24,31,35,57,72–83]. Using organoaluminium compounds, this alcohol was obtained practically



(22) (23)

TABLE 4. Influence of solvent on the proportions of allenic alcohol produced by organozinc synthesis[20]

$$H_2C{=}C{=}CHZnBr \xrightarrow[2.\ H_3O^+]{1.\ (i\text{-}Pr)_2CO} (i\text{-}Pr)_2C(OH)CH_2C{\equiv}CH + (i\text{-}Pr)_2C(OH)CH{=}C{=}CH_2$$

Solvent	Allenic alcohol (% in the mixture)
Dioxane	23
THF	36
1,2-Dimethoxyethane	38
THF + Dimethylformamide	45
Dimethylsulphoxide	45
THF + HMPA	56
HMPA	58
THF + LiBr	63
THF + HMPA + LiBr	78

pure[17,20,29,72-77]; while with organomagnesium derivatives, some of the allenic isomer **23** was obtained when the carbonyl compound was hindered, e.g. the mixture of isolated alcohols by condensation of allenylmagnesium bromide with 2,2,4,4-tetramethyl-3-pentanone contained 20% of allenic alcohol $(t\text{-Bu})_2C(OH)\text{-}CH{=}C{=}CH_2$ [20].

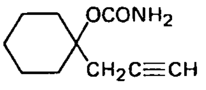
The allenic isomer **22** was principally observed with organozinc reagents[3,17,20,31,82]. The proportion of this isomer increased with the solvating strength of solvent (Table 4) and with the decrease of the electrophilic character of the carbonyl carbon atom (Table 5)[20]; the influence of the presence of LiBr was also noteworthy (Table 4).

Several propargyl carbinols have been prepared by these methods in order to study their parmacological activity. An interesting hypnotic activity has been observed particularly with 1-propargylcyclohexan-1-ol carbamate **24**[72] and with trichloromethyl propargyl carbinols **25**[75].

TABLE 5. Influence of carbonyl compounds on the proportion of allenic alcohol produced in the following reaction[20]:

$$R^1R^2CO + CH_2{=}C{=}CHZnBr \xrightarrow{\text{THF + HMPA}} R^1R^2C(OH)CH_2C{\equiv}CH + R^1R^2C(OH)CH{=}C{=}CH_2$$

R^1	R^2	Allenic alcohol (% in the mixture)
CCl_3	H	0
Me	H	<5
Pr	H	5
Me	Me	12
t-Bu	Me	20
Et	Et	25
i-Pr	*i*-Pr	56
Ph	H	7
Ph	Me	14
Ph	Ph	52



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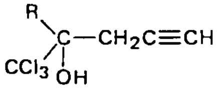
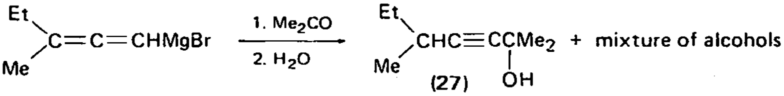


(25)

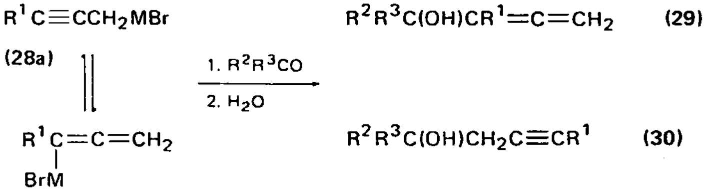
However, we have noted an anomaly; while Pasternak obtained the β-acetylenic alcohol 26 in 50% yield according to equation (16)[21], a recent work[33] on an analogous organomagnesium derivative furnished a mixture of alcohols where the β-acetylenic compound normally expected was absent, the alcohol 27 being the principal product (equation 17).

$$(CH_3)_2C{=}C{=}CHMgBr \xrightarrow[2.\ H_2O]{1.\ CH_3CHO} \underset{(26)}{CH_3CHOHC(CH_3)_2C{\equiv}CH} \qquad (16)$$



(27) (17)

b. Organometallics existing in both allenic and acetylenic forms. We have already seen that the organometallics from primary bromides of type $RC{\equiv}CCH_2Br$ are present as a rapid equilibrium mixture of forms 28a and 28b. Subsequent condensation with aldehydes or ketones gives mixtures of alcohols 29 and 30[3,32] (equation 18).



(28a) (28b) (29) (30) (18)

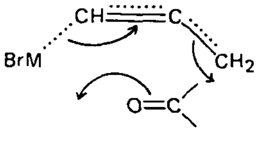
$$R^1C{\equiv}CCH_2MBr \rightleftharpoons R^1C(BrM){=}C{=}CH_2 \xrightarrow[2.\ H_2O]{1.\ R^2R^3CO} R^2R^3C(OH)CR^1{=}C{=}CH_2 + R^2R^3C(OH)CH_2C{\equiv}CR^1$$

Work in our laboratory[83] has showed that organozinc condensations are near-quantitative. For that reason, they are more advantageous than organomagnesium condensations which are limited by a concurrent Würtz reaction during the preparation of the organometallic derivative. This confirmed the advantage of zinc over magnesium observed previously by Gaudemar[31,74]. The proportions of isomers 29 and 30 depend chiefly of the structure of carbonyl compound; bulkiness in the latter favours the formation of β-acetylenic alcohol 30 (Table 6).

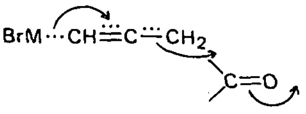
TABLE 6. Proportions of alcohols 29 and 30 by organozinc synthesis according to equation (18)[83]

R^1	R^2	R^3	Total yield (%) (29 + 30)	Acetylenic alcohol (30) (% of the mixture)
Me	Me	Me	95	25
Et	Me	Me	98	65
Et	Et	Et	96	54
Et	*i*-Pr	*i*-Pr	88	96
Et	Me	*i*-Bu	95	65
n-Bu	Et	Et	96	53
n-Pe	*i*-Pr	*i*-Pr	91	95

c. Processes of formation of alcohols. Since the β-acetylenic alcohol 22 is the main product obtained from allenic organometallics, it is currently assumed that it results from a reversing of the structure of the organometallic either by means of a six-centre electronic transfer (S_Ei' process)[3,4,17] or by electrophilic attack of the carbonyl carbon on the organometallic (S_E2' process)[84].

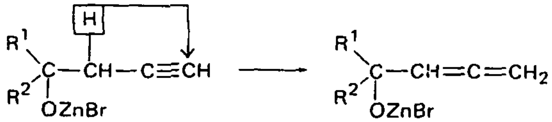


S_Ei' process

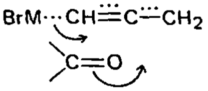


S_E2' process

The allenic alcohol 23, obtained sometimes in low quantities, could be the result of a prototropic migration in the alcoholate under the influence of the zinc salts present in the reaction mixture[17,32,82] (equation 19).

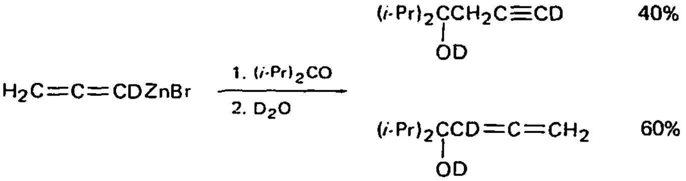


(19)



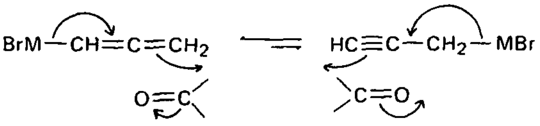
S_E2 process

Although it was observed in a special case (presence of HMPA and prolonged heating of the reaction mixture)[85,86], the possibility of such prototropic migration in the alcoholate was recently eliminated by the result shown in equaticn (20)[35,86],



$$H_2C{=}C{=}CDZnBr \xrightarrow[2.\ D_2O]{1.\ (i\text{-}Pr)_2CO} \begin{cases} (i\text{-}Pr)_2C(OD)CH_2C{\equiv}CD & 40\% \\ (i\text{-}Pr)_2C(OD)CD{=}C{=}CH_2 & 60\% \end{cases} \qquad (20)$$

Consequently S_E2 and S_E2' processes remained to explain the formation of allenic alcohol. Although the possibility of an S_E2 process cannot be excluded, we think now that both the α-allenic and the β-acetylenic alcohol arise from an S_E2' process, and involve an equilibrium between the two forms of the organometallic derivative (equation 21).



(21)

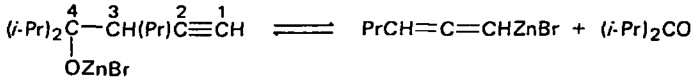
The results of Felkin and coworkers in the allylic series[87], the fact that the organozinc derivative of mesitylpropargyl bromide does not condense with acetone[82], and work in our laboratory all agree with this scheme. Analogous mechanisms could be envisaged for homologous organometallics.

d. Reversibility. We reported that condensations between organozincs from α-acetylenic bromides and ketones were reversible[35,83]. This was notably proved by experiences summerized in Schemes 4 and 5.

In Scheme 4, a β-acetylenic alcoholate (31) is formed by treatment of a β-acetylenic alcohol with an excess of allenylzinc bromide. First, the infrared absorption

$$\nu_{as}\ (>C=C=C<)$$

characteristic of the organometallic disappears and an absorption assigned to diisopropylketone appears at 1712 cm^{-1}; the intensity of the latter increases with time. After five days, one equivalent of allenylzinc bromide is added to the reaction mixture which is left standing for 8 days at room temperature. Two facts prove the regression of the preformed zinc alcoholate (31) to its precursors:

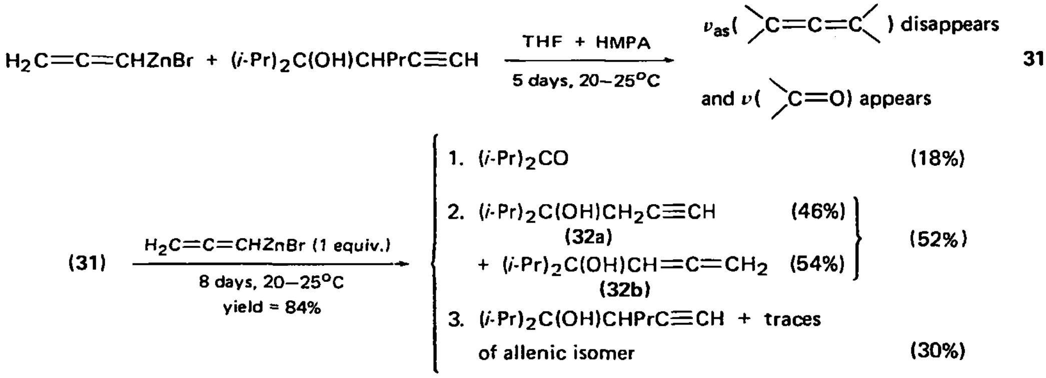


$$(i\text{-Pr})_2\underset{\substack{|\\ OZnBr}}{\overset{4}{C}}-\overset{3}{C}H(Pr)\overset{2}{C}\equiv\overset{1}{C}H \rightleftharpoons PrCH=C=CHZnBr + (i\text{-Pr})_2CO \qquad (22)$$

(31)

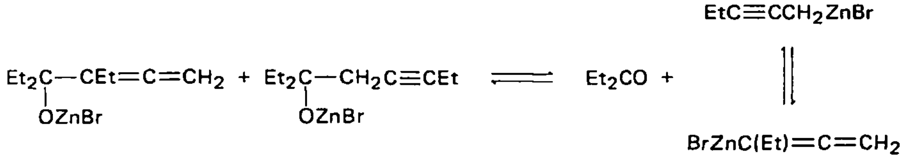
(i) A little diisopropylketone is isolated after hydrolysis. Also infrared spectroscopy reveals that this ketone is in the free state in the reaction mixture; this confirms the $C_{(3)}-C_{(4)}$ rupture.

(ii) The liberated diisopropylketone reacts with the added allenylzinc bromide to give a mixture of alcohols **32a** and **32b**.



SCHEME 4.

In Scheme 5, a mixture of α-allenic (46%) and β-acetylenic (54%) alcohols reacts with an excess of organozinc formed from ethyl bromoacetate; hydrolysis is carried out after 50 h at 50°C. The formation of the hydroxy ester **33** can be interpreted only by a regression of preformed zinc alcoholates to their precursors (equation 23). In this example, it also appears that the α-allenic alcoholate is less stable than



$$Et_2\underset{\substack{|\\ OZnBr}}{C}-CEt=C=CH_2 + Et_2\underset{\substack{|\\ OZnBr}}{C}-CH_2C\equiv CEt \rightleftharpoons Et_2CO + \begin{matrix}EtC\equiv CCH_2ZnBr\\ \Updownarrow\\ BrZnC(Et)=C=CH_2\end{matrix} \qquad (23)$$

the β-acetylenic alcoholate; it is reasonable to think that this last is the thermodynamically more stable compound because the steric stresses are lower.

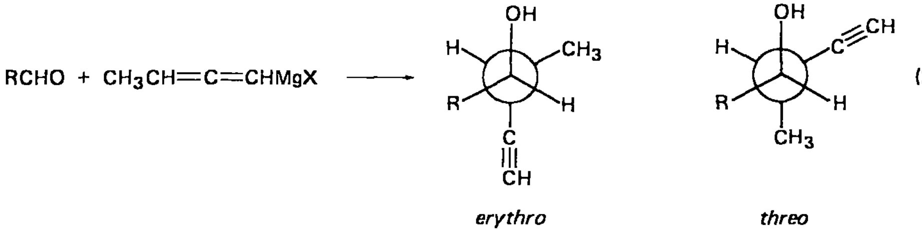
$$\underset{46\%}{\mathrm{Et_2C(OH)CEt{=}C{=}CH_2}} + \underset{54\%}{\mathrm{Et_2C(OH)CH_2C{\equiv}CEt}} \xrightarrow[\substack{\text{50 h, 50°C} \\ \text{yield} \simeq 90\%}]{\mathrm{BrZnCH_2CO_2Et\ (excess)}} \left[\begin{array}{ll} \mathrm{Et_2C(OH)CEt{=}C{=}CH_2} & (20\%) \\ \mathrm{Et_2C(OH)CH_2C{\equiv}CEt} & (68\%) \\ \mathrm{Et_2C(OH)CH_2CO_2Et} & (12\%) \end{array}\right.$$

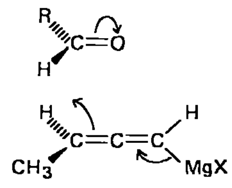
(33)

SCHEME 5.

e. Stereochemistry. Chodkiewicz and coworkers have made an important study of stereochemistry of condensations between allenic organometallics and some carbonyl groups in aldehydes, ketones, α-methoxylated ketones, terpenic ketones, cyclanones and quinones[88-105].

(*i*) Aliphatic aldehydes and aromatic carbonyl compounds. The reaction of aldehydes with 1,2-butadienylmagnesium halides has been carried out[88,89]. The *threo* : *erythro* product ratio depends on the size of the substituent group of the





(34)

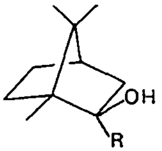
TABLE 7. *Threo:erythro* ratios according to equation (24)[89]

R	X	*Threo:erythro*
Me	Cl	70:30
Me	Br	76:24
Me	Br	56:44[a]
Et	Br	82:18
i-Pr	Br	90:10
t-Bu	Br	95:5

[a]Using the organoaluminium bromide.

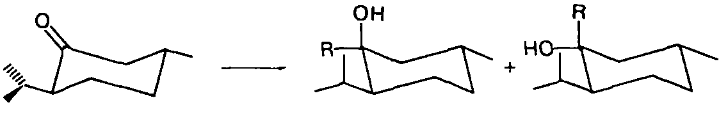
aldehyde (Table 7). The transition state 34 (S_E2' mechanism) permits a rationalization of the results. An apparent anomaly is observed: no stereoselectivity has been observed with benzaldehyde whereas the stereoselectivity of acetophenone was comparable to that of acetaldehyde.

(*ii*) Terpenic ketones. With (+)-camphor, allenyl-magnesium and -aluminium bromides gave exclusively the product 35 (R = $CH_2C{\equiv}CH$)[90].

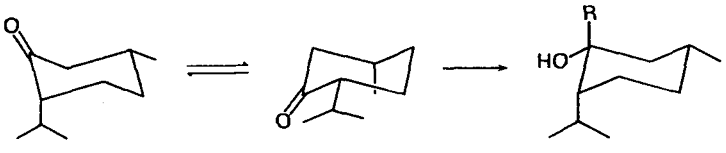


(35)

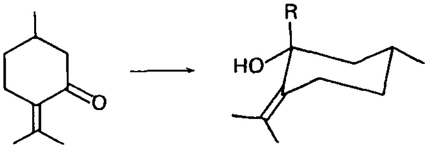
Allenylaluminium bromide reacts with (−)-menthone (36), (+)-isomenthone (37) and (+)-pulegone (38) to give in very good yields the alcohols 39 and 40, 41, 42 (R = $CH_2C{\equiv}CH$)[91], respectively. The stereochemistry of the addition was assumed to be a function of steric factors for menthone and isomenthone; stereoelectronic control was suggested as an essential factor of the condensation with pulegone.



(36) (39) 95% (40) 5% (25)

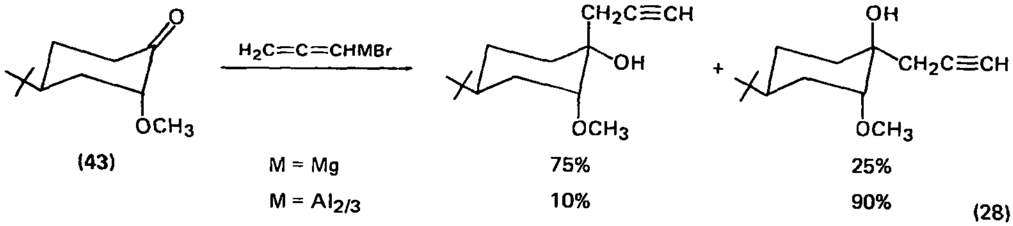


(37) (41) 100% (26)

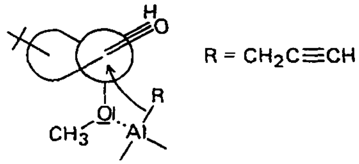


(38) (42) 100% (27)

(*iii*) α-Methoxylated ketones. Many studies have been carried out with different ketones[92–98]. *Cis*- and *trans*-4-*t*-butyl-2-methoxycyclohexanone have allowed the rationalization of the observed phenomena[98]. The *cis* cyclohexanone undergoes equatorial attack by the propargylic group whereas with the *trans* cyclanone (43), a spectacular inversion is observed when aluminium is substituted by magnesium (equation 28). The axial entering of the magnesium compound is justified by the



steric requirements of the methoxyl group. A favourable interaction between the metal of the organometallic derivative and the methoxyl group explains the equatorial attack according to transition state 44. In support of this hypothesis, the specificity of the attack is reduced in a more complexing solvent[98].



(44)

(*iv*) Substituted cyclanones. Diversely substituted cyclanones lead generally to mixtures of alcohols[72,99–106]. When the steric effect is important, it could determine the orientation of the reaction[105]. In the case of 4-*t*-butylcyclohexanone[48], Pearson's hard and soft acid and base (HSAB) principle rationalized the results. Axial attack by the organometallic compound increased with the hardness of the metal, while bulkiness favoured equatorial entry of the propargylic group (equation 29) (Table 8).

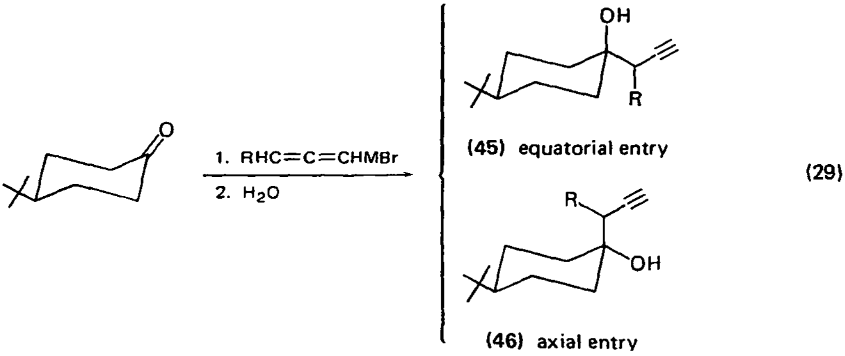
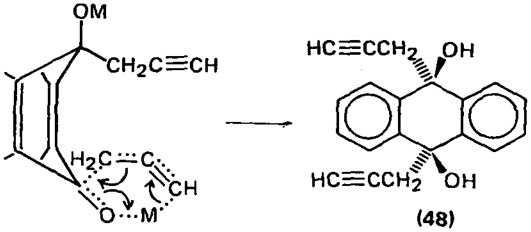


TABLE 8. Respective proportions of 45 and 46 according to equation (29)[48]

R	M	Yield (%)	45:46 (% in the mixture)
H	Mg	88	52:48
H	$Al_{2/3}$	85	70:30
H	Zn	83	79:21
Me	Mg	90	75:25
Me	$Al_{2/3}$	89	90:10
Me	Zn	92	88:12

(*v*) Quinones. The reaction has been studied with quinones[18,107-109]. Anthraquinone yields a mixture of *cis* and *trans* diquinols (*cis*:*trans* ratio = 3). The favoured transition state **47** leads preferentially to the *cis* diquinol **48**.

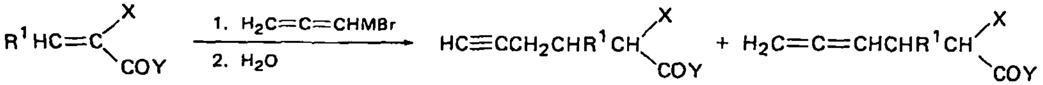


(47) (48) (30)

6. *Action of functional α-unsaturated compounds*

With α-ethylenic ketones, allenyl-magnesium[110,111] and -zinc[86,110] bromides and vinylallenic organomagnesium reagents[112,113] gave only products of 1,2-addition. The same is true for magnesium[68,114,115], zinc[116] and aluminium[68,114,115] compounds from propargyl bromide with aldehydes or α-acetylenic ketones, allenylmagnesium bromide with α-allenic ketones[117,118], allenyl- and 1,2-butadienylmagnesium bromides with γ-ether α-acetylenic ketones[119] and allenyl- and 1,2-butadienyl-magnesium or -zinc with α-ethylenic or α-acetylenic aldimines[120]. In all these examples, the main product of 1,2-addition is obtained by transposition of the organometallic derivative.

On the other hand, with alkylidene malonates (49)[110], alkylidene cyanoacetates (50)[121] and *N*-disubstituted α-ethylenic amides (51)[86,122], allenylic organometallics lead to mixtures of acetylenic and allenic products resulting exclusively from 1,4-addition of the organometallic compounds (equation 31). Acetylenic structures are predominant for substrates **49** and **50** whereas amides **51** give mainly allenic products. Moreover, it has been recently shown in our laboratory that the organozinc 1,4-addition complex **52** evolves a cyclopentenone under reflux of the solvent (equation 32)[123].

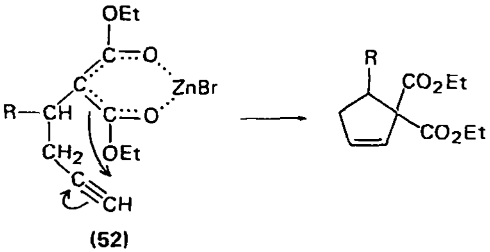


$$R^1HC{=}C(X)COY \xrightarrow[2.\ H_2O]{1.\ H_2C{=}C{=}CHMBr} HC{\equiv}CCH_2CHR^1CH(X)COY + H_2C{=}C{=}CHCHR^1CH(X)COY \qquad (31)$$

(49) X = CO_2Et, Y = OEt

(50) X = CN, Y = OEt

(51) X = H, Y = NR^2_2



(52) (32)

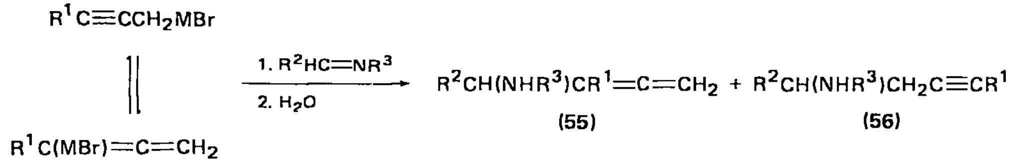
7. *Action of Schiff's bases*

Moreau and Gaudemar have studied in detail the reaction of Schiff's bases with allenic organometallics. Only a few results[124] were known before the publication of their first studies[125].

a. Organometallics of allenic structure. Usually the amine 53 is predominantly obtained (53 was isolated pure when $R^1 = H$ and $M = Al_{2/3}$). In general, substituting a hydrogen atom for the alkyl group R^1, under otherwise identical conditions, increases the percentage of this amine[37].

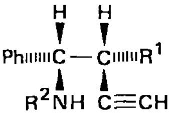
$$R^2HC{=}NR^3 \xrightarrow[2.\ H_2O]{1.\ R^1HC{=}C{=}CHMBr} \underset{(53)}{R^2CH(NHR^3)CHR^1C{\equiv}CH} + \underset{(54)}{R^2CH(NHR^3)CH{=}C{=}CHR^1} \qquad (33)$$

b. Organometallics from bromides $R^1C{\equiv}CCH_2Br$. In this case the condensation furnishes mixtures of β-acetylenic (56) and α-allenic (55) secondary amines, whose ratios depend of the experimental conditions. By fractional distillation one may obtain pure allenic amines (55)[37]. Similar results were reported by Nivert and Miginiac[126]. Allenylzinc bromide reacts similarly with imino ethers PhN=CHOEt to lead, with a low yield, to the expected secondary amine[127].

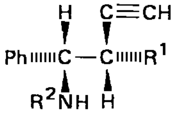


$$\begin{matrix} R^1C{\equiv}CCH_2MBr \\ \| \\ R^1C(MBr){=}C{=}CH_2 \end{matrix} \xrightarrow[2.\ H_2O]{1.\ R^2HC{=}NR^3} \underset{(55)}{R^2CH(NHR^3)CR^1{=}C{=}CH_2} + \underset{(56)}{R^2CH(NHR^3)CH_2C{\equiv}CR^1} \qquad (34)$$

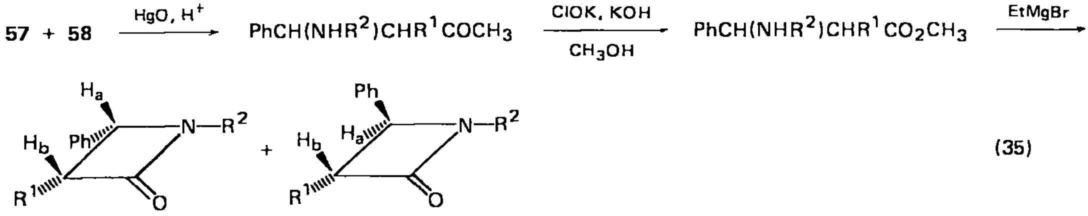
c. Stereochemistry. Schiff's bases of type $PhHC{=}NR^2$ react with allenic organo-magnesium and -zinc compounds ($R^1HC{=}C{=}CHMBr$) to give mixtures of diastereoisomeric secondary amines (*erythro*-57 and *threo*-58). The stereoisomers have been identified by the reaction sequence shown in equation (35)[128,129]. Since the last reaction is stereospecific[130], the *erythro* amine (57) gives finally the *cis* β-lactam 59 and the *threo* isomer (58) yields the *trans* β-lactam 60. *Cis* and *trans*



(*erythro*-57)



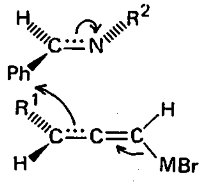
(*threo*-58)



(59) (60)

β-lactams are easily identified by the examination of the coupling constant $J(H_a-H_b)$ of the proton H_a.

Under reflux of the solvent, the reversibility of these reactions was proved[82], hence these condensations were under kinetic control in the reaction conditions used[129]. All these condensations are very stereoselective, and *threo* isomer **58** is always obtained in a preponderant way; the condensations between organozinc compounds and Schiff's bases are even more stereoselective than the same reactions with organomagnesium compounds. The sterically favoured transition state **61** accounts for the predominance of the *threo* isomer.

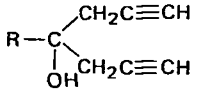


(61)

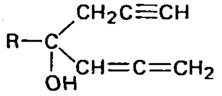
The stereochemical study was extended also to the reaction of *N*-methyl-4-*t*-butylcyclohexylimine[131].

8. *Action of esters*

Whereas organozinc derivatives do not react with esters, the allenylmagnesium bromide always leads to a mixture of alcohols **62** and **63**[74,133,134], even at low temperatures[132].



(62)



(63)

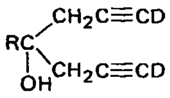
Ethyl formate reacts with allenic organomagnesiums to give mixtures of the bis-acetylenic alcohol **62** and the formate resulting from the transesterification of this alcohol[135]. At – 80°C in ether, these allenic organomagnesiums yield two mixtures: one contains ketones **64** and **65** and the other contains alcohols **62** and **63** (equation 36). This reaction has been utilized in the preparation of α-allenic ketones and α-allenic α′-halogenated ketones[136–138].

$$H_2C{=}C{=}CHMgBr \xrightarrow[\text{ether, }-80^{\circ}C]{R^1COOR^2} \left\{ \begin{array}{lll} (a) & R^1COCH_2C{\equiv}CH & + \; R^1COCH{=}C{=}CH_2 \\ & \quad (64) & \qquad (65) \\ (b) & \quad 62 \; + \; 63 & \end{array} \right. \qquad (36)$$

The mechanism of this reaction at – 80°C has been studied in detail using the deuterated magnesium compound $H_2C{=}C{=}CDMgBr$. The ketonic fraction contains two principal constituents: the β-acetylenic ketone **66** and the α-allenic ketone **67** obtained by prototropy from the β-acetylenic ketone **66** first formed[139]. The alcoholic fraction contains the bis-acetylenic alcohol **68** and the mixed alcohol **69**: the latter results from the reaction between the deuterated allenylmagnesium bromide

$RCOCH_2C{\equiv}CD$ (66) $\qquad$ $RCOCH{=}C{=}CHD$ (67)

and the ketone $RCOCD{=}C{=}CH_2$ initially formed, and shows an *apparent retention of structure* of the organometallic[140].



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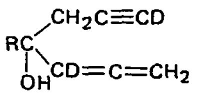
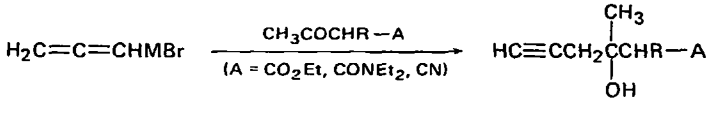


(69)

These different observations allowed the synthesis of β-hydroxylated δ-acetylenic esters, amides and nitriles (equation 37)[141].



$$H_2C{=}C{=}CHMBr \xrightarrow[\text{(A = CO}_2\text{Et, CONEt}_2\text{, CN)}]{CH_3COCHR-A} HC{\equiv}CCH_2\underset{\displaystyle OH}{\overset{\displaystyle CH_3}{C}}CHR-A \qquad (37)$$

9. Action of amides

Organomagnesium derivatives of α-acetylenic bromides react with *N,N*-dimethylbenzamide and give mixtures of acetylenic and allenic ketones (e.g. equation 38), but in this case the allenic ketone is not formed by prototropy from its acetylenic isomer[142].

$$BrCH_2C{\equiv}CCH_3 \xrightarrow[\text{2. PhCONMe}_2]{\text{1. Mg}} PhCOCH_2C{\equiv}CCH_3 + PhCOC(CH_3){=}C{=}CH_2 \qquad (38)$$

10. Action of orthoesters

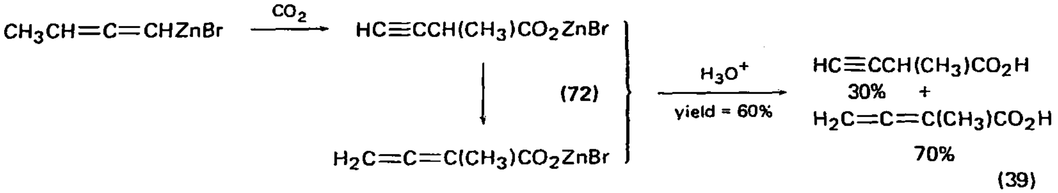
Allenylaluminium bromide on reaction with ethyl orthoformate yields the normally expected β-acetylenic acetal[18]. However, allenic magnesium compounds give a mixture of acetylenic and allenic acetals[22].

11. Carbonation

In general, carbonation leads to mixtures of acids[1,2,10,13-15,33]; for instance, the carboxylation of the Grignard reagent from propargyl bromide gives a mixture of acids **70** and **71**[1,13]. In order to determine the origin of allenic acid **71**, organozinc

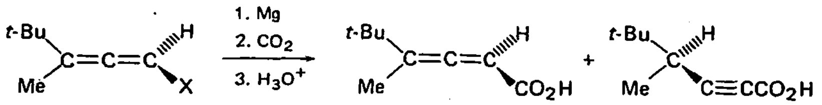
$HC{\equiv}CCH_2COOH$ (70) $\qquad H_2C{=}C{=}CHCOOH$ (71)

derivatives of secondary bromides ($RCHBrC{\equiv}CH$) were utilized[36]. Equation (39) shows that this acid results from prototropy in the intermediate zinc salt **72**.



$$CH_3CH{=}C{=}CHZnBr \xrightarrow{CO_2} \left.\begin{array}{c} HC{\equiv}CCH(CH_3)CO_2ZnBr \\ \Big\downarrow \quad (72) \\ H_2C{=}C{=}C(CH_3)CO_2ZnBr \end{array}\right\} \xrightarrow[\text{yield = 60\%}]{H_3O^+} \begin{array}{c} HC{\equiv}CCH(CH_3)CO_2H \\ 30\% \quad + \\ H_2C{=}C{=}C(CH_3)CO_2H \\ 70\% \end{array} \qquad (39)$$

Grignard reagents from allenic optically active halides **73** and **74**, treated by carbon dioxide give optically active acids **75** and **76** in poor yields (equation 40)[143]. The formation of the acetylenic acid **76** requires an unusual stereospecific



(73) X = Cl

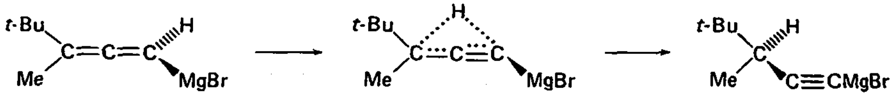
(74) X = Br

(75)

(76)

(40)

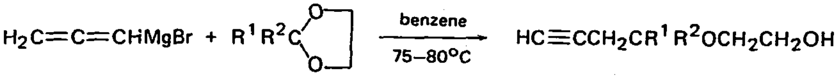
prototropic rearrangement, probably of the Grignard reagent, according to equation (41)[143].



(41)

12. *Miscellaneous reactions*

a. Dioxolanes. The Grignard reagents of propargyl bromide react with substituted 1,3-dioxolanes to give β-hydroxyethyl ethers of β-acetylenic alcohols (equation 42)[144].



(42)

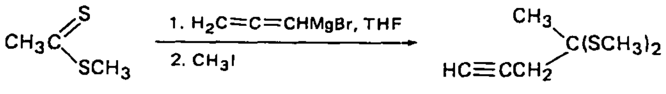
b. Thio ketones. The reaction of di-*t*-butyl thioketone (and of adamantane thione) with allenylmagnesium bromide leads to a mixture containing the addition compound **77** and the heterocycle **78**, which corresponds to the cyclization of the *C*-addition product[145].

(77)

(78)

(43)

c. Dithio esters. The reaction of allenyl Grignard reagent with methyl dithioacetate and subsequent action of methyl iodide gives dithio acetals **79** resulting from a carbophilic addition process[146].

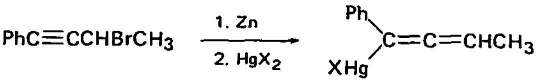


(79)

(44)

d. Ethyl chlorocarbonate and carbonate. Allenylaluminium bromide reacts with ethyl chlorocarbonate to form the normally expected tripropargylcarbinol (yield = 60%)[74, 133]. Tripropargylcarbinol and its isomer $(HC{\equiv}CCH_2)_2C(OH)$-$CH{=}C{=}CH_2$ are formed by the action of ethyl carbonate on the Grignard reagent from propargyl bromide[147].

e. Mercuric halides. Propargylic and allenic bromo- or chloro-mercury compounds are prepared in THF, from the appropriate organozinc compounds and mercuric halides, in good yields (e.g. equation 45)[31, 148].



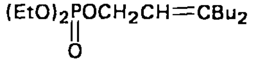
(45)

f. Halogeno dialkyl- or diaryl-arsine. Propargylic and allenic compounds of arsenic are formed simultaneously by reaction of halogeno dialkyl- or diarylarsines on a propargylic magnesium compound[39].

g. Esters of γ-halogenated α-acetylenic alcohols. Allenic organomagnesium derivatives react with both the ester and the halide functions, using up three moles of organometallic derivative per mole of halo ester. Mixtures of bis-acetylenic tertiary alcohols **80** and α-acetylenic δ-allenic alcohols **81** have been obtained (equation 46)[149,150].

$$\mathrm{BrCHR^2C{\equiv}CCHR^3OCOCH_3} \xrightarrow[\substack{2.\ \mathrm{Cu_2Cl_2} \\ 3.\ \mathrm{H_3O^+}}]{1.\ 3\ \mathrm{R^1HC{=}C{=}CHMgBr}} \begin{array}{c} \mathrm{CH_3C(OH)[CH(R^1)C{\equiv}CH]_2} \\ \mathbf{(80)} \quad + \\ \mathrm{R^1HC{=}C{=}CHCHR^2C{\equiv}CCHR^3OH} \\ \mathbf{(81)} \end{array} \qquad (46)$$

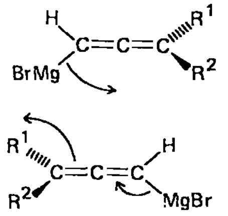
h. Monoallylphosphate ester. The monoallylphosphate ester (**82**) is rapidly alkylated by allenyl magnesium bromide in the presence of copper salts to give exclusively the allylallene **83** (equation 47)[151].



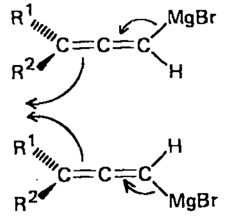
(82)

$$\mathrm{(EtO)_2\underset{\displaystyle \overset{\|}{O}}{P}OCH_2CH{=}CBu_2} \xrightarrow{\mathrm{H_2C{=}C{=}CHMgBr}} \underset{\mathbf{(83)}}{\mathrm{H_2C{=}C{=}CHCH_2CH{=}CBu_2}} \qquad (47)$$

i. Coupling reactions with oxygen. Allenyl Grignard reagents from tertiary propargylic bromides react with oxygen to yield coupling products which are best explained by postulating both 1,3-coupling (equation 48) and 3,3-coupling (equation 49)[33]. Similar coupling of copper (I) acetylides with oxygen is well known[152].



$$\xrightarrow{O_2} \mathrm{R^1R^2C{=}C{=}CHCR^1R^2C{\equiv}CH} \qquad (48)$$



$$\xrightarrow{O_2} \mathrm{HC{\equiv}CCR^1R^2CR^1R^2C{\equiv}CH} \qquad (49)$$

j. Esters of sulphinic acids. Reactions of 2-bromopent-3-yne with magnesium in THF and then with optically active menthyl esters of sulphinic acids give allenic sulphoxides which are asymmetric at sulphur and in the allene system[153].

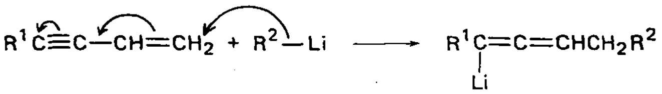
k. Addition to terminal acetylenic compounds and their magnesium derivatives. Organozinc compounds prepared from bromides $\mathrm{RC{\equiv}CCH_2Br}$ can be added once (equation 50) or twice to terminal acetylenic compounds and to their magnesium derivatives[154].

$$EtC{\equiv}CCH_2Br \xrightarrow[2.\ n\text{-}C_9H_{19}C{\equiv}CH]{1.\ Zn,\ THF} EtC{\equiv}CCH_2C(n\text{-}C_9H_{19}){=}CH_2 \qquad (50)$$

III. ALLENIC AND PROPARGYLIC DERIVATIVES OF LITHIUM

A. Addition of Alkyllithiums to Enynes

The 1,4-addition of primary, secondary, tertiary alkyl or aromatic lithium compounds to substituted enynes gives allenic lithium compounds 84 (equation 51)[155-157]. Yields are good in ether at temperatures lower than – 30°C.



$$R^1C{\equiv}C{-}CH{=}CH_2 + R^2{-}Li \longrightarrow R^1\underset{\displaystyle Li}{\underset{|}{C}}{=}C{=}CHCH_2R^2 \qquad (51)$$

(84)

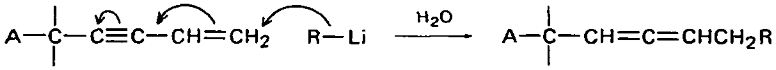
The regiospecific character of the addition as well as the absence of by-products are noteworthy[156]. In the case of unsymmetrical divinylacetylenes, steric factors are important; for instance, with vinylisopropenylacetylene, the methyl group screens the double bond in the isopropenyl group and addition of alkyllithiums takes place nearly exclusively at the vinyl group[158-160].

These allenic organolithiums (84) are very useful in synthesis. In various further reactions, the allenic structure is preserved. Mixtures of isolated acetylenic and allenic compounds are in some cases accounted for by the resonance-stabilized anion:

$$[R^1\bar{C}{=}C{=}CHCH_2R^2 \longleftrightarrow R^1C{\equiv}\bar{C}CHCH_2R^2]\,Li^+$$

1. Hydrolysis

The hydrolysis of the adducts 84 gives uniquely allenic hydrocarbons ($R^1HC{=}C{=}CHCH_2R^2$), in good yields[155-156]. The addition of organolithiums has been extended to a few functional vinylacetylenes (equation 52). Vinylacetylenic



$$A{-}\overset{|}{\underset{|}{C}}{-}C{\equiv}C{-}CH{=}CH_2 \quad R{-}Li \xrightarrow{H_2O} A{-}\overset{|}{\underset{|}{C}}{-}CH{=}C{=}CHCH_2R \qquad (52)$$

(85) A = OH

(86) A = Et_2N

(87) A = RS

alcohols (85) yield mainly allenic alcohols[167,168]. In the same way, amines[169] and α-allenic thio ethers[170] have been isolated from (86) and (87) respectively.

The addition of alkyllithiums to silicon-containing enynes and their germanium analogues gives on hydrolysis a mixture of allenic (88) and acetylenic (89) products (equation 53)[171,172]. To procure pure silicon-containing allenes (88, $R^1 = Ph$), Zubritskii and Bal'Yan added the triphenylsilyllithium to enynes[175,176]. Tin-containing vinylacetylenes undergo cleavage of the C–Sn bond[173]. With enynes, nascent

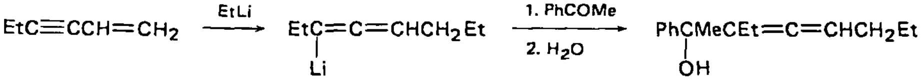
$$R^1_3XC{\equiv}CCH{=}CH_2 \xrightarrow[2.\ H_2O]{1.\ R^2Li} \underset{(89)}{R^1_3XC{\equiv}CCH_2CH_2R^2} + \underset{(88)}{R^1_3XCH{=}C{=}CHCH_2R^2} \qquad (53)$$

X = Si, Ge

alkyllithiums also give 1,4-addition products; at −40 to −60°C in ether or THF and, after hydrolysis, the expected allenic hydrocarbons are obtained in quantitative yields. However, at higher temperatures, this reaction produces mixtures of allenic and acetylenic hydrocarbons[174].

2. *Action of carbonyl compounds*

The treatment of adducts 84 with various aliphatic, aromatic, α-ethylenic, α-acetylenic aldehydes and ketones affords in good yields the expected α-allenic alcohols[177–181] (e.g. equation 54). No 1,4-addition of adducts 84 is observed[178,179].



$$\mathrm{EtC{\equiv}CCH{=}CH_2} \xrightarrow{\mathrm{EtLi}} \underset{\mathrm{Li}}{\mathrm{EtC}}\mathrm{{=}C{=}CHCH_2Et} \xrightarrow[\text{2. }\mathrm{H_2O}]{\text{1. PhCOMe}} \mathrm{Ph}\underset{\mathrm{OH}}{\mathrm{C}}\mathrm{MeCEt{=}C{=}CHCH_2Et} \qquad (54)$$

(84a)

Some carbonyl compounds lead to the formation of acetylenic glycols by reaction of adducts of alkyllithium and 2-methyl-5-hexen-3-yn-2-ol; this is caused by dual reactivity of the initially formed lithium hydroxyallenic compounds[181].

3. *Miscellaneous reactions*

Epoxides behave normally with 84, and β-allenic alcohols are isolated.

Oxidation of 84 with oxygen at −30°C leads to the predominant formation of acetylenic alcohols (equation 55)[180].

$$84 \xrightarrow[\text{2. }\mathrm{H_2O}]{\text{1. }\mathrm{O_2}} \mathrm{R^1CH(OH)C{\equiv}CCH_2R^2} \qquad (55)$$

The alcohol and the expected ketone are obtained when the adduct 84 is prepared from phenylvinylacetylene and ethyllithium[182]. The oxidation of adducts of alkyllithium and enynic hydrocarbons by *t*-butyl hydroperoxide gives mixtures of products[183].

Bromination or iodination of 84 at low temperatures entails a dimerization and tetraenes are isolated[180]. The reaction with α-haloacetylenes results in the same dimerization of allenic lithium compounds to tetraenes; on standing at room temperature, these tetraenes isomerize to allenynes (equation 56)[184].

$$\underset{(84)}{\mathrm{2\,LiCR^1{=}C{=}CHCH_2R^2}} + \mathrm{XC{\equiv}CR^3} \longrightarrow \begin{array}{l}\mathrm{R^2CH_2CH{=}C{=}CR^1CR^1{=}C{=}CHCH_2R^2} + \mathrm{LiX} \\ + \mathrm{LiC{\equiv}CR^3} \\ \qquad\qquad \Big\downarrow \text{room temperature} \\ \mathrm{R^2CH_2C{\equiv}CCHR^1CR^1{=}C{=}CHCH_2R^2}\end{array} \qquad (56)$$

The allenyllithiums react with esters, e.g. methyl formate, to give a mixture of α,α′-diallenic (90) and β-allenic (91) alcohols[185].

$$\underset{(90)}{\mathrm{R^2CH_2CH{=}C{=}CR^1CHOHCR^1{=}C{=}CHCH_2R^2}} \qquad \underset{(91)}{\mathrm{R^1CH{=}C{=}CHCHR^2CH_2OH}}$$

In the case of reactions of adducts **84** with chlorotriethyltin[186] and chlorotrimethylgermanium[187], the allenic structure is preserved, but with chlorotrimethylsilane, mixtures of allenic (**92**) and acetylenic (**93**) products are isolated[188, 189].

$$\underset{(92)}{\mathrm{Me_3SiCR^1{=}C{=}CHCH_2R^2}} \qquad \underset{(93)}{\mathrm{Me_3SiCHR^1C{\equiv}CCH_2R^2}}$$

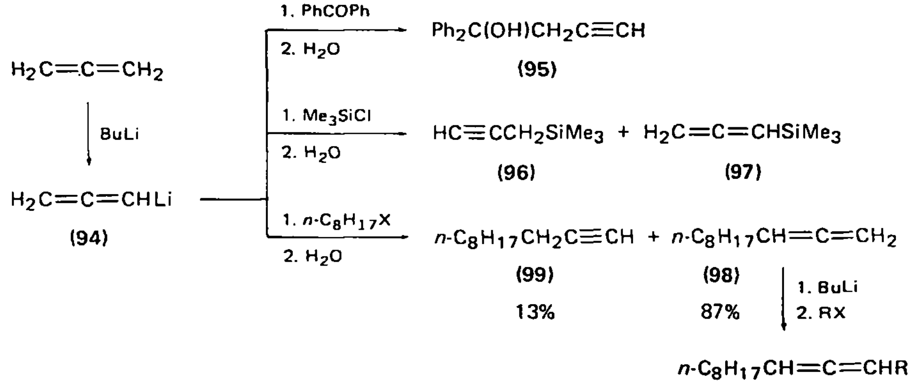
Enynes give rise to similar addition reactions with organocalcium[169, 190–197], diethylstrontium[198, 199] and organobarium compounds[200–205]; these organometallics behave similarly to alkyllithiums, and after the demetalation of the adducts with water, they form mainly the expected allenic hydrocarbons in moderate or low yields.

B. Metalation Reactions of Acetylenic and Allenic Hydrocarbons

1. Monometalation

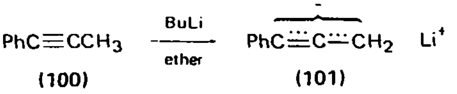
Alkyllithiums react very easily with allenic and acetylenic hydrocarbons and lead to polymetalated derivatives; for instance, the dimetalation of 1-phenylpropyne is faster than the monometalation and yields a dianion different from that of 3-phenylpropyne or phenylallene[206]. Nevertheless, many allenic monolithiums can be prepared.

Allenyllithium (**94**) is formed when allene is metalated with one equivalent of butyllithium, at −50°C in THF/hexane (mixture 1:1) or hexane at room temperature. The strong infrared absorption at 1890 $\mathrm{cm^{-1}}$ in the allenic region permits the assignment of an allenic structure to this organometallic[207]. The condensation of this reagent with benzophenone or chlorotrimethylsilane leads to the β-acetylenic alcohol **95** and to a mixture of the silylated compounds **96** and **97**, respectively[207]. Allenyllithium can also be alkylated[208], the isolated allenic hydrocarbon **98**, after separation from its acetylenic isomer **99**, can again be metalated and subsequently alkylated (Scheme 6).



SCHEME 6.

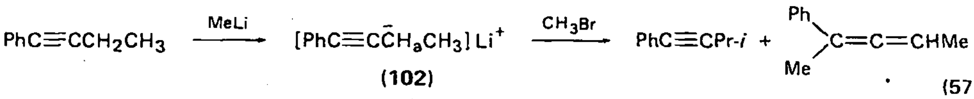
1-phenyl-1-propyne (**100**) treated with one equivalent of butyllithium gives a good yield of the monolithium compound **101**, the infrared spectrum of which shows a strong absorption at 1866 $\mathrm{cm^{-1}}$ (equation 56)[210]. The reaction of **101** with



$$\underset{(100)}{\mathrm{PhC{\equiv}CCH_3}} \xrightarrow[\text{ether}]{\text{BuLi}} \underset{(101)}{\overset{-}{\overbrace{\mathrm{PhC{\equiv}C{=}CH_2}}}}\ \mathrm{Li^+} \qquad (56)$$

electrophiles furnished pure β-acetylenic compounds (e.g., by action of Me_3SiCl) or mixtures of acetylenic and allenic products (hydrolysis, action of HCHO and MeCOMe)[210].

In contradiction to previous results, Klein and coworkers[206] discovered that the dimetalation of 1-phenyl-1-propyne (**100**) is faster than the monometalation when butyllithium was used; but, with methyllithium as metalating agent, they obtained preferentially the monolithium derivative[211]. Similar results were observed with 1-phenyl-1-butyne; alkylation, silylation and protonation of lithium derivatives were studied. For instance, methylation gave a mixture of hydrocarbons (equation 57)[211].



$$PhC{\equiv}CCH_2CH_3 \xrightarrow{MeLi} [PhC{\equiv}\bar{C}CH_aCH_3]\,Li^+ \xrightarrow{CH_3Br} PhC{\equiv}CPr\text{-}i + \overset{Ph}{\underset{Me}{>}}C{=}C{=}CHMe$$

(102) (57)

In ether or hexane, the organolithium **102** presents an infrared absorption at 1870 cm^{-1} [212] and ^1H-n.mr. shows $\delta = 1.61$ p.p.m. for the proton H_a; as for the organometallics presented in Section II, its real structure is certainly an equilibrium between two possible forms.

In general, aliphatic 2-alkynes are dimetalated in ether solution. Only 2-butyne undergoes monometalation exclusively (equation 58)[213]; acids **103** and **104** are obtained in ratio (**103**):(**104**) = 7.

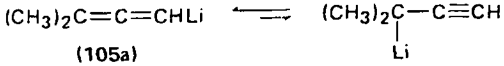
$$CH_3C{\equiv}CCH_3 \xrightarrow{BuLi} CH_3C{\equiv}CCH_2Li \xrightarrow{CO_2} \underset{(103)}{H_2C{=}C{=}C(CH_3)COOH} + \underset{(104)}{CH_3C{\equiv}CCH_2COOH} \qquad (58)$$

1,3-diphenylpropyne reacts with lithium diisopropylamide in a mixture of HMPA/benzene[214] and leads to an ambivalent anion[215]:

$$PhC{\equiv}\bar{C}CHPh \longrightarrow Ph\bar{C}{=}C{=}CHPh$$

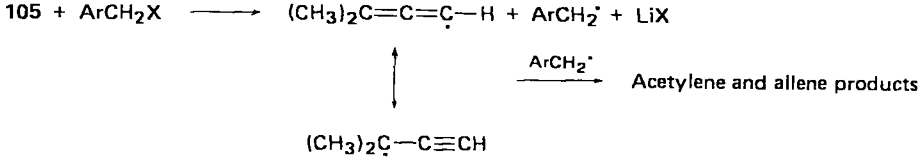
An interpretation based on the HSAB principle explains the reactivity of this anion; hard reagents (Me_3SiCl, H_2O) prefer to react with the allenic form whereas the softer acetylenic form prefers soft reagents (RI).

Some allenic organolithium compounds have been also prepared by halogen–metal exchange, at low temperature, between halogenoallenes and alkyllithiums[208, 209, 220]. 3,3-dimethylallenyllithium has been obtained by this method and also through the reaction of lithium diisopropylamide with 3,3-dimethylallene[220a]. The n.m.r. spectrum of the organometallic derivative in benzene shows a doublet at $\delta = 1.33$ p.p.m. and an heptet at $\delta = 4.70$ p.p.m. A similar spectrum is seen in ether[220a], showing that the contribution of the allenic structure **105a** is very important.



$$\underset{(105a)}{(CH_3)_2C{=}C{=}CHLi} \rightleftharpoons \underset{(105b)}{(CH_3)_2\underset{Li}{\underset{|}{C}}{-}C{\equiv}CH}$$

Very recently, the reagent **105** was thoroughly studied[220a]. The products of reaction of **105** with benzyl halides were acetylenes (major) and allenes (minor) and were rationalized in terms of an electron-transfer mechanism leading to the 3,3-dimethylallenyl radical–benzyl radical pair as in equation (59). Acetylenic and

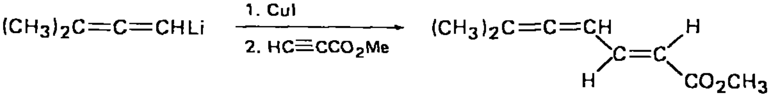


(59)

allenic alcohols were obtained by reaction of **105** with aldehydic and ketonic electrophiles. The HSAB principle explained the products of **105** with water, carbon dioxide and trimethylchlorosilane, but reaction with disulphides also gave allenic products which were inconsistent with the HSAB principle^{220a}.

The monometalation of alkynes has been extended to 1,4-enynes; the reaction is facile in ether with methyllithium^{216}; the formation of both the monoanion and the dianion has been studied by n.m.r. and ultraviolet spectroscopy$^{217-219}$. The monolithio compounds are alkylated with alkyl halides at the central 3-position only to give unconjugated enynes^{216}.

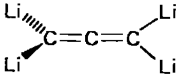
Finally, the first allenic cuprates were recently prepared by addition of one equivalent of copper (I) iodide to allenic lithium compounds at $-70°C^{209}$; after reaction with methyl propynoate, they gave the *trans* conjugated ester in excellent yields (equation 60). A very short synthesis of the pheromone of the parasitic bean weevil uses the same reaction.



(60)

2. *Polymetalation*

Acetylenic and allenic hydrocarbons give easily polymetalated compounds with an excess of alkyllithium$^{221-230}$. For instance, under reflux in hexane, four hydrogen atoms of propyne may be substituted^{221,223} and the tetralithioallene C_3Li_4 obtained. The infrared absorption of this compound at 1675 cm^{-1} is too low to be in agreement with an acetylenic structure; an allenic structure **106** was first proposed^{223}, but this tetralithio derivative can also be described either as a tetralithiopropargylide (**107**) or a tetralithiosesquiacetylene (**108**)^{225}. The sesquiacetylene structure and also the name for polylithiated acetylenes was first proposed by Klein and coworkers$^{217-219,237}$. Recently, *ab initio* molecular calculations have allowed the proposal of other curious structures for this lithiocarbon C_3Li_4^{231}. C_3Li_4 reacts to give either allene- or propyne-type products depending on the reagents and conditions. For instance, with chlorotrimethylsilane^{207,225} or chlorotrimethylgermane^{225}, tetrakis-(trimethyl-silyl or -germyl)allene is isolated, whereas alkylation be ethyl sulphate furnishes a mixture of tetraethylated compounds; the ratio acetylenic compound: allenic compound is four^{225}.



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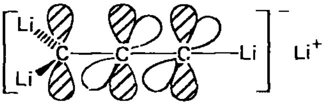

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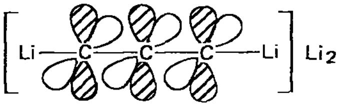
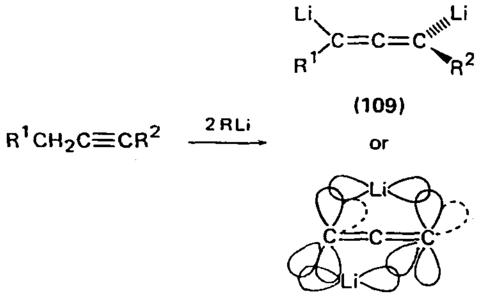


(108)

It is noteworthy to note that the dimetalation of internal acetylenes, terminal acetylenes and phenylallene is faster than the monometalation$^{212,232-236}$. The structure of the corresponding dilithio compounds seems now certain. Internal acetylenes give dianions of allenic **109**[212,225] or sesquiacetylenic **110**[212] structures (equation 61). SCF-MO calculations indicate that the sesquiacetylenic structure **110** is more stable than the allenic one **109**[237].

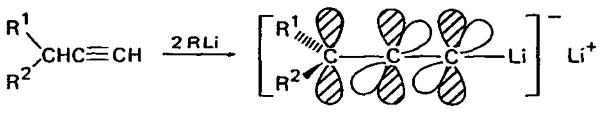


(109)

(110)

(61)

For dianions of terminal acetylenes, West and coworkers have proposed the propargylide structure **111**[225]. Some confusion in assignment of structure has resulted from the fact that the infrared absorption of the propargylide dianion occurs at the same frequency as that of the allenic monoanion.



(111)

(62)

3. 3-Lithio-1-trimethylsilylpropyne

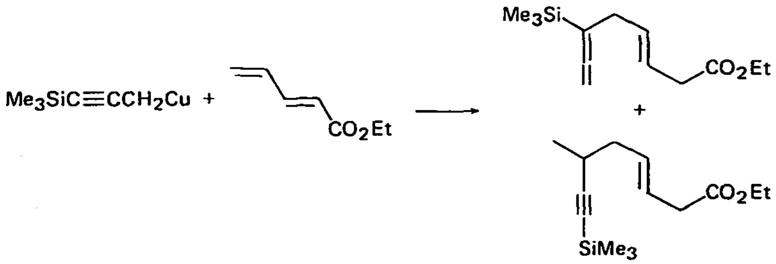
The coupling between an allylic halide and a propargylic reagent may constitute a method for the stereospecific elaboration of carbon chains containing the 1,5-diene system, via the 1-en-5-yne structure, but we have seen (Section II.C) that allenic organometallics often lead to mixtures of acetylenic and allenic products. So allenyllithium furnishes important quantities of allenic hydrocarbons. With a view to avoiding this inconvenience, Corey and Kirst have prepared the 3-lithio-1-trimethylsilylpropyne **113**; the treatment of 1-trimethylsilylpropyne (**112**) in ether at – 50°C with tetramethylethylenediamine (TMEDA) and an equivalent amount of butyllithium under argon led to complete metalation in 15 minutes (equation 63)[238].

$$\underset{(112)}{CH_3C{\equiv}CSiMe_3} \xrightarrow[TMEDA]{BuLi} \underset{(113)}{LiCH_2C{\equiv}CSiMe_3} \xrightarrow{RX} RCH_2C{\equiv}CSiMe_3 + H_2C{=}C{=}CRSiMe_3 \qquad (63)$$

The structure of this reagent has been not studied, but it is probable that it is an ambivalent anion. The reaction of **113** with primary halides was found to give the acetylene with only small amounts of the isomer allene; acetylene:allene ratios are between 10 and 20[238]. The trimethylsilyl group is easily removable and treatment with silver nitrate at 25°C followed by sodium cyanide[239] afforded the expected acetylene. This coupling reaction constituted an important step in the stereospecific total syntheses of *trans,trans*-farnesol[238], *dl*-C_{18} Cecropia juvenile hormone[240] and α-santalol[241].

The protonation of **113** gave exclusively 1-trimethylsilylpropyne (**112**) whereas the condensation with acetone led to a 9:1 mixture of acetylenic:allenic carbinols[242]. Reaction of **113** with methyl sorbate produced a complex mixture of the products of 1,4- or 1,6-addition[242].

The addition of one equivalent of copper(I) iodide to **113** at −78°C leads to the corresponding copper(I) derivative, which treated by the ethyl *trans*-2,4-pentadienoate furnishes only products of 1,6-addition having the *trans* stereochemistry (equation 64). A 4:1 ratio of allenic and acetylenic products is formed in 42% yield[243]. This reaction constitutes a simple route to 1,5-enynes and 1,4,5-trienes.



(64)

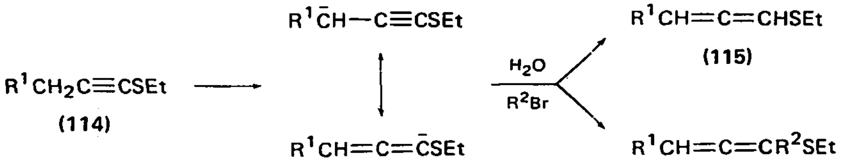
C. Functional Organolithium Compounds

Acetylenic and allenic thio ethers, silylated or unsilylated propargylic and allenic ethers are very easily metalated and can give one, and sometimes two, successive metalations; in the same way, the 1-triphenylsilylpropyne has undergone three successive lithiations[224]. These anions are interesting because some of them correspond to masked acyl anions[245]; for instance, 1-lithiummethoxypropadiene is equivalent to the acyl anion from acrolein:

$$H_2C{=}C{=}C\begin{matrix}OCH_3\\ Li\end{matrix} \quad \text{equivalent to} \quad H_2C{=}CH{-}C\begin{matrix}{}^{\nearrow}O\\ {}^{-}\end{matrix}$$

1. Thio ethers

Acetylenic thio ethers **114** are metalated by sodium amide in liquid ammonia[247]; hydrolysis and alkylation lead to allenic thio ethers (equation 65). The isomeric



(114)

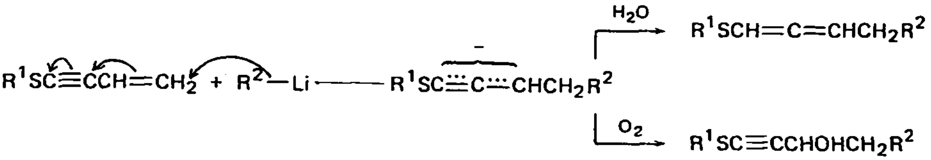
(115)

(65)

allenic thioethers **115** give the same mesomeric anion by treatment with lithium amide in liquid ammonia[248] or with alkyllithium in ether[249]. Subsequent reaction with carbonyl compounds leads to the expected carbinols.

By analogy with 1,4-addition of organolithium compounds to vinylacetylenes (see Section III.A) lithiumallenyl thioethers have been obtained by action of alkyllithiums on alkylthiovinylacetylenes. The hydrolysis of the resulting adducts furnishes allenic thio ethers[250] and oxidation by oxygen of air gives exclusively (alkylthio)ethynyl carbinols[251] (equation 66).

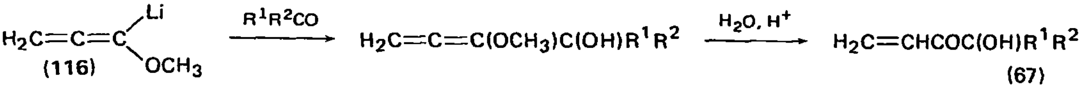
In the same way, addition of diethylbarium to alkylthiovinylacetylenes results, after hydrolysis, in allenic thio ethers in poor yield[252].



(66)

2. *Allenic ethers*

The metalation of methoxypropadiene and other alkoxypropadienes with butyllithium in ether gives allenic monoanions of type **116**. The α-lithiation is demonstrated by treatment with deuterium oxide at – 20°C which produces α-deuterated allenyl ether $H_2C{=}C{=}CDOR$[253]. During the reaction of anion **116** with alkyl halides[253], dimethyl disulphide[246] or carbonyl compounds[246], the allenic structure of the lithium derivative is preserved. Acid catalysed hydrolysis of the isolated allenic carbinols gives nearly quantitative yields of unsaturated ketols (equation 67)[246].

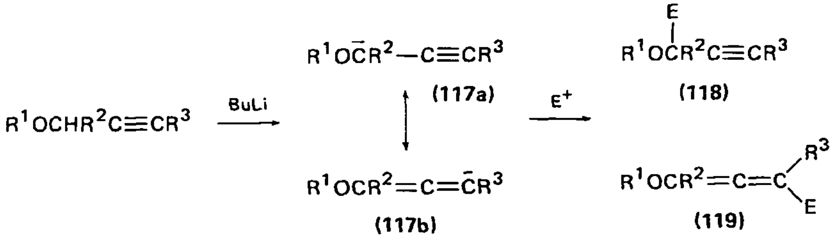

(116)

$$H_2C{=}C{=}C(Li)OCH_3 \xrightarrow{R^1R^2CO} H_2C{=}C{=}C(OCH_3)C(OH)R^1R^2 \xrightarrow{H_2O,\ H^+} H_2C{=}CHCOC(OH)R^1R^2 \quad (67)$$

The use of liquid ammonia as solvent and lithium amide as metalating agent is unsatisfactory: such alkylations led to a mixture of two allenic ethers[253] and the action of diethylketone led to a mixture of three isomeric carbinols in low total yields[246]. Similar results were obtained from $CH_3OCH{=}C{=}C(R)C_5H_{11}$[254], and from mono- and di-silylated *t*-butoxyallenes[255,256].

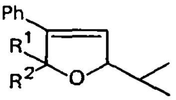
3. *Propargylic ethers*

Propargylic ethers $R^1OCHR^2C{\equiv}CR^3$ (R^3 = alkyl, phenyl or Me_3Si; R^2 = alkyl or H) are metalated by butyllithium at low temperature in ether (equation 68). The



(68)

obtained carbanions are stable below 0°C. According to the nature of the electrophile E^+, they react either in the acetylenic form (**117a**) or in the allenic form (**117b**). Expected allenic products **119** have been isolated in a great number of reactions, for instance with the anion from $PhC{\equiv}CCHR^2OR^1$; acid hydrolysis of condensation products furnished α-ethylenic ketones[257]. The organolithium derivative from the ether $PhC{\equiv}CCH(i\text{-}Pr)OCH_3$ gives dihydrofurans **120**, tetrahydrofurans **121** and the hemiacetal lactone **122** by reaction with ketones (R^1R^2CO), aldehydes (R^1CHO) and carbon dioxide, respectively[258].



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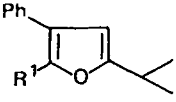

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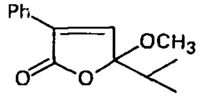


(122)

α-Ethylenic aldehydes have been prepared from propargylic alcohols via organolithium compounds as shown in equation (69)[259].

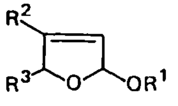
$$C_5H_{11}C\equiv CCH_2OH \longrightarrow C_5H_{11}C\equiv CCH_2OR \longrightarrow [C_5H_{11}C\overset{..}{=}C\overset{..}{=}CHOR]\,Li \longrightarrow$$

$$\underset{30\%}{C_5H_{11}C\equiv CCH_2OR} + \underset{70\%}{C_5H_{11}CH{=}C{=}CHOR} \longrightarrow C_5H_{11}C\equiv CCH_2OR + C_5H_{11}CH{=}CHCHO \qquad (69)$$

Allenic products **119** are principally obtained by action of methyl iodide[255,256], chlorotrimethylsilane[254–256] or dimethyl or diethyl sulphate[256] on allenic organolithiums from propargylic ethers; on the other hand, condensation with carbonyl compounds furnishes a mixture of hydroxylated acetylenic ethers **123** and dihydrofurans **124**. These last probably result from the intermediary allenic alcoholate[260]. A pure acetylenic compound **123** is obtained if the reaction takes place in the presence of zinc iodide; tertiary propargylic amines metalated by butyllithium lead to analogous results[260].

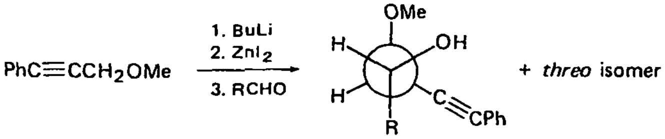
$R^3CHOHCH(OR^1)C\equiv CR^2$

(123)



(124)

The reaction with carbonyl compounds in the presence of zinc salts has been improved and its stereochemistry has been very well studied[261,262]. The *erythro* isomer **125** is always predominantly obtained (equation 70)[262].

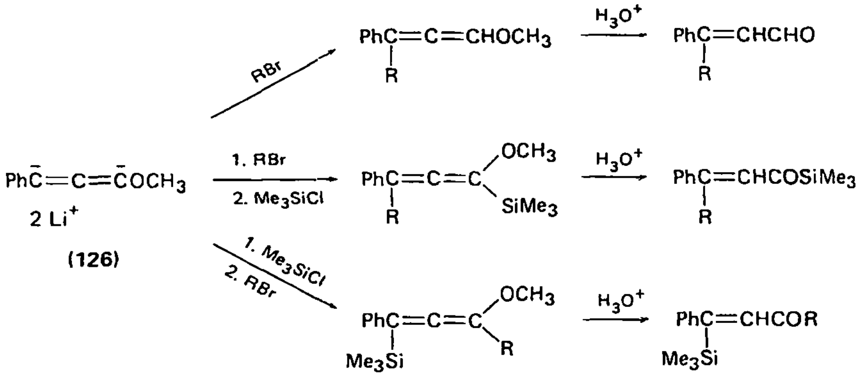


(125) (70)

Moreover, alkoxypropargylation of 17-keto steroids is nearly stereospecific[263], the isolated compounds being present in the (17*S*)(20*R*) configuration[264].

4. *Allenic dianions*

3-Methoxy-1-phenyl-1-propyne treated at −75°C by two equivalents of butyllithium in ether gives a dianion whose structure is allenic (126). This dianion

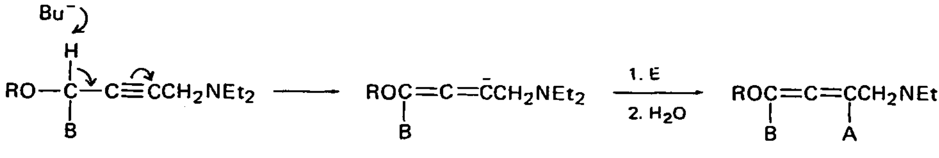


SCHEME 7.

presents a peculiar relationship between its selectivity and reactivity: the first alkylation always takes place on the carbon atom near the phenyl group, whatever the nature of the alkylating agent. Selective mono- and di-alkylations are thus effected as shown in Scheme 7[265,266]. The yields of allenic products are excellent and α-ethylenic carbonyl compounds are formed by simple acid-catalysed hydrolysis.

5. *Miscellaneous functional anions*

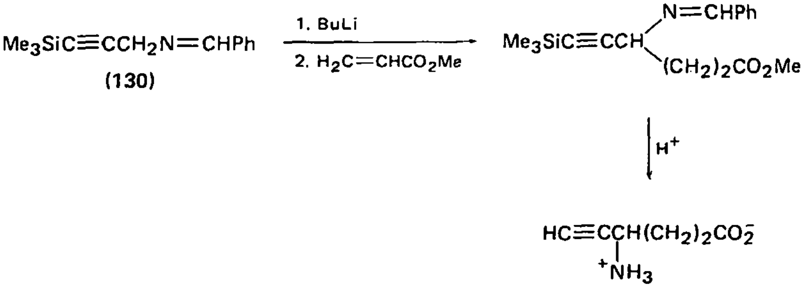
Whereas α,α′-acetylenic diethers lead to cummulenic lithium derivatives by action of two equivalents of butyllithium[267], α-diethylamino-α′-alkoxyacetylenes (127) give organolithiums 128. In this case, the metalation is regiospecific, the hydrogen on the carbon bearing the ether function being removed (equation 71)[268]. The subsequent condensations of these functional lithioallenes with electrophiles and allenic compounds result in 129 with good yields (B = H, Me or Me_3Si; A = H, D, Me, Me_3Si, Me_2COH)[268].



(127) (128) (129) (71)

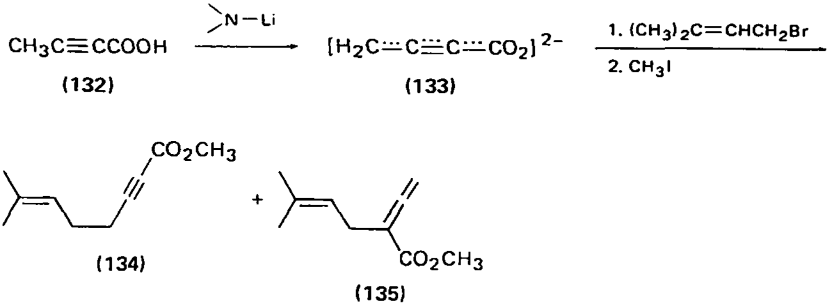
Allenic carbanions were obtained through the metalation by lithium dialkylamides of 3,3-diethoxy-1-methylthiopropyne[269] and of 1-methylthio-3-methoxypropyne[270]. These anions allow the introduction, respectively, of an acylacetate unit and of β-keto aldehyde or β-diketone units.

The propargylic anion derived from the aldimine 130 undergoes a regiospecific Michael reaction with methyl acrylate in high yield; the desired synthon 131 is easily obtained (equation 72)[271].



(130) (131) (72)

Methyl-2-butynoate is metalated by lithium *N*-isopropylcyclohexylamide. Quenching of the anion derived from this ester provides a simple synthesis of the methyl-2,3-butadienoate[272]. On the other hand it has been shown that treatment of 2-butynoic acid (132) with slightly more than two moles of lithium 2,2,6,6-tetramethylpiperidide yields a dianion (133) which, when alkylated with 1-bromo-3-methyl-2-butene, yields a mixture of the salts of two acids. These acid salts are methylated with methyl iodide to form esters 134 and 135 (equation 73). The ratio of ene-yne ester (**134**) to ene-allene ester (**135**) is 70:30; The ester **134** obtained in 53–59% yield is easily transformed into nerol[273].



(73)

The 2-butynoic acid dianion **133** reacts with cinnamic aldehyde at −100°C to give 80% of a 1:1 mixture of α- and γ-condensation products; (±)-goniothalamine has been easily synthesized from the γ-condensation product

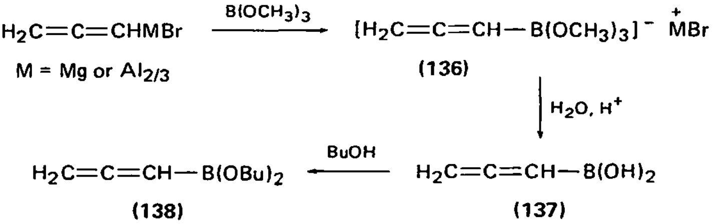
$PhCH{=}CHCHOHCH_2C{\equiv}CCO_2H$[274].

α-Ynamines of type $CH_3C{\equiv}CNR_2$ can be metalated by alkyllithium TMEDA complexes to form lithium derivatives which undergo alkylation upon treatment with a variety of halides[275]. Octadecynyl alcohols and their methyl ethers were metalated with BuLi in ether and yielded on carbonation mono- and diacid mixtures[276] (see Note added to proof, p. 413).

IV. ALLENIC AND PROPARGYLIC DERIVATIVES OF BORON

A. Preparation

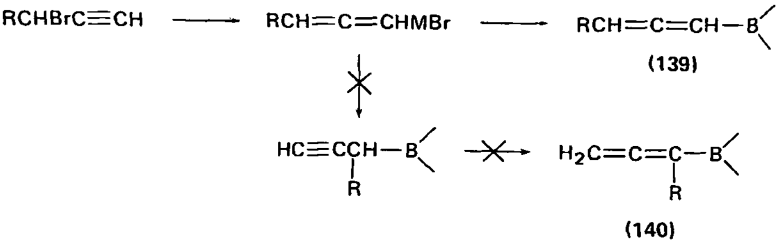
The first allenic boronate described in 1966[277] was the dibutylallenyl boronate **138**; it had been obtained by action of the allenyl-magnesium or -aluminium bromide on methyl borate. First, a tetracoordinated complex **136** is formed, then hydrolysis of this complex liberates the boronic acid **137** which is esterified to yield the boronate **138** by 1-butanol. The fact that a tetracoordinated complex of type **136** may be isolated is good support in favour of the reaction scheme shown in equation (74).



(74)

Treatment of an organometallic derivative of a propargylic bromide with an alkyl borate is a general method for the preparation of alkyl propargylic and allenic boronates[34,279–282]. The structure of boronates, obtained generally in medium yields, depends of the nature of the organometallic. It has been shown that the unsaturated chain structure of the boronate is determined as soon as the tetracoordinated complex is formed; the latter has been isolated in several cases in excellent yields[279,281,282]. In summary, organometallics from bromides like

$BrCH_2C{\equiv}CH$ and $RCHBrC{\equiv}CH$ lead essentially to allenic boronates, those derived from $PhC{\equiv}CCH_2Br$ and $PhC{\equiv}CCHBrCH_3$ lead to acetylenic boronates and those obtained from primary bromides $RC{\equiv}CCH_2Br$ give mixtures of acetylenic and allenic boronates. Moreover, it has been proved that boronic esters are never formed by prototropic transposition of initially formed boronates; so, for instance, allenic boronates prepared from secondary bromides $RCHBrC{\equiv}CH$ always afford linear structure **139** and no ramified structure **140** (equation 75)[277-282].



(139)

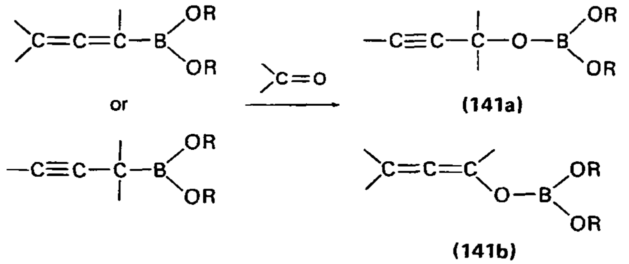
(140)

(75)

Allenic cyclic aminated derivatives of boron have been obtained following an analogous method[282].

B. Reactivity towards Carbonyl Compounds

Allenic boronates behave towards carbonyl compounds as Grignard reagents[283]. They add on the carbonyl group to lead to dissymmetrical borates **141a** and **141b** (equation 76).



(141a)

(141b)

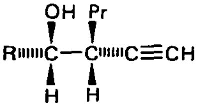
(76)

These dissymmetrical borates are not generally distillable as they dissociate on heating in mixtures of symmetrical borates[283]. Nevertheless they can be isolated with a degree of satisfactory purity after evaporation of the solvent and the excess of carbonyl compound in vacuo and without heating[284]. Dissymmetrical borates behave similarly to magnesium alcoholates: hydrolysis liberates, besides butanol ($R = n$-Bu), the expected β-acetylenic and/or α-allenic alcohols; the structure of the latter is the same as that of borates **141a** and/or **141b**.

The condensation of aldehydes in ether solution at 20°C and slightly bulky ketones in autoclave at 200°C with boronates is always carried out with total transposition of boronate[279-285]. So, allenic boronates lead to propargylic borates (**141a**) and propargylic boronates furnish allenic borates (**141b**). This is in conformity with an S_E2' or S_Ei' reaction mechanism[280,281].

A systematic study of the reaction of the dibutyl allenyl boronate with ketones has been performed by Favre and Gaudemar[286]. Acetone, acetophenone and cyclohexanone only lead to β-acetylenic borates, but with other ketones, these authors obtain a mixture of acetylenic and allenic borates. The proportion of allenic product increases notably with the bulkiness of the carbonyl compound and decreases with the solvating strength of the solvent. Moreover, it has been shown that allenic compounds result from a retention of the structure of the boronic ester[286].

Finally, the stereochemistry of the condensation of dibutyl hexa-1,2-diene-1-yl boronate has been studied[287]. These condensations are very stereoselective and, except in the case of benzaldehyde, *threo* alcohols **142** are predominantly formed. The authors think that a transition state obtained via an S_Ei' mechanism fits best with their experimental results[287].



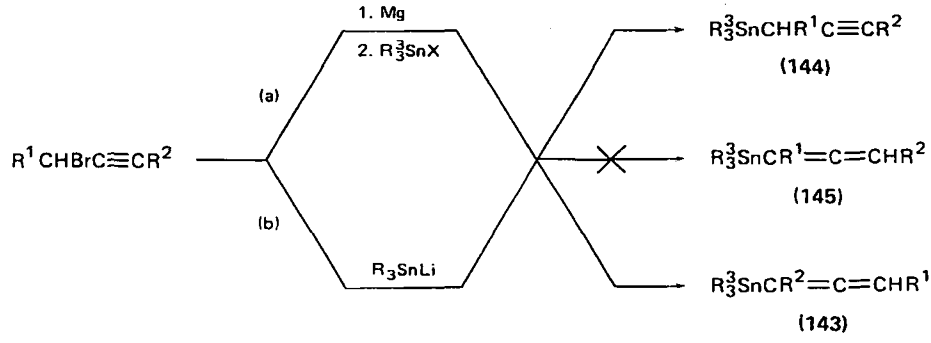
(142)

V. ALLENIC AND PROPARGYLIC DERIVATIVES OF GROUP IVb ELEMENTS

The preparation of allenic compounds of silicon by the action of chlorotrialkylsilane on allenic lithium derivatives was discussed in Section III.

A. Preparation and Isomerization

Allenic (**143**) and propargylic (**144**) compounds of tin are prepared from α-acetylenic bromides according to routes (a) and (b) in equation (77). Yields are generally good but no compound of structure **145** has ever been observed[288].



(77)

Route (a) has been extended to the elements of Group IVb (C, Si, Ge, Sn, Pb)[289]. The proportion of allenic compound in the mixture is greatly increased, with the increasing metallic character of the heteroatom; this is particularly obvious with lead. The proportion of allenic isomer also increases when aromatic groups are substituted by aliphatic ones in the R_3M moiety. These results are summarized in Table 9.

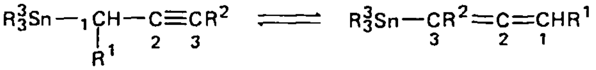
Propargylic organotin compounds can isomerize into their allenic isomers[292–294] according to an equilibrium as shown in equation (78)[295]. The establishment of this equilibrium necessitates either a nucleophilic assistance on the heteroatom by means of an electron-donor solvent or an electrophilic assistance on the triple bond through the medium of a Lewis acid. This type of transposition is also observed for lead compounds, but not for those of silicon and germanium[292].

TABLE 9. Allenic products[289-291] in the reaction

$$BrCH_2C{\equiv}CH \xrightarrow[2.\ R_3MX]{1.\ Mg} R_3MCH_2C{\equiv}CH + R_3MCH{=}C{=}CH_2$$

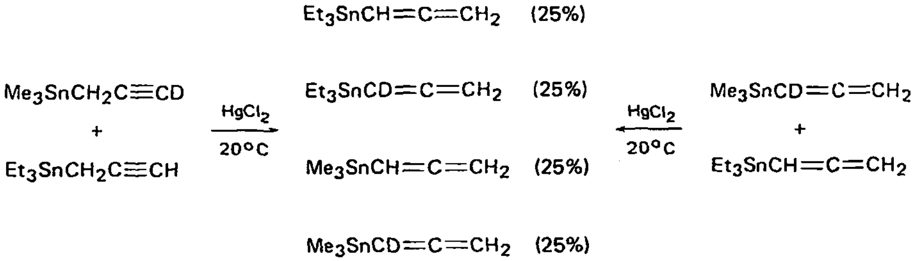
	Allenic compound (% in the mixture)				
R	M = C	Si	Ge	Sn	Pb
Me, Et	–	10	20	70	95
Ph	0	10	20	10	92

In all cases the process involves a rearrangement of the unsaturated chain (equation 78). The equilibrium has been studied starting from mixtures with either, two



$$R^3_3Sn{-}{}_1\underset{R^1}{CH}{-}\overset{}{C}_2{\equiv}CR^2_3 \rightleftharpoons R^3_3Sn{-}CR^2_3{=}C_2{=}CHR^1_1 \qquad (78)$$

triethylated and trimethylated propargylic compounds with the insaturated chain differentiated by a deuterium atom, or the corresponding allenic compound pair. Four allenic compounds in identical proportions have been obtained without proton–deuterium exchange (equation 79)[295].

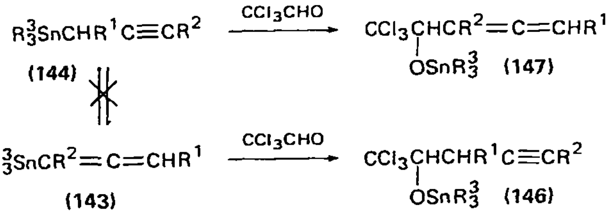


(79)

B. Reactivity

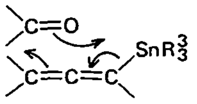
The electrophilic displacement reactions of allenyltins produces allenes (S_E reaction) by direct displacement of the organotin function or acetylenes (S_E' reaction) by an attack at the γ-carbon[296,298].

Recently, a kinetic study of the condensation of propargylic and allenic tin derivatives with chloral was carried out (equation 80)[297]. These condensations yielded two isolable stannic alcoholates **146** and **147**; they were obtained by propargylic or retropropargylic transposition while there was no observable equilibrium between the tin compounds **143** and **144**. The corresponding alcohols are formed by decomposition of the alcoholates by malonic acid.



(80)

Several factors influence the reactivity of these organotin derivatives towards chloral, such as the nature of the R^3 group and the structure of the unsaturated chain[297]; quantitative investigations have been made and kinetic data have been calculated. The authors have likewise found an important entropy contribution during these reactions; this would be in favour of a cyclic mechanism ($S_E i'$):



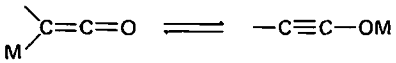
VI. ORGANOMETALLIC DERIVATIVES OF KETENES

Organometallic derivatives from ketenes are not numerous; only compounds of the general formulae $R_3XCH{=}C{=}O$ and $(R_3{}^1X^1)(R_3{}^2X^2)C{=}C{=}O$ in which X^1 and X^2 are elements of Group IVb (Si, Ge, Sn) are well known, and only a few studies on this subject have been reported.

By analogy with the familiar enolate–carbeniate equilibrium (equation 81), an

$$-\underset{\mathrm{M}}{\underset{|}{\overset{|}{\mathrm{C}}}}-\underset{|}{\overset{|}{\mathrm{C}}}{=}\mathrm{C} \rightleftharpoons -\overset{|}{\mathrm{C}}{=}\underset{|}{\mathrm{C}}-\mathrm{OM} \qquad (81)$$

analogous equilibrium between ketonate–ynolate forms of organometallics from ketenes can be conceived (equation 82).

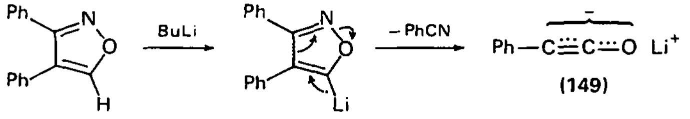


(82)

On treatment with an electrophile, such mixtures could react either at the oxygen or at the carbon. However, contrary to aldehyde or ketone enolates, ketene ynolates are almost unknown. They were sought for but could not be isolated as intermediates during the reaction of ethylmagnesium bromide with methyl propiolate[299]; only lithium phenylethynolate has been recently prepared[300]. However, compounds of similar structure such as alkyne-thiolates $RC{\equiv}CSM$, -selenolates $RC{\equiv}CSeM$ and -tellurolates $RC{\equiv}CTeM$ (M = Li or Na) are well known[301]. They are mainly obtained by insertion of sulphur, selenium and tellurium in alkynyllithiums $RC{\equiv}CLi$[302–307]. The alkynethiolates have been particularly studied; they react at the sulphur atom[301–312].

A. Lithium Phenylethynolate

Lithium phenylethynolate **149** has been obtained by elimination of benzonitrile from 5-lithio-3,4-diphenylisoxazole (**148**) in THF at −60°C (equation 83)[300]. An



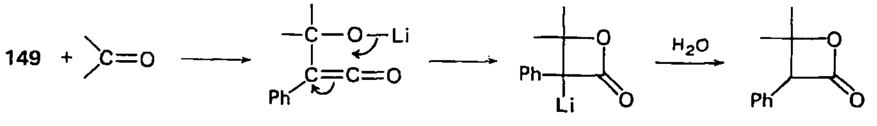
(149)

(148)

(83)

analogous cleavage reaction was observed and the lithium phenylethynethiolate $PhC{\equiv}CSLi$ prepared during the reaction between 4-phenyl-1,2,3-thiadiazole and butyllithium[313].

149 is trapped with chlorotrimethylsilane to form phenyl trimethylsilylketene $(Me_3Si)(Ph)C{=}C{=}O$ (yield = 41%). Reaction with aldehydes and ketones affords the β-lactone **150** after hydrolysis, in acceptable yields (equation 84). The addition



(84)

(151) **(150)**

of lithium phenylethynolate **149** to the carbonyl group has been proposed, with a metalated β-lactone **151** as an intermediate; however, a concerted cycloaddition cannot be ruled out[300]. Before quenching, the lithiated β-lactone (**151**) can be alkylated or hydroxyalkylated.

B. Ketene Derivatives of Group IVb (Si, Ge, Sn)

For a good review on this subject, see Reference 314.

1. Preparation

The first ketene derivative in which a hydrogen atom was replaced by a homologue of carbon was reported by Shchukovskaya and coworkers in 1965 who obtained trimethylsilylketene by pyrolysis of trimethylsilylethoxyacetylene (equation 85)[315].

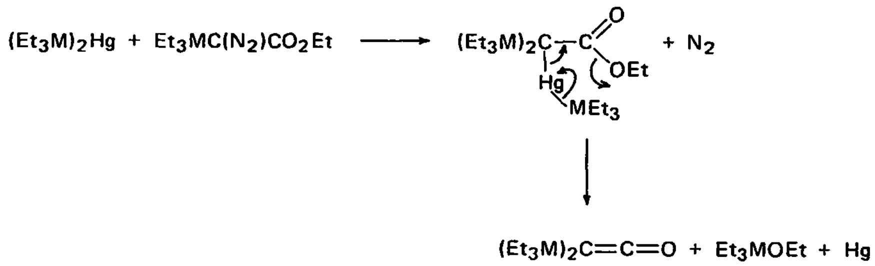
$$Me_3SiC{\equiv}COEt \xrightarrow[\text{yield = 90\%}]{120\text{–}130\,^{\circ}C} Me_3SiCH{=}C{=}O \qquad (85)$$

Trichloro- and trialkylsilyl-ketenes[316] and trialkylgermylketene[317–319] have been analogously synthesized, but the expected products were sometimes mixed with disubstituted ketenes and only bis(trimethylstannyl)ketene was formed on pyrolysis of ethoxy(trimethylstannyl)acetylene[319,320]. Dimetalated ketenes $(R_3M)_2C{=}C{=}O$ (M = Si, Ge, Sn) were isolated in 40–80% yield when trialkylheteroorganic (Si, Ge, Sn) alkoxyacetylenes were treated with trialkylheteroorganic halides in the presence of magnesium bromide; various mixed dimetalated ketenes have also been synthesized[317–323].

Trialkyl-silyl or -germyl ketenes are also obtained from α-metalated carboxylic acids[324–327], either by pyrolysis of (trialkyl-silyl or -germyl) acetic anhydride or by action of triethylamine on the acid chloride (equation 86).

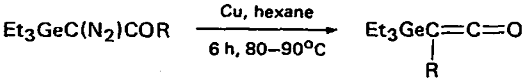
$$\begin{tikzcd}
R_3MCH_2COOH \arrow[r, "H_2C{=}C{=}O"] \arrow[d, "PCl_3"] & R_3MCH_2COOCOMe \arrow[r] & (R_3MCH_2CO)_2O \arrow[r] & R_3MCH{=}C{=}O \\
R_3MCH_2COCl \arrow[r, "Et_3N"] & R_3MCH{=}C{=}O & &
\end{tikzcd} \qquad (86)$$

Newer methods of obtaining metalated ketenes have been described; bis(triethylgermyl)-, bis(triethylsilyl)- and (triethylgermyl)(triethylsilyl)-ketenes can be prepared according to the equation (87)[328,329].



(87)

Monogermylated disubstituted ketenes have been isolated in 53–71% yields (equation 88)[330].

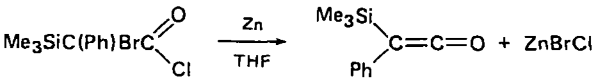


$$Et_3GeC(N_2)COR \xrightarrow[6\text{ h, }80\text{–}90^{\circ}C]{Cu,\text{ hexane}} Et_3Ge\underset{R}{\underset{|}{C}}{=}C{=}O \qquad (88)$$

Bis(trimethylsilyl)ketene is obtained from the decomposition of the ester enolate **152** obtained by addition of *t*-butyl bis(trimethylsilyl)acetate to an equivalent amount of lithium diisopropylamide[331] (equation 89):

$$(Me_3Si)_2CHCO_2Bu\text{-}t + LiN(i\text{-}Pr)_2 \longrightarrow \underset{(152)}{(Me_3Si)_2C(Li)CO_2Bu\text{-}t} \xrightarrow[\text{yield} = 60\%]{r.t.} (Me_3Si)_2C{=}C{=}O \qquad (89)$$

Phenyl(trimethylsilyl)ketene has been prepared by the zinc dehalogenation of phenyl (trimethylsilyl)bromoacetyl chloride (equation 90)[332].



(90)

Bis(trimethylsilyl)thioketene has been prepared via the trimethylsilylethynethiolate (equation 91)[333].

$$Me_3SiC{\equiv}CH \xrightarrow[2.\ 1/8\ S_8]{1.\ BuLi} Me_3SiC{\equiv}CSLi \xrightarrow{Me_3SiCl} (Me_3Si)_2C{=}C{=}S \qquad (91)$$

2. *Structure*

A tautomeric mixture of trialkyl(heteroelement)ketene **153a** and trialkyl(heteroelement)oxyacetylene **153b** had been initially postulated:

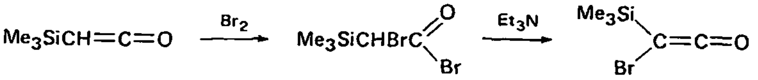
$$\underset{(153a)}{R_3MCH{=}C{=}O} \rightleftharpoons \underset{(153b)}{HC{\equiv}COMR_3}$$

On the basis of infrared and n.m.r. data[316,317,319,334], the ketenic structure **153a** has been assigned. For example, the n.m.r. spectrum of $Et_2SiHCH_a{=}C{=}O$ shows for the proton H_a a doublet at $\delta = 1.65$ p.p.m., this proton resonates in the region of acetylenic protons ($\delta_{HC\equiv} = 1.15$ p.p.m. for $CH_3OC{\equiv}CH$), but the fact that it appears as a doublet argues for structure **153a** since **153b** would require coupling through five bonds[316]. Moreover a strong infrared absorption is observed in the ketenic region. Infrared, ultraviolet and n.m.r. data also indicate the ketenic structure for mono- and digermylated ketenes[317].

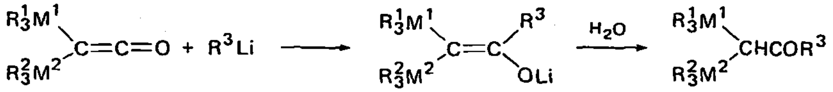
3. *Reactivity*

a. Addition reactions. Mono- and di-heterosubstituted ketenes containing elements of Group IVb (Si, Ge, Sn) give quickly in nearly quantitative yields addition reactions characteristic of the ketene group. Water[315,335,336], alcohols[317,330,337], ammonia, and primary and secondary amines[317,319,336,338] lead to acids, esters and amides, respectively.

Ketenes and silylketenes (but not germylated ketenes[317]) add bromine; for instance, bromine readily adds to trimethylsilylketene to yield trimethylsilylbromoacetyl bromide[315] which yields trimethylsilylbromoketene by action of triethylamine (equation 92)[339].


(92)

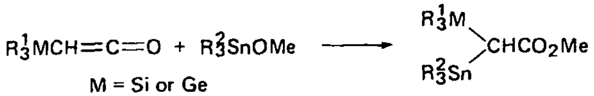
Di(trialkylsilyl)-, di(trialkylgermyl)- and mixed (trialkylsilyl)(trialkylgermyl)-ketenes react with organolithium compounds on heating, and after hydrolysis, the dimetalated ketones are obtained (equation 93)[320,340].


(93)

However, with trimethylstannylketene, alkyllithiums induce cleavage of the tin–carbon bond. In contrast, butyllithium has been added, at – 100°C in THF, to trimethylsilylketene to form, presumably, the ketene ynolate 154; quenching this solution with an equivalent amount of trimethylchlorosilane gives 80–90% yields of bis(trimethylsilyl)ketene (equation 94)[344].

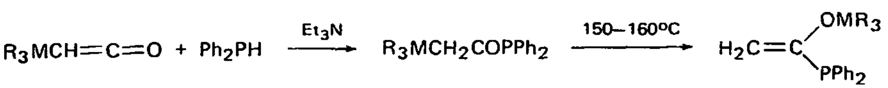
$$\mathrm{Me_3SiCH{=}C{=}O} \xrightarrow{\mathrm{BuLi}} \underset{(154)}{\mathrm{Me_3SiC{\equiv}COLi}} \xrightarrow{\mathrm{Me_3SiCl}} \mathrm{(Me_3Si)_2C{=}C{=}O} \qquad (94)$$

Dimetalated acetic esters 155 are obtained by addition of trialkylmethoxytins with trialkyl-silyl or -germyl ketenes[345,346] (equation 95) while trialkylmethoxygermanes furnish derivatives of 3-hydroxy-3-butanoic acid[345].


(95)

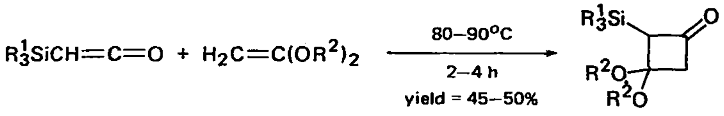
(155)

In the presence of catalytic amounts of triethylamine, diphenylphosphine adds to trialkyl-silyl or -germyl ketenes with formation of stable trialkyl-silyl or -germyl phosphines[342,343] which rearrange into the corresponding *O*-isomers on heating (equation 96).

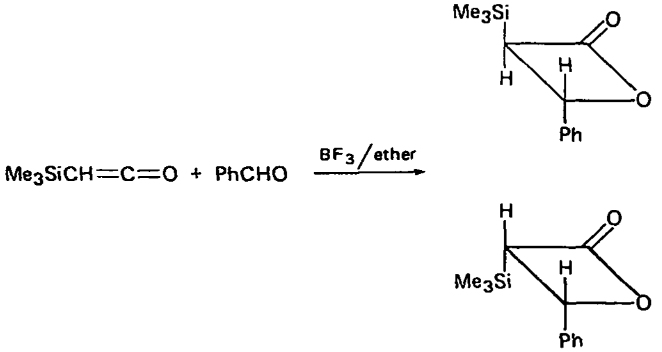

(96)

On the other hand, instead of the expected *C*-derivatives, only *O*-substituted products are obtained by action of diphenylphosphinous acid, dialkyl hydrogen phosphites and *O,O*-dimethyl hydrogen phosphorothioite[341–343].

b. Cycloadditions. Numerous cycloaddition reactions of ketenes have been described; but, contrary to ketenes and to (trimethylsilylmethyl)ketene[349], trimethylsilylketene does not undergo cycloaddition reactions with dienes and olefins[337]. This ketene only gives cycloadducts with the dimethyl and diethyl acetals of ketene (equation 97)[347] and with benzaldehyde (equation 98)[348] under rather vigorous conditions. In the last case, *cis-* and *trans*-4-phenyl-3-trimethylsilyl-2-oxetanones are obtained in 2:1 proportions. Trimethylsilylbromoketene gives cycloaddition reactions easily[339].

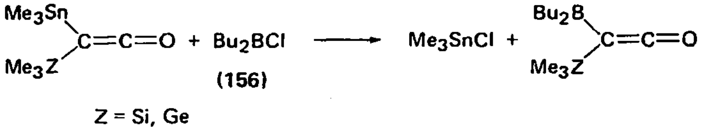


(97)



(98)

c. Miscellaneous reactions. Stannylsilyl- or stannylgermyl-ketenes react readily with boryl chloride (**156**), the stannyl groups being replaced by boryl groups (equation 99)[350].

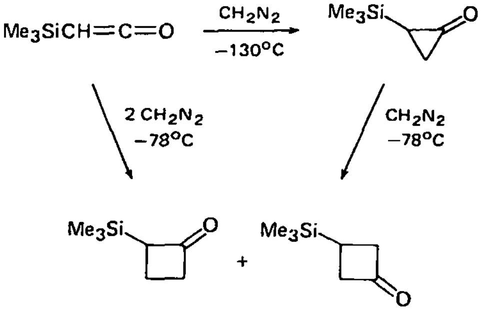


$$(Me_3Sn)(Me_3Z)C{=}C{=}O + Bu_2BCl \longrightarrow Me_3SnCl + (Bu_2B)(Me_3Z)C{=}C{=}O \qquad (99)$$

(156)

Z = Si, Ge

The treatment of trimethyl-silyl- and -germyl-ketenes[351] and phenyltrimethylsilylketene[332] with diazomethane leads to the corresponding trimethyl-silyl- and -germyl-cyclopropanones; an excess of diazomethane affords the silylated and germylated cyclobutanones (equation 100).



(100)

Monometalated ketenes also undergo olefination with stabilized phosphorus ylides to give allenic compounds in good yields (equation 101)[337,352]. Ozonation of trialkylsilylketene yields trialkylsilyl formates (equation 102)[353].

$$\mathrm{Me_3MCH{=}C{=}O + Ph_3P{=}CHA \longrightarrow Me_3MCH{=}C{=}CHA + Ph_3PO} \qquad (101)$$

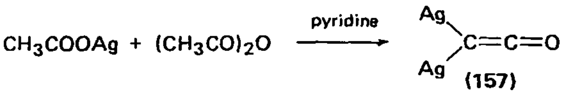
$$\mathrm{M = Si, Ge} \qquad \mathrm{A = CO_2Me, CO_2Et, CN, COCH_3}$$

$$\mathrm{R_3SiCH{=}C{=}O} \xrightarrow[\text{yield = 40–60\%}]{\mathrm{O_3}} \mathrm{HCOOSiR_3} \qquad (102)$$

C. Metal Ketenides $M_2C{=}C{=}O$

Finally, we shall mention a recent class of organometallic compounds, the metal ketenides of formula $M_2C{=}C{=}O$ where M = Ag, Cu, Au. These ketenides are very attractive because they can act as powerful oxidation catalysts[354,355].

The most easily prepared compound of this group is silver(I) ketenide 157[356-359]. The reaction of acetic anhydride with a silver salt, e.g., the acetate, in the presence of pyridine is a particularly convenient high yield procedure (equation 103)[358]. The



$$\mathrm{CH_3COOAg + (CH_3CO)_2O \xrightarrow{pyridine} Ag_2C{=}C{=}O} \qquad (103)$$

(157)

structure of silver ketenide (157) has been well studied[354,356]. Gold(I)[360] and copper(I)[361] ketenides have also been prepared.

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Note added to proof (see p. 396)

Allenic carbanion $PhC{=}C{=}C(OEt)_2$ was obtained from the propargylic acetal $PhC{\equiv}CCH(OEt)_2$ and reacted with electrophiles[362]. Allenic phosphoramides $(RO)_2P(O)N(CH_3)CH{=}C{=}CH_2$ have been alkylated after metalation[363]; the latter anions are equivalent to acyl anions.

Since the submission of this chapter to the editor, numerous articles using allenic organometallic derivatives have been published. Interesting syntheses were realized mainly from allenic lithium compounds[364], allenic ethers[365–367] and thio ethers[368]. These results reflect the growing interest in this field.

The Chemistry of Ketenes, Allenes and Related Compounds
Edited by Saul Patai

CHAPTER 11

Preparation and uses of isotopically labelled allenes

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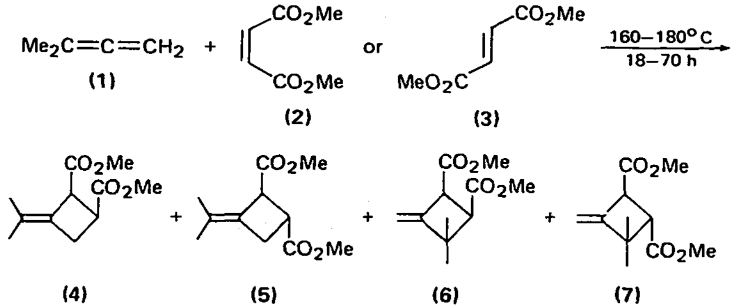
I. INTRODUCTION AND SCOPE

Within the past ten years a surge of general interest in the chemistry of molecules containing the allenic functional group[1] has generated a number of detailed mechanistic investigations of the preparative methods and subsequent reactions of the title moiety. A multitude of mechanistic probes have been employed in the pursuit of such information. Only recently, however, have syntheses of the allenic functional group become of sufficient scope to allow the convenient introduction of various isotopes in or directly attached to the three carbon group (C=C=C) or in groups immediately adjacent to it.

This chapter will concentrate on the utilization of allenes isotopically labelled at $C_{(1)}$ or $C_{(3)}$ or at the atoms or groups directly attached to $C_{(1)}$ and $C_{(3)}$ to elucidate the mechanisms of reaction of that functional group. For the sake of completeness the reactions of other functional groups which result in the formation of isotopically labelled allenes are also included. Solvent isotope effects in reactions of the allenic functional group are not included. The literature is complete through 1977.

II. CYCLOADDITION REACTIONS

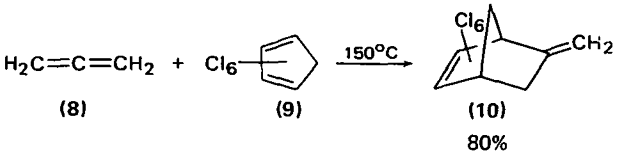
Early kinetic and stereochemical studies of [2 + 2] cycloaddition reactions of allenes led some workers to the conclusion that such reactions occurred via a concerted, antarafacial, multicentre process. For example, the high degree of stereospecificity of the reaction of 1,1-dimethylallene (1) with dimethyl maleate (2) or fumarate (3) was considered to be strong evidence favouring the classification



(1)

of this reaction as a counterexample of the Woodward–Hoffmann[2] formulation. In this case reaction of 1 with 3 was found to be 99% stereospecific giving only 5 and 7 in the ratio 11.5:1. Reaction of 1 with 2 produced all four possible adducts in the ratio (4 + 5):(6 + 7) = 5 but was also >90% stereospecific.

In an elegant series of papers Dolbier and coworkers investigated a broad spectrum of allene [2 + 2], [2 + 3] and [2 + 4] cycloadditions[3–6] (equations 2–8).



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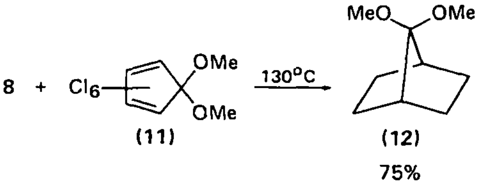

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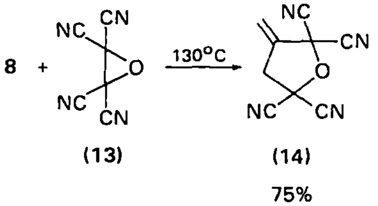

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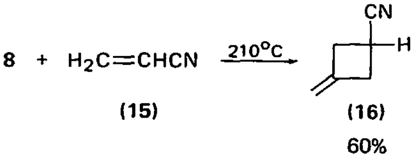

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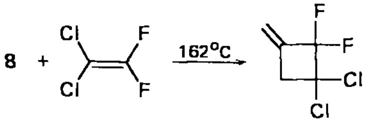
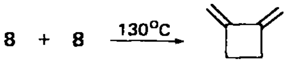


(17) (18)

75%

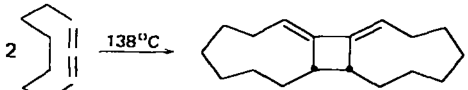
(6)



(19)

91%

(7)



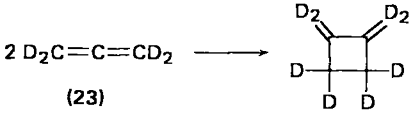
(20) (21)

95%

(8)

They determined both *intra*molecular [allene-1,1-d_2 (22) substituted for 8] and *inter*molecular [allene-d_4 (23) substituted for 8] kinetic secondary isotope effects for a number of these reactions.

In a *concerted* cycloaddition (equation 9) allene essentially behaves as two identical, isolated double bonds and unsymmetrically deuterated allenes, such as allene-1,1-d_2 should give rise to *intra*molecular secondary isotope effects of the same magnitude and direction as those obtained *inter*molecularly in experiments using mixtures of deuterated and undeuterated alkenes[7-11]. In a stepwise cycloaddition the central sp-hybridized carbon atom is attacked (equation 10) giving rise



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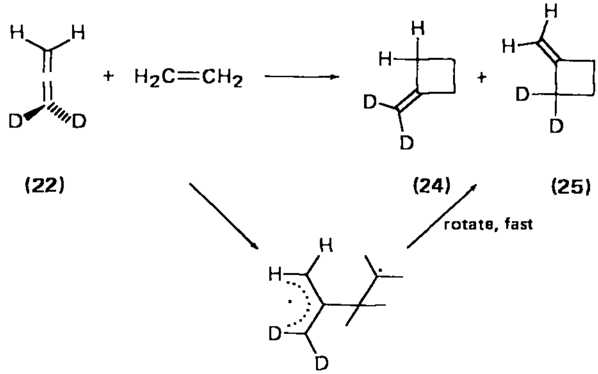
(9)



(22) (24) (25)

(26)

(10)

to an allylic radical where unsymmetrical labelling may result in an isotope effect on the product-forming step. Synchronous formation of new σ bonds involving

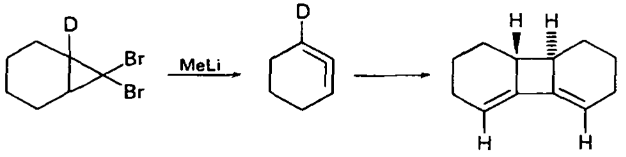
TABLE 1. Secondary deuterium isotope effects in allene cycloadditions[6]

Cycloaddition	System	k_H/k_D(*intra*)	k_H/k_D(*inter*)
[2 + 2]	8–15	1.13–1.21	1.05
[2 + 2]	8–17	1.17	
[2 + 2]	8– 8	1.14	1.02
[2 + 2]	20–20	1.10	
[2 + 3]	8–13	0.93	
[2 + 4]	8– 9	0.90	0.90
[2 + 4]	8–11	0.92	

rehybridization at $C_{(1)}$ or $C_{(3)}$ from sp^2 to sp^3 almost invariably results in inverse *intra*- and *inter*-molecular secondary isotope effects, $k_H/k_D < 1$, whereas a two-step mechanism (first step rate-limiting) involves no change in hybridization at $C_{(1)}$ or $C_{(3)}$ and should give rise only to a small, normal *inter*molecular isotope effect. A small intramolecular isotope effect might also be expected in this case owing to relief of torsional and/or nonbonded interactions in the planar allylic radical (26).

A normal *intra*molecular isotope effect was observed in all [2 + 2] cycloadditions studied (equations 5–8; Table 1). In addition, relatively small *inter*molecular isotope effects were observed. These results suggest strongly that these [2 + 2] cycloadditions are stepwise reactions. In contrast the results for the [2 + 3] and [2 + 4] cycloaddition reactions studied strongly imply a concerted mechanism.

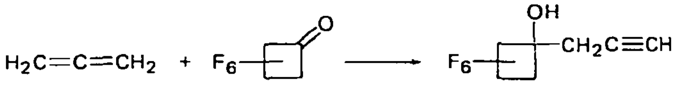
Moore and coworkers studied the dimerization (equation 11) of 1,2-cyclohexadiene-1-d (27) generated from dibromide-1-d (28)[12]. Dimer (29)-d_2 was isolated and analysed by deuterium magnetic resonance. This system exhibits a normal *intra*molecular secondary isotope effect and thus provides independent corroboration of Dolbier's work.



(28) (27) (29)

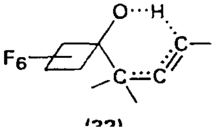
(11)

In a somewhat related study the allene–perfluorocyclobutanone (30) ene reaction (equation 12) has been examined[13,14]. The intramolecular isotope effect for reaction of allene-1,1-d_2 with **30** was found to be $k_H/k_D = 3.54 \pm 0.03$. It differs from that observed in the reaction of allene-1,3-d_2 with **30** where $k_H/k_D = 2.17 \pm 0.05$. The intermolecular isotope effect using the reaction of **30** with allene-1,1,3,3-d_4 is found to be $k_H/k_D = 1.99 \pm 0.07$. In a concerted process involving intermediate **32** a significant primary isotope effect is expected due to



(30) (31)

(12)



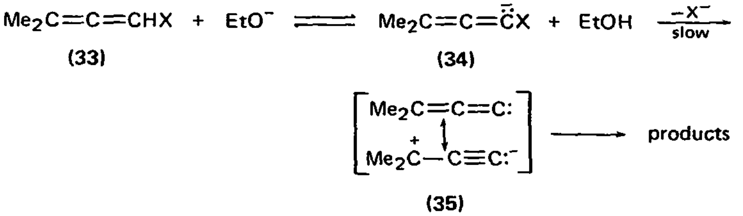
(32)

proton transfer. In addition secondary isotope effects due to hybridization changes at $C_{(1)}$ ($sp^2 \rightarrow sp^3$ with $k_H/k_D < 1$) and $C_{(3)}$ ($sp^2 \rightarrow sp$ with $k_H/k_D > 1$) are predicted. These three factors combine uniquely to produce the observed effect for the three deuterated allenes studied. The magnitude and direction of each contribution can thus be calculated from the observed effects. This treatment yields a calculated primary isotope effect for the process of $k_H/k_D = 2.41$, a secondary isotope effect for $sp^2 \rightarrow sp^3$ rehybridization of $k_H/k_D = 0.868$, and a secondary isotope effect for $sp^2 \rightarrow sp$ rehybridization of $k_H/k_D = 1.10$. These are shown to be consistent only with the concerted, symmetry-allowed process implied by **32**.

III. SOLVOLYSIS OF HALOALLENES

The solvolysis of trisubstituted bromo- and chloro-allenes and 3,3-disubstituted bromoallenes has been studied extensively.

Shiner and Humphrey examined the base-catalysed hydrolysis of 1-bromo-3-methyl-1,2-butadiene (**33**)[15]. A mechanism similar to that proposed for the hydrolysis of terminal propargyl halides[23,24] is proposed (equation 13). The



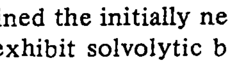
$$Me_2C{=}C{=}CHX + EtO^- \rightleftharpoons Me_2C{=}C{=}\bar{C}X + EtOH \xrightarrow[\text{slow}]{-X^-} \left[\begin{array}{c} Me_2C{=}C{=}C: \\ \updownarrow \\ Me_2\overset{+}{C}{-}C{\equiv}C:^- \end{array}\right] \longrightarrow \text{products} \qquad (13)$$

(**33**) (**34**) (**35**)

rate of allenyl hydrogen exchange with deuterated medium is 10–20 times faster than the formation of products. This is in accord with the preequilibrium proton loss proposed but not with a concerted α elimination or simple S_N1 solvolysis mechanism. Furthermore a common-ion rate depression with added 0.2M Br^- of 17% strongly suggests loss of Br^- from **34** as the rate-limiting step. The β secondary isotope effect reported is also consistent with this interpretation. For **34a** $k_H/k_{D_6} = 1.15$ whereas **35a** exhibits $k_H/k_{D_6} = 1.31$. These are to be contrasted with that

$(CD_3)_2C{=}C{=}CHBr$

(**34a**)



$$(CD_3)_2\overset{X}{\overset{|}{C}}{-}C{\equiv}C{-}H$$

(**35a**)

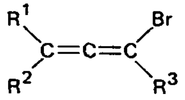
observed for solvolysis of *t*-butyl chloride-d_6 where $k_H/k_{D_6} = 1.71$[25]. These results imply a transition state in which the degree of vacancy at $C_{(3)}$ is substantially lower than is expected for a simple S_N1 process, i.e. the carbene zwitterion (**35**) is implicated.

Schiavelli and coworkers[16–22] have examined the initially neutral solvolysis of a wide variety of haloallenes. The substrates exhibit solvolytic behaviour typical of unimolecular bond heterolysis as the slow step. These compounds exhibit *m* values vs *Y* between 0.80 and 1.06 in aqueous ethanol, k_{Br}/k_{Cl} leaving-group ratios of 20–58, $\Delta S^\ddagger$ values from −10 to +9 e.u., ρ values against σ^+ of −2.0 and CH_3/H ratios of $10^{4.5}$ in 60% aqueous ethanol (60E). Typical of this behaviour is the solvolysis of **34** in aqueous ethanol which shows $m = 0.88$ and the 'expected' secondary isotope effect values for α- and β-deuterium substitution in aqueous ethanol. It is interesting to note that the magnitude of these secondary isotope effects is strongly dependent upon solvent and substituent as shown in Table 2. It was concluded that these data are indicative of considerable involvement by solvent

TABLE 2. Secondary deuterium isotope effects in solvolysis of disubstituted bromoallenes 36–43[20–22]

$(k_H/k_D)_\alpha$	$k_H/k_{\beta\text{-}CD_3}$
36/37 = 1.28, 50E (75°C)	38/39 = 1.17, 60E (65°C)
38/40 = 1.20, 50E (65°C)	= 1.33, 97T (65°C)
= 1.22, 70T (65°C)	41/42 = 1.15, 60E (65°C)
41/43 = 1.20, 50E (55°C)	= 1.15, 97T (65°C)
= 1.28, 97T (65°C)	= 1.15, 97T (65°C)

during solvolysis most likely at an ion-pair intermediate stage. Salt effects on the titrimetric and polarimetric rates of solvolysis of (*R*)-(−)-44 have been reported.



(36) $R^1 = R^2 = t\text{-Bu}, R^3 = H$

(37) $R^1 = R^2 = t\text{-Bu}, R^3 = D$

(38) $R^1 = t\text{-Bu}, R^2 = CH_3, R^3 = H$

(39) $R^1 = t\text{-Bu}, R^2 = CD_3, R^3 = H$

(40) $R^1 = t\text{-Bu}, R^2 = CH_3, R^3 = D$

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

(42) $R^1 = R^2 = CD_3, R^3 = H$

(43) $R^1 = R^2 = CH_3, R^3 = D$

(44) $R^1 = Et, R^2 = CH_3, R^3 = H$

A marked increase in k_{rac} with added Br^- in 97:3 (w/w) 2,2,2-trifluoroethanol–water (97T) and $k_{rac} \neq 0$ in the absence of added nucleophile are key findings in this study. These findings are detailed below:

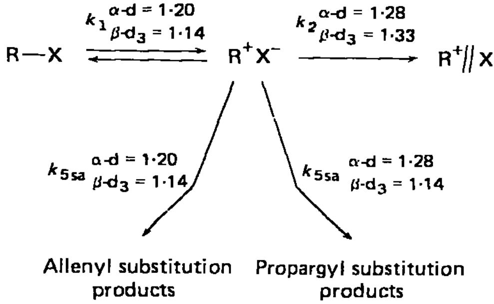
(1) The ratio k_α/k_t remains constant with changing solvent nucleophilicity, 10^5 $k_{rac}^{97T} = 0.43$ and 10^5 $k_{rac}^{60E} = 0.55$.
(2) No common ion effect is observed.
(3) No special salt effect is observed.
(4) k_α shows substantial enhancement upon addition of Br^- in 97T; k_t does not, i.e. 10^5 k_{rac} increases from 0.43 in the absence of Br^- to 4.1 at $[Br^-] = 0.1$ M. In 60E k_{rac} is constant with added Br^-.

The results can best be interpreted in terms of a mechanism of solvolysis which involves an ion pair. It is thus possible to interpret the secondary isotope effects in the light of this more recent work. For aqueous ethanolysis of 35[a], $k_H/k_{\beta\text{-}CD_3} = 1.33$, which is comparable to the β secondary isotope effect observed for *t*-butyl chloride, $k_H/k_{\beta\text{-}CD_3} = 1.31$. These compounds are known to solvolyse by a mechanism in which conversion of a tight ion pair to a solvent-separated ion pair is rate-limiting[26]. For a similar process, therefore, the fractionation factor[27] between $R_2C{=}C{=}CHBr$ and $R_2C{=}C{=}\overset{+}{C}H$ should also be 1.33/CD_3. It is significant that this value is obtained in solvolysis of 38 in 97T thus implying a similar mechanism of solvolysis for this substrate. Where β-CD_3 effects are substantially reduced from this value there must be some nucleophilic attachment at either the allenyl or the propargyl centre in cation **45** in the rate-determining step.

$$[R_2C{=}C{=}\overset{+}{C}H \longleftrightarrow R_2\overset{+}{C}{-}C{\equiv}CH]$$

(45)

Shiner and Buddenbaum have calculated[28] the expected fractionation factor for α-deuterium substitution for sp^2-hybridized carbon → sp-hybridized carbon and obtained the value 1.28 – the exact value obtained for $(k_H/k_D)_\alpha$ in the solvolysis of **36** in 50E and **41** in 97T. A simplified scheme can be constructed combining these data (Scheme 1). Rate-limiting attack via $k_{5\,s}$ at either allenyl or propargyl site



SCHEME 1.

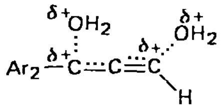
should reduce the hyperconjugative β-d_3 effect to about half its k_2 value; the same reduced value should apply if k_1 is rate-limiting. On the other hand, the α-d effect is only reduced from its maximum value of 1.28 if nucleophilic attack is at $C_{(1)}$, the allenyl centre. This obtains if k_1 or $k_{5\,sa}$ is rate-limiting but not if $k_{5\,sp}$ is slow. For $k_{5\,sp}$ rate-limiting α-d should be a maximum.

Therefore $k_{5\,sp}$ must be rate-limiting for **41** in 97T. In aqueous ethanol k_1 becomes rate-limiting. For hindered substrates in aqueous 2,2,2-trifluoroethanol k_2 becomes rate-determining since $k_{5\,sp} \ll k_2$. Thus **38** and possibly **36** follow this pathway. A mixed mechanism probably obtains for hindered substrates in aqueous ethanol.

It should be noted further that the Meyer–Schuster rearrangement (equation 14) has been shown[29] to occur via rate-limiting nucleophilic attack at the allenyl

$$Ar_2C(OH)C{\equiv}C{-}H(D) \xrightarrow{H^+} Ar_2C{=}CHCHO \qquad (14)$$

(46)



$$Ar_2\overset{\overset{\delta+}{OH_2}\;\vdots\;\delta+}{C}{\cdots}C{\equiv}\overset{\overset{\delta+}{OH_2}\;\delta+}{C}{-}H$$

(47)

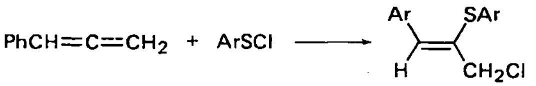
centre of an ion-dipole pair, **47**. Substitution of deuterium as indicated in **46** results in an inverse α secondary isotope effect of $k_H/k_{\alpha\text{-}D} = 0.92$. Since the propargyl centre of cation **45** generated solvolytically from an allenyl on propargyl halide is the almost exclusive site of nucleophilic attack by water, the carbonium ion formed by loss of water from protonated **46** must return more rapidly than it rearranges. This is consistent with the mechanism proposed for the Meyer–Schuster rearrangement.

IV. ADDITION REACTIONS

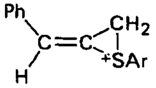
While the mechanism of ionic and radical additions to allenes has been the subject of much study[1], the use of isotopic labelling experiments to substantiate the accepted pathways for these reactions has been minimal.

Okuyama and coworkers have examined the hydrochlorination[30], hydrobromination[30] of, and addition of 2,4-dinitrobenzenesulphenyl chloride[31] to, phenylallene. Phenylallene was found to give the hydrochlorination product arising from addition to the terminal bond, i.e. the 2,3-adduct, cinnamyl chloride (equation 15). Their evidence shows that this product is formed by electrophilic attack at the 1,2-bond, specifically at $C_{(2)}$, followed by allylic rearrangement and attachment of nucleophile at $C_{(3)}$. Jacobs and collaborators showed that allylic rearrangement could not be involved in the sulphenylation of aliphatic allenes[32]. Okuyama has measured the kinetic secondary isotope effects for addition of 2,4-dinitrobenzenesulphenyl chloride to phenylallene (Table 3). These results substantiate a mechanism involving the episulfonium ion, 48. The rate enhancement from 3,3-dideuteration is interpreted in terms of partial rehybridization at $C_{(3)}$ as required by 48 and is similar to those reported in the sulphenylation of styrene[33]. No rehybridization at $C_{(1)}$ is implied by the lack of effect upon deuteration at that site.

$$\mathrm{PhCH{=}C{=}CH_2 + HX \longrightarrow PhCH{=}CHCH_2X} \qquad (15)$$

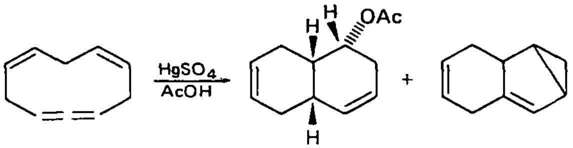


(16)



(48)

The oxymercuration of cyclodeca-1,2,5,8-tetraene (49) gives only rearranged products[34] (equation 17). The formation of 50 and 51 represents a transannular rearrangement during the reaction. Since the reaction is highly stereospecific a



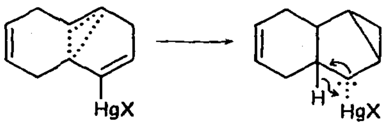
(49) (50) (51)

(17)

TABLE 3. Secondary isotope effects in addition of ArSCl to phenylallene[31]

Allene pair	k_H/k_D
$PhCH{=}C{=}CH_2/PhCD{=}C{=}CH_2$	1.01 ± 0.03
$PhCH{=}C{=}CH_2/PhCH{=}C{=}CD_2$	0.92 ± 0.02/deuterium

bridged intermediate 52 which undergoes homoallylcyclopropylcarbinyl rearrangement to the metal-complexed carbene 53 is proposed (equation 18). These intermediates are known to undergo the hydride shift shown[35] to yield 51. Oxymercuration of 49 with $HgSO_4$ in CH_3COOD results in deuterium incorporation into 50 at $C_{(4)}$ as required by the accepted addition–elimination mechanism whereby mercury is lost. No deuterium is found in 51 as required by the proposed mechanism.

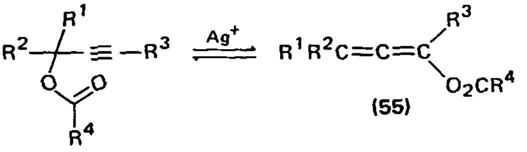


(52) (53)

(18)

V. PROPARGYL–ALLENYL REARRANGEMENTS

The mechanism of the Ag(I)-catalysed propargyl ester/allenyl ester rearrangement (equation 19) has been investigated by Schmid and coworkers[36]. ^{14}C and ^{18}O-labelling experiments were done in conjunction with stereoisomeric labelling. These workers report that 54 ($R^4 = p$-$O_2NC_6H_4$-) ⇌ 55 ($R^4 = p$-$O_2NC_6H_4$-) occurs in an Ag(I) complex formed in a preequilibrium step. Kinetic experiments support this conclusion. Most notably, added cyclohexene strongly decreases the rate of rearrangement. This is also the case in solvents known to form Ag(I) complexes. The Ag(I) complex involved here is described as a π complex with the triple bond in 54 or with one of the two double bonds in 55.

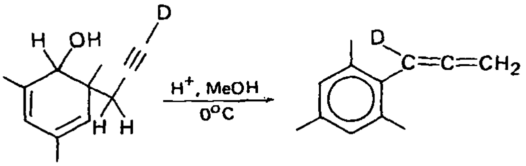


(54) (55)

(19)

Furthermore the shift of the carboxyl moiety occurs *intra*molecularly. *p*-Nitrobenzoic acid (carboxyl-^{14}C) is not incorporated in reactant or product in the course of rearrangement. An internal ion pair having equivalent oxygens is ruled out because an ^{18}O-carbonyl label in 54 is found exclusively in the alkoxyl oxygen in 55. Optically active propargyl esters lead to racemic allenyl esters. Rearrangement of *erythro*-54 (carbonyl-^{18}O) and *threo*-54 (carbonyl-^{18}O) shows that the stereospecifically *formed* allenyl esters epimerize without ^{18}O-scrambling 2 and 40 times as rapidly respectively as the rearrangement occurs. The reaction is best described as a [3s, 3s]-sigmatropic reaction.

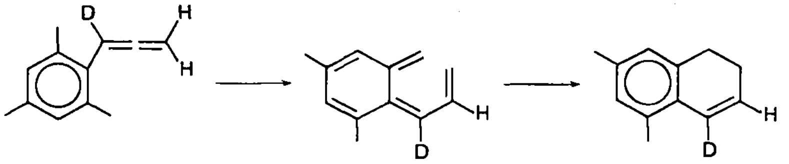
Isotopically labelled mesitylallene (57) has been prepared by the rearrangement of 56 (equation 20)[37,38] and rearranges cleanly in *n*-decane at 150–190° C via a



(56) (57)

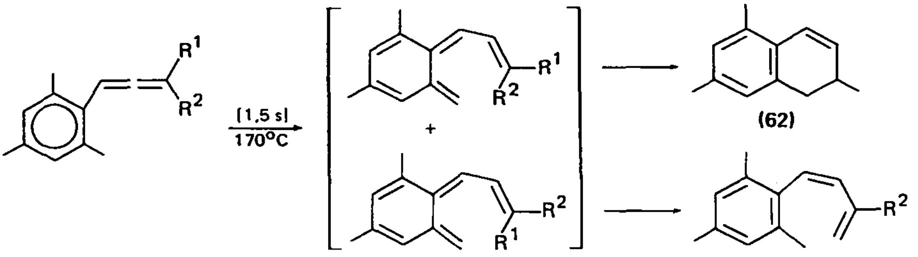
(20)

[1,5s]-sigmatropic hydrogen shift to yield **58** which cyclizes under the same conditions yielding **59**, (equation 21). Allenes **60** and **61** undergo similar rearrangement/cyclization to 1,2-dihydronaphthalene (**62**) in one case or undergo [1, 7a]-sigmatropic hydrogen shifts to 1-mesityl-(*Z*)-buta-1,3-dienes, (*Z*)-**64** and (*Z*)-**65**, in quantitative yields (equation 22). Deuterium-labelling experiments show that the rate-limiting step is a [1, 5s] hydrogen shift from an sp^3-hybridized carbon in the side-chain to the sp-hybridized central carbon of the allene moiety. When labelled 2′-isopropylphenyl allenes **66** and **67** (equation 23) are rearranged to the corresponding 1-(*Z*)-propenyl-2-isopropenyl benzenes, the primary kinetic isotope effect observed is $k_H/k_D = 3.45$ (**68**/**66**). The secondary isotope effect (**68**/**67**) is found to be $k_H/k_{D_6} = 1.20$. These are reported to be consistent only with the rate-limiting step proposed.



(57) (58) (59)

(21)



(62)

(22)

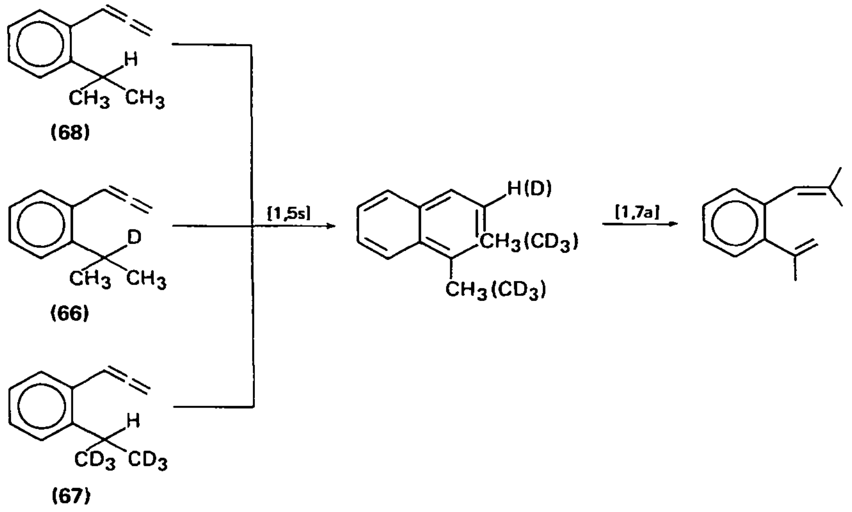
R^1 = Me, R^2 = H (60)

R^1 = R^2 = Me (61)

(63)

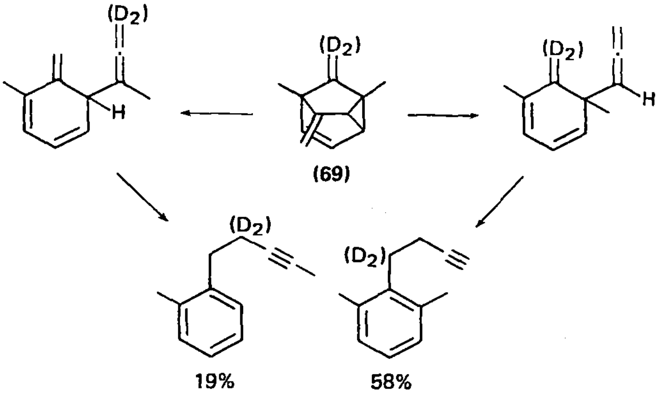
R^2 = H (*Z*)-(64)

R^2 = Me (*Z*)-(65)



(23)

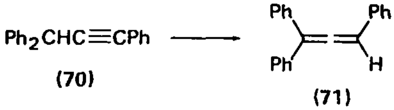
Schmid and coworkers have reported[39] that the tricyclic dimethylene hydrocarbons thermally rearrange to 4-aryl-1-butynes via an unstable 6-allenyl-1-methylenecyclohexa-2,4-diene intermediate. Rearrangement of labelled 69 (equation 24) allowed these workers to demonstrate that the allenyl moiety was formed by a cycloreversion (retro-Diels–Alder) reaction which then rearranges with complete inversion.



(24)

VI. BASE-CATALYSED ISOMERIZATION OF ACETYLENES

The base-catalyzed isomerization of monoalkynes was first reported by Favorskii who suggested that allenic intermediates were involved[40]. Since then a number of workers have examined the isomerization of 1,3,3-triphenylpropyne (70) to triphenylallene (71). The intramolecularity of the isomerization 70-3-d → 71-3-d



(70) (71)

(25)

ranges from >90% in DMSO/methyl sulphenyl anion/triethylenediamine[41,42] to 19% in methanol/potassium methoxide[43]. The primary kinetic isotope effect associated with the rearrangement, $k_H/k_D = 6.7-8.2$ in DMSO/tetramethylammonium hydroxide at 30° C, strongly indicates a rate-determining step involving proton abstraction by the base and a highly advanced transition state[41].

Klein and Brenner[44] observed that dimetalation of 1-phenylpropyne (72) by *n*-BuLi occurs faster than monometalation and further yields a dianion different from the dianion derived from 3-phenylpropyne (73) or from phenylallene (74). Thus deuteration of the dianion derived from 72 yields 75 indicating that a 1,3-hydrogen shift has occurred during the dimetalation or subsequent deuteration. The transfer could not have occurred at the dianion stage since the dianion formed from 72 is different from that formed from 73 and 74 and the dianion from 72

$PhC{\equiv}C{-}CH_3$ (72) $PhCH_2C{\equiv}CH$ (73) $PhCH{=}C{=}CH_2$ (74) $PhCHDC{\equiv}CD$ (75)

does not rearrange to that derived from 73 or 74. Further since the dianion from 72 forms faster than the monoanion, the rearrangement must occur at the monoanion stage during the deuteration. Formation of 75 thus proceeds by equation (26). On the other hand, 74 yields undeuterated 76 in the first stage of metalation which

$$\mathbf{72} \xrightarrow{2\,n\text{-BuLi}} \mathrm{PhC{\equiv}CCH^{2-}} \xrightarrow{\mathrm{D_2O}} \mathrm{PhCD{=}C{=}\bar{C}H} \longleftrightarrow \underset{\mathbf{(76)}}{\mathrm{Ph\bar{C}DC{\equiv}CH}} \xrightarrow{\text{H-shift}}$$

$$\underset{\mathbf{(77)}}{\mathrm{PhCHDC{\equiv}C^-}} \xrightarrow{\mathrm{D_2O}} \underset{\mathbf{(75)}}{\mathrm{PhCHDC{\equiv}CD}} \tag{26}$$

rapidly isomerizes to undeuterated 77 and yields 78 on further metalation. Metalation of 3-phenylpropyne-1,3,3-d$_3$ (79) with two equivalents of *n*-BuLi and subsequent protonation yields 3-phenylpropyne-3-d$_1$ (80) as required by the proposed mechanism. In a related study[45] hepta-2,4-diynoic acid (81) isomerizes to hepta-3,5-diynoic acid (84) by the sequence given in equation (28). Of interest here is that n.m.r. studies of the rate of isomerization of 82 in aqueous NaOH show that deuterium incorporation at $C_{(4)}$ occurs prior to isomerization.

$$\underset{\mathbf{(78)}}{\mathrm{Ph\bar{C}HC{\equiv}C^-}}$$

$$\underset{\mathbf{(79)}}{\mathrm{PhCH_2C{\equiv}CD}} \xrightarrow{2\,n\text{-BuLi}} \xrightarrow{\mathrm{H_2O}} \underset{\mathbf{(80)}}{\mathrm{PhCHDC{\equiv}CH}} \tag{27}$$

$$\underset{\mathbf{(81)}}{\mathrm{CH_3CH_2C{\equiv}CC{\equiv}CCOOH}} \longrightarrow \underset{\mathbf{(82)}}{\mathrm{CH_3CH{=}C{=}CHC{\equiv}CCOOH}} \longrightarrow$$

$$\underset{\mathbf{(83)}}{\mathrm{CH_3CH{=}C{=}C{=}C{=}CHCOOH}} \longrightarrow \underset{\mathbf{(84)}}{\mathrm{CH_3C{\equiv}CC{\equiv}CCH_2COOH}} \tag{28}$$

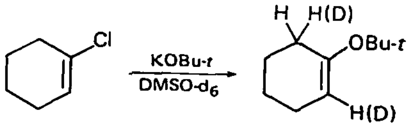
Schiavelli and Wann[46] have measured the rate of allenic hydrogen exchange for phenylallene and *p*-chlorophenylallene in ethanol-*O*-d/0.1 M sodium ethoxide solution at 35° C. These studies indicate that the terminal protons of such compounds are exchanged exclusively. The ρ for the reaction is -3.4. The difference in kinetic acidity observed is expected in light of the resonance stabilization available to anion 85 which is not available to anion 86 without rotation of the aryl group and concomitant loss of styrene-like conjugation.

$$\underset{\mathbf{(85)}}{\mathrm{ArCH{=}C{=}\bar{C}H}} \qquad \underset{\mathbf{(86)}}{\mathrm{Ar\bar{C}{=}C{=}CH_2}}$$

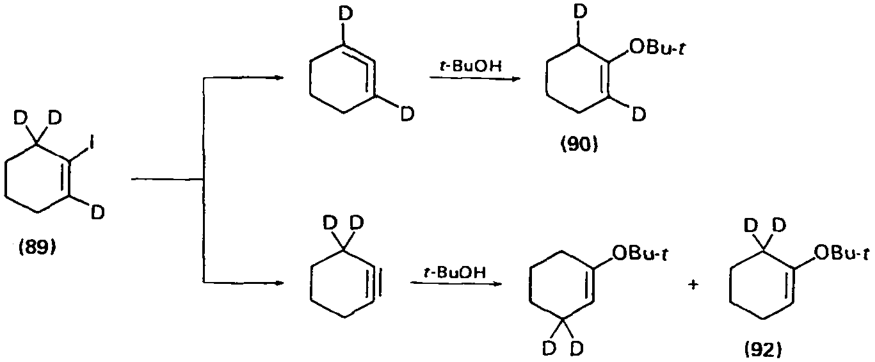
VII. MISCELLANEOUS REACTIONS

The reduction of propargyl halides by lithium aluminium hydride provides a convenient preparation of the corresponding allenic hydrocarbon[47]. Thus, reduction of $\mathrm{Me_2C(Cl)C{\equiv}CH}$ affords $\mathrm{Me_2C{=}C{=}CH_2}$ in 47% yield. Lithium aluminum deuteride reduction of the same propargyl halide affords $\mathrm{Me_2C{=}C{=}CHD}$ containing 94% d$_1$.

1,2-Cyclohexadiene intermediates have been implicated in the reaction of 1-halo-cyclohexene with KOBu-*t* in DMSO or DMSO–*t*-BuOH media[48]. When 1-chlorocyclohexene (87) is treated with KOBu-*t* in DMSO-d_6, 88 is obtained with incorporation of *one* deuterium from the solvent at $C_{(2)}$ or $C_{(6)}$. Treatment of 1-iodocyclohexene-2,6,6-d_3 (89) under identical conditions yields enol ethers 90,



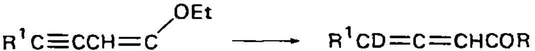
(87) (88) (29)



(89) (90) (91) (92) (30)

91 and 92 by means of two concurrent elimination–addition pathways involving the 1,2-cyclohexadiene and cyclohexyne shown in equation (30).

The preparation of certain deuterated allenic ketones has been reported. Bertrand and Rouvier[49,50] have studied the hydration of a number of ethoxyenynes (equation 31). In 0.3 M D_3PO_4 the specifically deuterated allenic ketones shown result.



$$\underset{(93)}{R^1C\equiv CCH{=}C\begin{matrix}\diagup OEt\\ \diagdown R^2\end{matrix}} \longrightarrow \underset{(94)}{R^1CD{=}C{=}CHCOR} \qquad (31)$$

$R^1 = H, R^2 = Me$

$R^1 = D, R^2 = H, Et, n\text{-}Pr$

Couffignal and Gaudemar[51] have observed the formation of deuterated allenic ketones from the reaction of the Grignard reagent derived from 95 (equation 32) with simple aliphatic esters (equation 33).

$$\underset{(95)}{BrCH_2C\equiv CD} \xrightarrow{Mg} \underset{(96)}{[BrMgCH_2C\equiv CD + H_2C{=}C{=}CDMgBr]} \qquad (32)$$

$$\begin{array}{lll} MeCO_2Et + 96 \longrightarrow & MeCOCH_2C\equiv CD & 32\% \qquad (33a)\\ & MeCOCH{=}C{=}CHD & 56\% \\ & MeCOCD{=}C{=}CH_2 & 4\% \\ & MeCOCH{=}C{=}CH_2 & 8\% \end{array}$$

$$\mathrm{EtCO_2Et} + \mathbf{96} \longrightarrow \begin{array}{ll} \mathrm{EtCOCH_2C{\equiv}CD} & 63\% \\ \mathrm{EtCOCH{=}C{=}CHD} & 30\% \\ \mathrm{EtCOCD{=}C{=}CH_2} & 4\% \\ \mathrm{EtCOCH{=}C{=}CH_2} & 3\% \end{array} \qquad (33b)$$

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The Chemistry of Ketenes, Allenes and Related Compounds
Edited by Saul Patai

CHAPTER 12

Electrochemistry of allenes and cumulenes

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I. INTRODUCTION

Presented in this chapter is a discussion of the electrochemistry of allenes and cumulenes. Almost all the available information dealing with these species pertains to the electrolytic reduction of phenyl-substituted allenes as well as nominally electroinactive allenes possessing other reducible sites. In addition, there are several reports in which allenes have been detected during the electrochemical reduction of alkynes or in which allenes are postulated as transient intermediates. Although only a small number of investigations dealing with cumulenes have appeared in the literature, these compounds offer interesting possibilities for the electrosynthesis of other unsaturated hydrocarbons, and there are at least two examples of the use of electrochemistry to produce cumulenes. To the best of our knowledge, papers concerned with the electrochemical behaviour of ketenes, ketene acetals, ketene imines and carbodiimides are nonexistent.

Polarographic half-wave potentials and potentials employed in controlled-potential electrolyses are cited throughout this chapter. Because a variety of reference electrodes have been utilized in the work to be discussed, it is difficult to compare the electrochemistry of a compound examined in one study with that of the same or a related substance in another investigation. Therefore, to achieve consistency we have taken the liberty of quoting all potentials with respect to the familiar aqueous saturated calomel electrode (SCE). Details about the actual reference electrodes used in the original research can be found in the papers listed at the end of the chapter.

II. ALLENES

Unless the allene moiety is conjugated to one or more phenyl groups or bonded to another activating substituent, the allene site itself cannot be electrolytically reduced. However, allenes which are themselves inherently electroinactive may possess functional groups, such as carbon–halogen bonds, that can undergo reduction and thereby induce chemical reactions of the allene site.

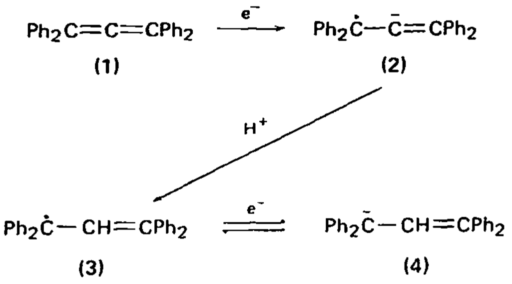
A. Allene

Although allene is not reducible electrolytically, the potentiostatic and galvanostatic oxidation of allene at platinum anodes in both sulphuric acid and sodium hydroxide media at 80° C has been observed by Bockris, Wroblowa, Gileadi and Piersma[1]. Under these conditions, allene is destructively and nearly quantitatively converted into carbon dioxide (equation 1) as is true for other unsaturated hydrocarbons, including 1-butene and 1,3-butadiene. From a consideration of the kinetics of the electrochemical process, these workers concluded that the rate of oxidation of allene is controlled by the anodic discharge of water to form adsorbed hydroxyl radicals which interact chemically with adsorbed molecules of the hydrocarbon to yield the products.

$$H_2C{=}C{=}CH_2 + 6\,H_2O \longrightarrow 3\,CO_2 + 16\,H^+ + 16\,e^- \qquad (1)$$

B. Tetraphenylallene

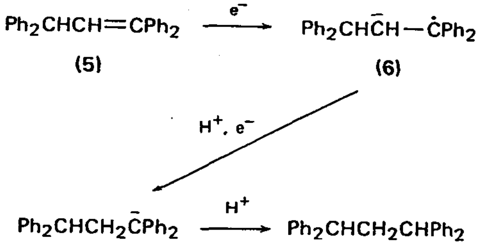
There have been at least four publications in which the electrochemical reduction of tetraphenylallene is discussed[2-5]. In a comprehensive examination of the electrochemistry of tetraphenylallene (1), Dietz, Peover and Wilson[2] found that the parent compound exhibits a single two-electron polarographic wave with a half-wave potential of −2.11 V vs SCE in dimethylformamide containing 0.2 M tetra-*n*-butylammonium perchlorate, the product being the relatively stable, red-coloured tetraphenylallyl anion (4) (equation 2) which was identified with the aid of visible spectrophotometry. Tetra-*n*-butylammonium cation is conceivably the



(2)

source of protons for the rapid conversion of the strongly basic radical anion (2) to radical (3), but the Hofmann elimination products (tri-*n*-butylamine and 1-butene) arising from the deprotonation of the tetraalkylammonium ion were not detected.

If phenol, a better proton donor, is added to the system consisting of dimethylformamide and tetra-*n*-butylammonium perchlorate, two polarographic waves are seen for tetraphenylallene; the first wave is attributable to the sequence of reactions just outlined and the second wave, which has a half-wave potential of –2.47 V vs SCE, corresponds to the two-electron reduction of 1,1,3,3-tetraphenylpropene (5) produced upon protonation of the tetraphenylallyl anion (4) (equation 3). Large-scale controlled-potential electrolytic reduction of the starting material (1) at a mercury cathode in an aprotic medium can be utilized to generate the tetraphenylallyl anion (4); addition of water to the solution yields 1,1,3,3-tetraphenylpropene (5). As part of this study[2], the authors utilized the technique of chronoamperometry to obtain rate constants of approximately 1000 and 200 s^{-1}, respectively, for the protonation of radical anions (2) and (6). In addition, it was demonstrated that the tetraphenylallyl anion (4) can be oxidized at a potential of –0.80 V vs SCE to yield a yellow species, presumably the tetraphenylallyl radical (3).



(3)

Through the use of cyclic voltammetry with a platinum microelectrode, Dietz and Larcombe[3] subsequently confirmed the results of the preceding workers pertaining to the electrochemical oxidation of the tetraphenylallyl anion (4) to the tetraphenylallyl radical (3). Moreover, it was discovered that the tetraphenylallyl radical (3) can undergo further oxidation in either dimethylformamide or acetonitrile to a species thought to be a carbonium ion; a cyclic voltammetric peak for apparent reduction of the carbonium ion was detected only in the acetonitrile medium, an observation consistent with the lower reactivity of such a species in that solvent.

In developing an all-glass, closed-loop, two-stage flow cell for the electrolytic generation of organic radicals and for the characterization of these species with the aid of e.s.r. spectroscopy, Forno[4] utilized tetraphenylallene as a test system. Tetraphenylallene in oxygen-free dimethylformamide containing tetra-*n*-butylammonium iodide was electrolytically reduced at a large platinum gauze cathode in order to form the tetraphenylallyl anion (4). Next, the resulting solution flowed from the first cell directly into a second electrochemical cell, and the tetraphenylallyl anion was subjected to controlled-potential oxidation at another platinum gauze electrode to yield the tetraphenylallyl radical (3). Finally, the radical-containing solution passed into a cell positioned in an e.s.r. spectrometer so that a spectrum could be recorded immediately; the e.s.r. spectrum of the tetraphenylallyl radical agreed with that reported earlier by Dietz, Peover and Wilson[2].

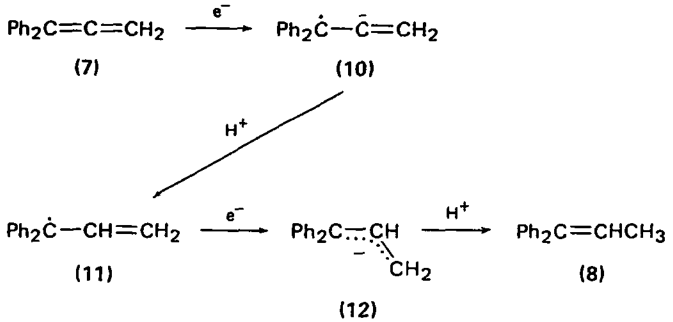
Attempting to produce the dianion of tetraphenylallene, Zweig and Hoffmann[5] observed a single polarographic wave in dimethylformamide and concluded that two-electron reduction of the starting material takes place at a potential of –2.09 V vs SCE. Although details of the electrochemical experiments are lacking, it seems probable that the process occurring involved addition of two electrons and one proton to yield the tetraphenylallyl anion (4) as described earlier[2]. If formation of the dianion were to be observed, one would expect to see two polarographic waves: a wave due to the one-electron reduction of tetraphenylallene (1) to the radical anion (2) and another wave, at a more negative potential, corresponding to the one-electron reduction of the radical anion to the dianion. However, if protonation of the radical anion (2) is rapid, the latter is converted to a neutral allyl radical (3) which is easier to reduce than tetraphenylallene itself.

C. 1,1-Diphenylallene

A polarogram for the reduction of 1,1-diphenylallene (7) in dimethylformamide containing 0.1 M tetraethylammonium bromide has been observed by Doupeux, Martinet and Simonet[6] to exhibit two waves with half-wave potentials of approximately −2.33 and −2.72 V vs SCE. According to these workers, the starting material is reduced in a pair of two-electron steps leading to the formation of 1,1-diphenyl-1-propene (8) and 1,1-diphenylpropane (9), respectively (equation 4).

$$\underset{(7)}{Ph_2C{=}C{=}CH_2} \xrightarrow[2\,H^+]{2\,e^-} \underset{(8)}{Ph_2C{=}CHCH_3} \xrightarrow[2\,H^+]{2\,e^-} \underset{(9)}{Ph_2CHCH_2CH_3} \qquad (4)$$

Though no mechanistic features of the reduction process were probed, it is reasonable to presume that the allene is initially converted into a radical anion (10) which is quickly protonated to form a neutral radical (11) that accepts another electron and a proton to yield 1,1-diphenyl-1-propene (8) (equation 5). A similar sequence of electron-transfer and proton-transfer reactions can be written to account for the second polarographic wave, which ostensibly corresponds to the reduction of 1,1-diphenyl-1-propene (8) to 1,1-diphenylpropane (9).



(5)

Comparison of the work by Dietz, Peover and Wilson[2] dealing with tetraphenylallene and the report by Doupeux, Martinet and Simonet[6] concerning 1,1-diphenylallene presents a dilemma. Whereas a good proton donor (phenol) must be present in order to observe the second stage of reduction of tetraphenylallene – that is, the conversion of 1,1,3,3-tetraphenylpropene to 1,1,3,3-tetraphenylpropane – it is apparently possible to see the second step in the reduction of 1,1-diphenylallene in the absence of a proton donor. In addition, the two polarographic waves shown by Doupeux, Martinet and Simonet[6] for the reduction of 1,1-diphenylallene have significantly different instead of identical heights, but no rationale is offered in explanation of this fact. Moreover, although 1,1-diphenyl-1-propene (8) can be formed upon electrolytic reduction of 1,1-diphenylallene (7), it is possible that protonation of the allylic anion intermediate (12) can produce some 1,1-diphenyl-2-propene; indeed, as discussed later in this chapter, the electrochemical reduction of 1-phenyl-1,2-hexadiene yields *trans*-1-phenyl-1-hexene, *trans*-1-phenyl-2-hexene and *cis*-1-phenyl-1-hexene, the phenyl-conjugated olefins being predominant. Unfortunately, the products formed upon electrolytic reduction of 1,1-diphenylallene have not been isolated and identified.

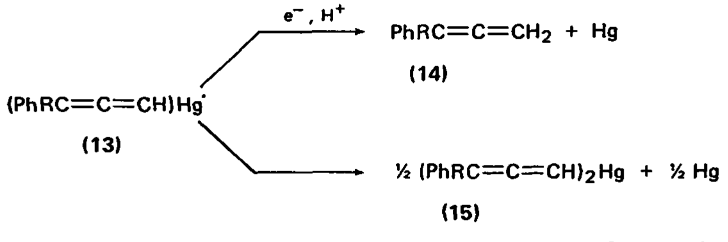
D. 1,1-Diphenyl-3-bromoallene, 1-Methyl-1-phenyl-3-bromoallene, 1-Bromo-3-phenylallene and 1,1-Diphenyl-3-chloroallene

As part of the preceding study, Doupeux, Martinet and Simonet[6] investigated the polarographic and coulometric behaviour of a series of allenes having the general formula PhRC=C=CHX, where R was chosen to be phenyl, methyl or hydrogen and where X was either a bromine or chlorine atom.

In dimethylformamide containing 0.1 M tetraethylammonium bromide, reduction of each of the three bromine-containing compounds gives four polarographic waves; half-wave potentials are −0.58, −1.12, −2.32 and −2.72 V vs SCE for 1,1-diphenyl-3-bromoallene and are −0.58, −1.17, −2.41 and −2.74 V vs SCE for both 1-methyl-1-phenyl-3-bromoallene and 1-bromo-3-phenylallene. Spontaneous insertion of mercury from the cathode into the carbon—bromine bond of each compound (equation 6) was proposed to precede any electron-transfer step and the first polarographic wave was attributed to an irreversible one-electron process leading to production of an organomercury radical (13) (equation 7). This organomercury radical undergoes two competing reactions; it can accept an electron and a proton, causing the second polarographic wave as well as giving a phenyl-substituted allene (14), or it can disproportionate to yield a diorganomercury compound (15) and an atom of mercury (equation 8). At more negative potentials, the third and fourth polarographic waves are associated with reduction of the allene (14), the electrochemistry of which mimics that described earlier for 1,1-diphenylallene.

$$\mathrm{PhRC{=}C{=}CHBr + Hg \longrightarrow (PhRC{=}C{=}CH)HgBr} \qquad (6)$$

$$\mathrm{(PhRC{=}C{=}CH)HgBr \xrightarrow{e^-} \underset{(13)}{(PhRC{=}C{=}CH)Hg^{\bullet}} + Br^-} \qquad (7)$$



$$\underset{(13)}{\mathrm{(PhRC{=}C{=}CH)Hg^{\bullet}}} \begin{cases} \xrightarrow{e^-,\,H^+} \underset{(14)}{\mathrm{PhRC{=}C{=}CH_2}} + \mathrm{Hg} \\ \longrightarrow \tfrac{1}{2}\,\underset{(15)}{\mathrm{(PhRC{=}C{=}CH)_2Hg}} + \tfrac{1}{2}\,\mathrm{Hg} \end{cases} \qquad (8)$$

Processes involving the formation, disproportionation and reduction of the organomercury radical (13) are similar to those invoked in a number of studies of the electrochemical reduction of organic halides at mercury[7] and do not truly pertain to the electrochemistry of allenes. One detail deleted from the mechanistic scheme suggested by Doupeux, Martinet and Simonet[6] is that, prior to disproportionation, the organomercury radical is stabilized by adsorption onto the surface of the electrode. In solution, the strength of the carbon—mercury bond of such a radical is so meagre (approximately 6 kcal/mol) that the organomercury radical persists no longer than perhaps 10^{-8} s, a time too short to permit significant accumulation of the diorganomercury compound; on the other hand, adsorbed organomercury radicals[8] have a lifetime as long as 10^{-2} s. Most probably, organomercury radicals in the adsorbed state are those which disproportionate into elemental mercury and a diorganomercury species.

In dimethylformamide containing both tetraethylammonium bromide and lithium perchlorate, the large-scale electrolytic reduction of 1,1-diphenyl-3-bromoallene at a mercury pool cathode kept at a potential (–0.88 V vs SCE) corresponding to the plateau region of the first polarographic wave results in the transfer of one electron to each molecule of starting material and in the formation of an isolable diorganomercury compound, which was found to be $(Ph_2C{=}C{=}CH)_2Hg$. A polarogram for reduction of the diorganomercury species exhibits four waves. Half-wave potentials for the first and second waves are –1.12 and –1.92 V vs SCE, but the electron-transfer processes responsible for these waves are unknown. However, the half-wave potentials for the third and fourth polarographic waves for reduction of the diorganomercury compound are –2.34 and –2.74 V vs SCE, and these values coincide with the half-wave potentials observed for 1,1-diphenylallene. When large-scale reduction of 1,1-diphenyl-3-bromoallene is performed at a controlled potential of –1.53 V vs SCE, two electrons are added to each molecule of the parent compound and 1,1-diphenylallene is recovered as the electrolysis product.

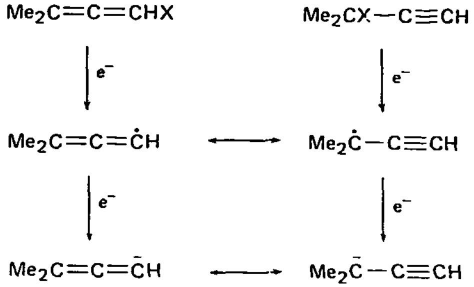
In contrast to the behaviour of the preceding group of bromoallenes, a polarogram for 1,1-diphenyl-3-chloroallene (**16**) shows only three waves in dimethylformamide containing 0.1 M tetraethylammonium bromide, the half-wave potentials being –1.53, –2.33 and –2.72 V vs SCE. Based on the results of a large-scale electrolysis, it appears that the first stage of reduction entails two-electron cleavage of the carbon–chlorine bond, followed by protonation of the resultant anion to yield 1,1-diphenylallene (**7**) (equation 9) and that the second and third electron-transfer

$$\underset{(16)}{Ph_2C{=}C{=}CHCl} \xrightarrow{2\,e^-,\ H^+} \underset{(7)}{Ph_2C{=}C{=}CH_2} + Cl^- \qquad (9)$$

steps correspond to those seen for 1,1-diphenylallene. No evidence for the formation of organomercury radicals or diorganomercury compounds was observed.

E. 1,1-Dimethyl-3-bromoallene and 1,1-Dimethyl-3-chloroallene

Polarographic and coulometric investigation of the behaviour of 1,1-dimethyl-3-bromoallene and 1,1-dimethyl-3-chloroallene in dimethylformamide containing 0.1 M tetraethylammonium bromide as supporting electrolyte indicates that reduction of each compound proceeds through a pair of one-electron steps. Half-wave potentials for the first polarographic waves for the bromoallene and chloroallene are –1.48 and –2.32 V vs SCE, respectively, whereas the half-wave potentials for the second wave for each compound are identical (–2.73 V vs SCE). For similar experimental conditions, two polarographic waves are observed for the reduction of both 3-bromo-3-methyl-1-butyne and 3-chloro-3-methyl-1-butyne; the half-wave potentials for the bromobutyne are –1.11 and –2.73 V vs SCE and those for the chlorobutyne are –2.06 and –2.75 V vs SCE. Controlled-potential coulometry has revealed that each stage in the reduction of the bromobutyne and chlorobutyne involves the transfer of a single electron. Because the half-wave potentials for the second polarographic waves for all four compounds are virtually identical, Simonet and coworkers[9,10] proposed that electrolytic reduction of these substances occurs via a common pathway (equation 10). However, it should be stressed that neither



(17) (18)

(10)

the allenic nor the acetylenic sites are reducible and that the carbon–halogen bonds are responsible for the electroactivity of these compounds.

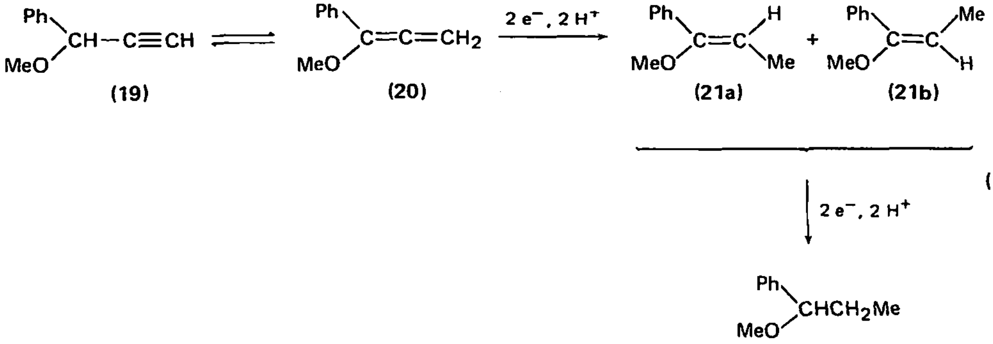
Presumably, transfer of a proton from the tetraethylammonium cation to anions (**17**) and (**18**) would yield a mixture of 1,1-dimethylallene and 3-methyl-1-butyne. Thus, one should be able to prepare 3-methyl-1-butyne by electrolytic reduction of either the bromoallene or chloroallene; conversely, 1,1-dimethylallene could be electrogenerated from 3-bromo-3-methyl-1-butyne or 3-chloro-3-methyl-1-butyne. Unfortunately, the relative yields of allene and alkyne obtainable by means of these reactions have not been measured, so that the possible usefulness of these electrochemical processes for synthetic purposes cannot be assessed.

In the presence of a twofold excess of phenol, the bromoallene and chloroallene exhibit polarographic behaviour consistent with the occurrence of a one-step, two-electron reduction to 1,1-dimethylallene; the half-wave potentials for the bromoallene and chloroallene are −1.61 and −2.36 V vs SCE, respectively. This change in the mechanism of reduction in the presence of excess phenol has been verified by means of controlled-potential coulometry; electrolysis of the bromoallene at a potential of −1.93 V vs SCE indicated that 1.61 electrons are transferred to each molecule of starting material, and electrolysis of the chloroallene at −2.53 V vs SCE showed that 2.02 electrons are added to each molecule of the parent compound.

Large-scale electrolytic reduction of 1,1-dimethyl-3-bromoallene at mercury in dimethylformamide containing 0.1 M tetraethylammonium bromide at a potential (−2.03 V vs SCE) corresponding to the plateau region of the first polarographic wave results in the addition of one electron to each molecule of starting material and in the formation of two products. One species, the very unstable $Me_2C{=}C{=}CHCH{=}C{=}CMe_2$, appears to arise from coupling of a pair of $Me_2C{=}C{=}\dot{C}H$ intermediates, but the existence of the dimer has only been inferred from the appearance of two new polarographic waves during the exhaustive electrolysis of 1,1-dimethyl-3-bromoallene. However, the same radical intermediate interacts strongly with the mercury cathode to form $(Me_2C{=}C{=}CH)Hg^{\cdot}$ which disproportionates to yield $(Me_2C{=}C{=}CH)_2Hg$, an isolable diorganomercury compound. A polarogram for this diorganomercury species in dimethylformamide containing 0.1 M tetraethylammonium bromide exhibits a single wave for an unidentified electron-transfer reaction with a half-wave potential of −2.16 V vs SCE; this value differs from any of the half-wave potentials for reduction of $(Ph_2C{=}C{=}CH)_2Hg$.

F. Allenic Ethers

If 3-methoxy-3-phenyl-1-propyne (**19**) is added to dimethylformamide containing 0.1 M tetra-*n*-butylammonium iodide along with a trace of some proton acceptor, a polarogram exhibiting two waves of identical height can be recorded; the half-wave potentials are approximately –2.67 and –2.84 V vs SCE. Santiago and Simonet[11] attribute this behaviour to stepwise reduction of the 1-methoxy-1-phenylallene (**20**) formed by base-catalysed rearrangement of the propyne (equation 11). Whereas carbon–oxygen bonds of benzylic and allylic ethers usually



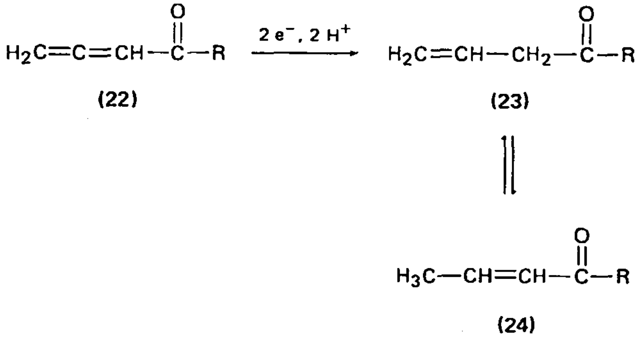
(11)

suffer electrolytic scission, an allenic ether, such as 1-methoxy-1-phenylallene (**20**), is not cleaved; instead, electroreductive saturation of the β carbon–carbon double bond occurs preferentially, giving a mixture of *cis* and *trans* olefins. Taking advantage of this fact, Santiago and Simonet demonstrated that electrolysis of 3-methoxy-3-phenyl-1-propyne (**19**) at a mercury pool cathode in dimethylformamide containing 0.1 M tetra-*n*-butylammonium iodide and an excess of phenol and at a potential (approximately –2.70 V vs SCE) corresponding to the first stage of reduction results in the formation of a one-to-one mixture of (*Z*)-1-methoxy-1-phenylpropene (**21a**) and (*E*)-1-methoxy-1-phenylpropene (**21b**). Conceivably, it is the tiny amount of phenoxide ion in equilibrium with the phenol which promotes the rearrangement of the propyne (**19**) to the electroactive allene (**20**). Without added phenol (but probably with an inevitable trace of water present which upon electrolytic reduction can furnish hydroxide ions to induce the propyne-to-allene isomerization), the yields of the *Z* and *E* isomers were 70% and 30%, respectively. Although the cause of the differing distribution of products in the presence and absence of phenol has not been elucidated, the synthetic usefulness of these reactions should not be discounted.

G. Allenic Aliphatic Ketones

A report by Martinet, Simonet and Morenas[12] describes the electrochemical reduction at mercury electrodes of three allenic aliphatic ketones (**22**) – namely, 1,2-pentadien-4-one, 5-methyl-1,2-hexadien-4-one and 5,5-dimethyl-1,2-hexadien-4-one – and compares the behaviour of these species in both aqueous and nonaqueous media.

In aqueous buffers of various pH values, polarograms for the allenic aliphatic ketones exhibit a single diffusion-controlled wave corresponding to a two-electron process, and large-scale controlled-potential electrolyses at mercury pool cathodes indicate that each compound undergoes a two-electron reduction accompanied by uptake of a pair of protons to give both a β,γ-unsaturated ketone (**23**) and an α,β-unsaturated ketone (**24**) (equation 12). Typical of the behaviour of the three



$$H_2C{=}C{=}CH{-}\overset{O}{\overset{\|}{C}}{-}R \xrightarrow{2\,e^-,\,2\,H^+} H_2C{=}CH{-}CH_2{-}\overset{O}{\overset{\|}{C}}{-}R \rightleftharpoons H_3C{-}CH{=}CH{-}\overset{O}{\overset{\|}{C}}{-}R \qquad (12)$$

(22) (23) (24)

R = Me, *i*-Pr, *t*-Bu

allenic aliphatic ketones is that seen for 5,5-dimethyl-1,2-hexadien-4-one. In a buffer with a pH of 5.80, the polarographic half-wave potential for the starting material is −0.91 V vs SCE; under the same conditions, the half-wave potential for further reduction of the α,β-unsaturated ketone (24) is −1.57 V vs SCE, whereas the half-wave potential for further reduction of the β,γ-unsaturated ketone (23) is −2.85 V vs SCE. A large-scale electrolysis of the starting material at a potential of −1.50 V vs SCE leads to the recovery of the α,β- and β,γ-unsaturated ketones in relative yields of 60% and 40%, respectively. It should be interjected here that, in an aqueous medium, as much as 60% of the original amount of starting material is lost by reaction with water to form a β-diketone. Interestingly, a polarogram for a solution initially containing only the allenic aliphatic ketone (22) shows two waves. There is one wave corresponding to reduction of the starting material and another wave signalling reduction of the β,γ-unsaturated ketone; no polarographic wave denoting reduction of the α,β-unsaturated ketone is observed.

Of the two products obtained from a large-scale controlled-potential electrolysis of 5,5-dimethyl-1,2-hexadien-4-one, the α,β-unsaturated ketone (24) is thermodynamically more stable than the β,γ-unsaturated ketone (23). This fact, coupled with the results of the polarographic and electrolytic experiments described above, allows one to conclude that electrochemical reduction of the starting material produces only the β,γ-unsaturated ketone; the α,β-unsaturated ketone recovered upon reduction of the parent compound must be formed chemically by isomerization of the less stable β,γ-unsaturated ketone.

Various mechanisms for electrolytic reduction of the allenic aliphatic ketones were invoked for aqueous solutions of different pH values. Because the polarographic half-wave potentials depend on pH in an acidic medium, protonation of the starting material is proposed to occur prior to addition of the first electron; then, in a concerted process, a second electron and another proton are accepted by the radical intermediate to yield the β,γ-unsaturated ketone. In neutral and alkaline buffers, for which the half-wave potentials are unaffected by pH, one electron is accepted by the starting material before uptake of the first proton, and the second electron and second proton are added essentially simultaneously.

In dimethylformamide containing tetraethylammonium bromide, it appears on the basis of polarographic and cyclic voltammetric evidence that the allenic aliphatic ketones accept just one electron and that the rate of protonation of the resulting radical anion (conceivably by transfer of a hydrogen ion from the supporting electrolyte cation) is slow. However, the fate of the intermediate produced by addition of one electron to the starting material is unclear. On the other hand, if enough phenol is introduced into the system to provide a phenol-to-ketone ratio of three or more, polarography and controlled-potential electrolyses reveal that two electrons and two protons are transferred to each molecule of starting material and that the products are the same as those obtained in aqueous media.

H. Allenic Sulphones

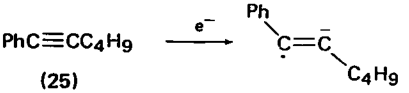
Polarographic half-wave potentials for allenyl *p*-tolyl sulphone and buta-1,2-dienyl *p*-tolyl sulphone (as well as numerous alkenes and alkynes bearing sulphonyl, sulphinyl and sulphonium groups) in a methanolic solution of tetramethylammonium bromide at pH 9.2 have been measured by Howsam and Stirling[13]. A polarogram for each allenic sulphone exhibits two well-resolved waves, and the half-wave potentials are −1.36 and −2.09 V vs SCE for allenyl *p*-tolyl sulphone and −1.35 and −2.10 V vs SCE for buta-1,2-dienyl *p*-tolyl sulphone.

Controlled-potential electrolytic reduction of allenyl *p*-tolyl sulphone at a potential (−1.40 V vs SCE) on the rising portion of the first polarographic wave causes transfer of two electrons to the starting material and results in the formation of allyl *p*-tolyl sulphone in high yield (84%). Further reduction of allyl *p*-tolyl sulphone cleaves the carbon–sulphur bond in a two-electron process, the products being 1-propene and *p*-tolylsulphinate. No large-scale electrolyses of buta-1,2-dienyl *p*-tolyl sulphone were performed, but it is reasonable to presume that the first stage of reduction should produce but-2-enyl *p*-tolyl sulphone and that scission of the carbon-sulphur bond would occur during the second stage of reduction to yield 2-butene and *p*-tolylsulphinate.

Starting with the knowledge that the thermodynamic stabilities as well as the reactivities toward nucleophilic addition of allenyl *p*-tolyl sulphone, prop-2-ynyl *p*-tolyl sulphone and prop-1-ynyl *p*-tolyl sulphone decrease in the order written, Howsam and Stirling sought to determine if the polarographic behaviour of the three species reflects these trends. Because the half-wave potentials for the first polarographic waves for allenyl *p*-tolyl sulphone and prop-2-ynyl *p*-tolyl sulphone are almost identical (−1.36 and −1.32 V vs SCE, respectively), it was concluded that the latter compound undergoes rapid electrolytically induced isomerization to the former substance and that reduction of the acetylenic sulphone actually proceeds via the allenic sulphone; this behaviour is consonant with the observation that nucleophilic addition to prop-2-ynyl *p*-tolyl sulphone occurs only after isomerization to allenyl *p*-tolyl sulphone. However, the first polarographic wave for prop-1-ynyl *p*-tolyl sulphone has a half-wave potential (−1.46 V vs SCE) which differs from those for the other two species examined; this finding is consistent with the relatively slow rearrangement of prop-1-ynyl *p*-tolyl sulphone to allenyl *p*-tolyl sulphone, from which it follows that the acetylenic sulphone itself is reduced directly. Indeed prop-1-ynyl *p*-tolyl sulphone does undergo nucleophilic addition, but it is less reactive than allenyl *p*-tolyl sulphone.

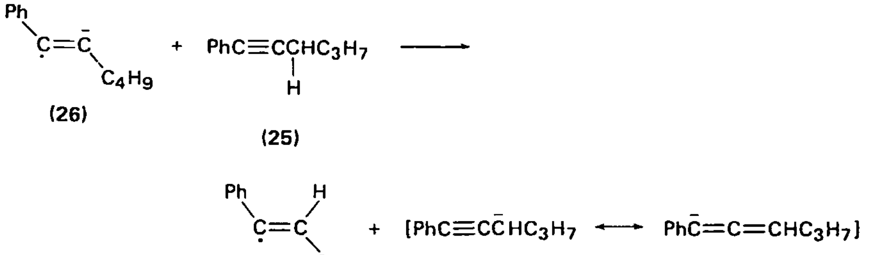
I. Electrolytically-induced Isomerization of Alkynes to Allenes

In an investigation of the electrochemical reduction of 1-phenyl-1-hexyne at a mercury pool cathode in dimethylformamide containing 0.1 M tetra-*n*-butylammonium perchlorate, Moore and Peters[14] discovered that the starting material can undergo rapid conversion to 1-phenyl-1,2-hexadiene within minutes after the start of a prolonged large-scale electrolysis. This isomerization is a base-catalysed propargylic rearrangement triggered through abstraction of an α proton from 1-phenyl-1-hexyne (**25**) by an electrolytically formed radical anion (**26**) (equations 13 and 14). Reabstraction of a proton by the propargylic anion (**27**) can result in the



(25) (26)

(13)



(26) (25) (27)

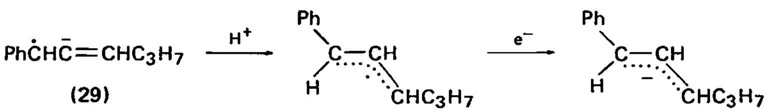
(14)

formation of either 1-phenyl-1,2-hexadiene or starting material.

In dimethylformamide containing 0.1 M tetra-*n*-butylammonium perchlorate, a polarogram for 1-phenyl-1-hexyne exhibits a single wave corresponding to the overall four-electron reduction of starting material to 1-phenylhexane; the half-wave potential is –2.63 V vs SCE. A polarogram for 1-phenyl-1,2-hexadiene consists of two waves with half-wave potentials of –2.42 and –2.64 V vs SCE; in the first step, the allene is reduced to *trans*-1-phenyl-1-hexene, *cis*-1-phenyl-1-hexene and *trans*-1-phenyl-2-hexene, whereas the second step corresponds formally to the conversion of the phenyl-conjugated olefins to 1-phenylhexane. Reduction of 1-phenyl-1,2-hexadiene (**28**) occurs more readily than its acetylenic precursor and probably involves initially the addition of an electron to the phenyl-conjugated double bond (equation 15). Proton abstraction by the carbanion (**29**) produces an

$$\underset{(28)}{\mathrm{PhCH{=}C{=}CHC_3H_7}} \xrightarrow{e^-} \underset{(29)}{\mathrm{Ph\dot{C}H\bar{C}{=}CHC_3H_7}} \qquad (15)$$

allyl radical (**30**) which is further reduced electrochemically to an allylic anion (**31**) (equation 16). Protonation of the latter anion (**31**) leads to *trans*-1-phenyl-1-



(29) (30) (31)

(16)

hexene, *trans*-1-phenyl-2-hexene and *cis*-1-phenyl-1-hexene; none of the *cis*-1-phenyl-2-hexene has been detected in this system. During a large-scale exhaustive electrolysis at a potential of –2.70 V vs SCE, the two phenyl-conjugated olefins are directly reducible to 1-phenylhexane; furthermore, loss of a benzylic proton from *trans*-1-phenyl-2-hexene regenerates the allylic anion (**31**) which can accept a hydrogen ion to yield one of the reducible olefins.

Inasmuch as the formation of 1-phenyl-1,2-hexadiene is at least a bimolecular reaction, electrolysis of a sufficiently dilute solution of 1-phenyl-1-hexyne proceeds without isomerization to the allene, which can be distinguished from the starting material by its characteristic polarographic wave as well as its infrared and n.m.r. spectra. For initial concentrations of 1-phenyl-1-hexyne of the order of 2.6×10^{-4} M, when formation of the allene does not occur to a significant extent, a large-scale electrolysis, done at a potential of −2.70 V vs SCE in such a way that an average of only two electrons is transferred to each molecule of starting material, yields mainly 1-phenylhexane (47%), along with small amounts of *trans*-1-phenyl-1-hexene (11%), *cis*-1-phenyl-1-hexene (4%), and *trans*-1-phenyl-2-hexene (1%), and considerable 1-phenyl-1-hexyne (37%) remains unreduced.

However, it is possible to generate reasonably large concentrations of 1-phenyl-1,2-hexadiene by means of the rapid electrolytically induced isomerization of 1-phenyl-1-hexyne and to study just the reduction of the allene by subsequent adjustment of the electrolysis potential. In one experiment, a solution containing a maximal concentration of 0.0067 M 1-phenyl-1,2-hexadiene was prepared by controlled-potential electrolysis of a 0.010 M solution of 1-phenyl-1-hexyne at −2.75 V vs SCE. Immediately, the potential was stepped back to −2.35 V vs SCE at which only 1-phenyl-1,2-hexadiene undergoes reduction, and an exhaustive electrolysis of the allene was performed. At the end of the electrolysis, which involved addition of two electrons to each molecule of the allene, the principal products were *trans*-1-phenyl-1-hexene (73%), *trans*-1-phenyl-2-hexene (19%) and *cis*-1-phenyl-1-hexene (4%), and only a trace of 1-phenylhexane (1%) was formed – a dramatically different result from that obtained upon electrolytic reduction of 1-phenyl-1-hexyne.

In an extension of the preceding studies of 1-phenyl-1-hexyne and 1-phenyl-1,2-hexadiene, an examination of the electroreductive cyclization reactions of 6-chloro-1-phenyl-1-hexyne and 6-chloro-1-phenyl-1,2-hexadiene at mercury cathodes in dimethylformamide was carried out by Moore, Salajegheh and Peters[15].

If a polarogram is recorded for 6-chloro-1-phenyl-1-hexyne in dimethylformamide containing 0.1 M tetra-*n*-butylammonium perchlorate, two waves are observed with half-wave potentials of −2.52 and −2.80 V vs SCE and with respective diffusion currents in an approximate two-to-one ratio. Reduction of the carbon–carbon triple bond is responsible for the first polarographic wave, whereas the second wave is caused by two different reactions – reduction of benzylidenecyclopentane (which results from intramolecular cyclization of an intermediate formed during the process corresponding to the first wave) and reduction of the carbon–chlorine bond of 6-chloro-1-phenyl-1-hexyne.

Because reduction of the phenyl-activated carbon–carbon triple bond of 6-chloro-1-phenyl-1-hexyne occurs more easily than that of the carbon–chlorine moiety, this system offers an opportunity for study of nucleophilic displacement reactions involving intramolecular attack of electrochemically generated radical anions on the terminal alkyl chloride site. However, more relevant from the standpoint of the present discussion is the effect of the initial concentration of 6-chloro-1-phenyl-1-hexyne on the course of the electrolysis and on the identities and yields of products. For sufficiently low concentrations, 6-chloro-1-phenyl-1-hexyne can be reduced without isomerizing to 6-chloro-1-phenyl-1,2-hexadiene. At concentrations larger than approximately 0.002 M, isomerization to and reduction of 6-chloro-1-phenyl-1,2-hexadiene become important, and the product distribution changes markedly.

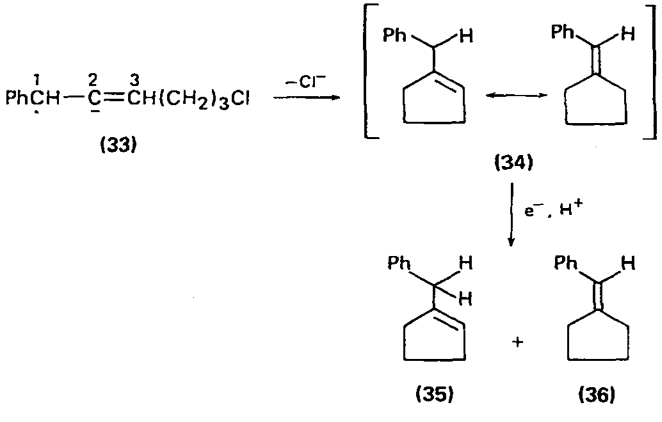
If an exhaustive electrolysis of a 2.5×10^{-4} M solution of 6-chloro-1-phenyl-1-hexyne in dimethylformamide containing 0.1 M tetra-*n*-butylammonium perchlorate is performed at a controlled potential of −2.50 V vs SCE, no evidence for isomerization of acetylene to allene can be observed; the electrolysis current exhibits a normal exponential decay with time, and polarograms recorded at intermediate stages of the electrolysis show no wave for reduction of the allene. At the end of the electrolysis, there is an abundance of benzylidenecyclopentane (81%) as well as smaller amounts of benzylcyclopentane (6%), 1-phenyl-1-hexyne (4%), *trans*-1-phenyl-1-hexene (3%), *cis*-1-phenyl-1-hexene (2%), *trans*-1-phenyl-2-hexene (2%), 1-phenylhexane (1%) and 1-benzylcyclopentene (<1%). Mechanistic schemes for the formation of products derived from the electrolytic reduction of 6-chloro-1-phenyl-1-hexyne are proposed in the original paper[15].

Early during a large-scale controlled-potential electrolysis at −2.50 V vs SCE of a 0.01 M solution of 6-chloro-1-phenyl-1-hexyne in dimethylformamide, rapid isomerization of the starting material to 6-chloro-1-phenyl-1,2-hexadiene is indicated by the appearance of a pronounced maximum in the current–time curve and by the development of a dark-green colour. In addition, polarography reveals the presence of a new wave with a half-wave potential of −2.30 V vs SCE due to reduction of 6-chloro-1-phenyl-1,2-hexadiene, and the presence of the allene can be confirmed with the aid of infrared and n.m.r. spectroscopy. Gas chromatographic analysis demonstrates that, at the maximum in the current–time curve, the quantities of the alkyne and allene isomers are nearly identical. At the completion of the electrolysis, the final distribution of products was as follows: 1-benzylcyclopentene (37%), benzylidenecyclopentane (29%), benzylcyclopentane (14%), *trans*-1-phenyl-2-cyclobutylethene (9%), 1-phenylcyclohexene (3%), 3-phenylcyclohexene (2%), *trans*-1-phenyl-1,5-hexadiene (3%), *trans*-1-phenyl-2-hexene (2%) and *trans*-1-phenyl-1-hexene (1%). It has been shown that this distribution of products is quite similar to what is obtained when 6-chloro-1-phenyl-1,2-hexadiene is reduced at potentials where 6-chloro-1-phenyl-1-hexyne is electroinactive. Indeed the electrolytic reduction of 6-chloro-1-phenyl-hexyne at initial concentrations higher than 0.0025 M proceeds largely through the allene isomer.

Base-catalysed isomerization responsible for the production of 6-chloro-1-phenyl-1,2-hexadiene begins soon after the start of an electrolysis of the starting material and is analogous to the rearrangement of 1-phenyl-1-hexyne described earlier. Once formed, 6-chloro-1-phenyl-1,2-hexadiene (32) is reduced by addition of one electron to the phenyl-conjugated double bond (equation 17). Radical anion

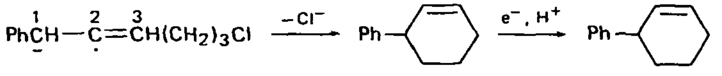
$$\underset{(32)}{\mathrm{PhCH{=}C{=}CH(CH_2)_3Cl}} \xrightarrow{e^-} \underset{(33)}{\mathrm{Ph}\overset{1}{\underset{\cdot}{\mathrm{C}}}\mathrm{H}{-}\overset{2}{\underset{-}{\mathrm{C}}}{=}\overset{3}{\mathrm{C}}\mathrm{H(CH_2)_3Cl}} \qquad (17)$$

(33) can undergo intramolecular cyclization with displacement of chloride, and the resulting cyclic allyl radical (34) is further reduced and protonated to yield both 1-benzylcyclopentene (35) and benzylidenecyclopentane (36) (equation 18). Ex-



(18)

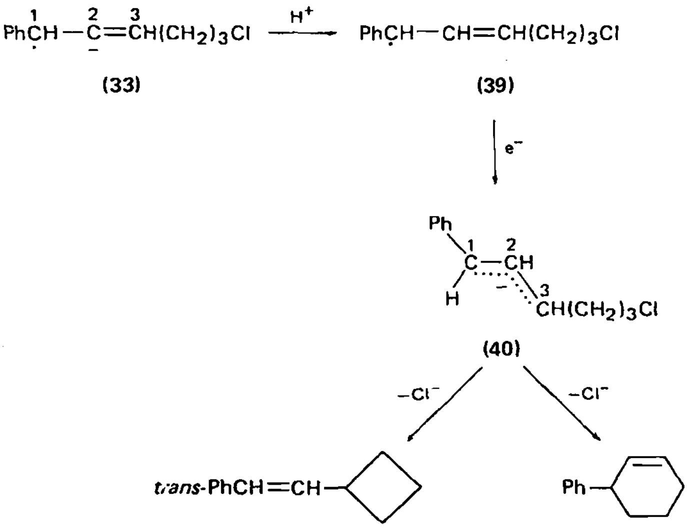
perimental evidence indicates that a small fraction of the negative charge on (**33**) resides on $C_{(1)}$ and that 3-phenylcyclohexene (**38**) may arise by the intramolecular cyclization reaction shown in equation (19). However, because the yield of five-



(**33**) (**37**) (**38**) (19)

membered carbocycles derived from 6-chloro-1-phenyl-1,2-hexadiene greatly exceeds that of six-membered rings, the radical anion initially formed from 6-chloro-1-phenyl-1,2-hexadiene is best represented by the resonance structure in which the negative charge is located on $C_{(2)}$.

After radical anion (**33**) is formed, there is competition between protonation and intramolecular cyclization. Protonation of (**33**) at $C_{(2)}$ yields an allyl radical (**39**) which is further reduced to an allylic anion (**40**) (equation 20). Subsequent

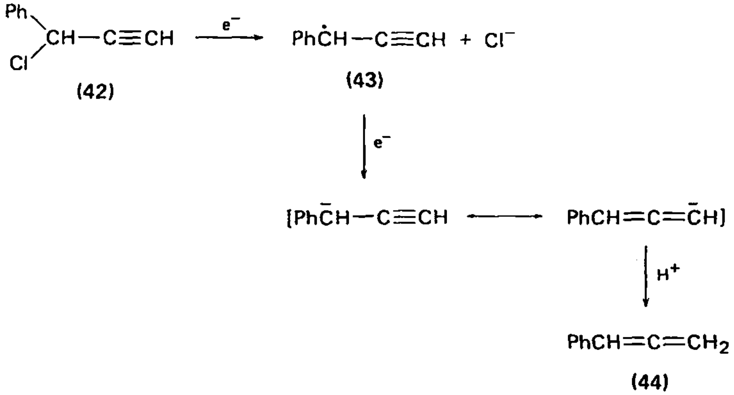


(**33**) (**39**) (**40**) (**41**) (**38**) (20)

intramolecular displacement of chloride by (**40**) gives either *trans*-1-phenyl-2-cyclobutylethene (**41**) or 3-phenylcyclohexene (**38**), the latter also being formed from radical anion (**33**). Formation of *trans*-1-phenyl-2-cyclobutylethene is the favoured process, suggesting that the majority of negative charge resides on $C_{(3)}$ of the allylic anion (**40**). Further discussion of the processes leading to formation of some of the minor electrolysis products is available[15].

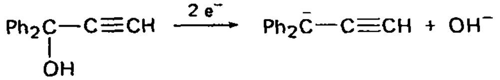
Besides the preceding studies in which alkynes are shown to undergo electrolytically induced rearrangement to allenes and in which direct proof is available to verify the presence of the allene and to demonstrate that the course of reduction of an allene can differ from that of its acetylenic counterpart, there have been other investigations where the generation of an allene upon electrochemical reduction of an alkyne is strongly inferred or at least postulated[6,16,17].

While studying the electrolytic reduction of several halogen-substituted phenylallenes and diphenylallenes, Doupeux, Martinet and Simonet[6] examined the polarographic and coulometric behaviour of 3-chloro-3-phenyl-1-propyne in dimethylformamide containing 0.1 M tetraethylammonium perchlorate. Four polarographic waves with half-wave potentials of −1.14, −1.87, −2.41 and −2.74 V vs SCE were observed for this compound, and controlled-potential electrolyses established that each of the first two polarographic waves corresponds to a one-electron transfer. Although the half-wave potentials for the first two polarographic waves are characteristic of 3-chloro-3-phenyl-1-propyne itself, the half-wave potentials for the third and fourth waves are nearly the same as the half-wave potentials measured for 1,1-diphenylallene[6]. These results can be interpreted as signifying that the first step in the reduction of 3-chloro-3-phenyl-1-propyne (42) is the one-electron cleavage of the carbon–chlorine bond to produce a radical (43) capable of being further reduced and then protonated to yield 1-phenylallene (44) (equation 21). Presumably, stepwise reduction of 1-phenylallene (44) is responsible for the third and fourth polarographic waves seen for 3-chloro-3-phenyl-1-propyne. There is no reason to expect the polarography of 1-phenylallene to differ significantly from that of 1,1-diphenylallene.

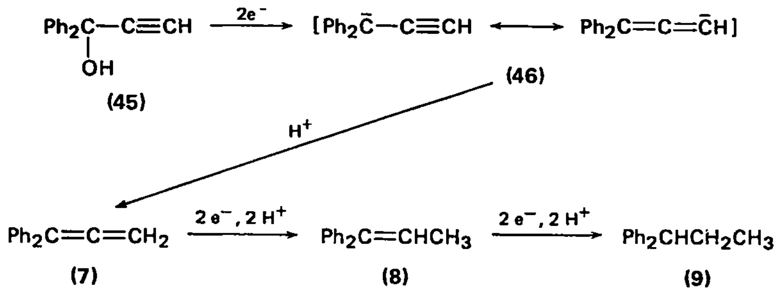


(21)

In a study by Lund, Doupeux, Michel, Mousset and Simonet[16], allenes have been suggested as intermediates in the electrochemical reductions of 3-hydroxy-3,3-diphenyl-1-propyne, 3-hydroxy-3-phenyl-1-propyne and 3-hydroxy-3-phenyl-1-butyne in dimethylformamide containing 0.1 M tetra-*n*-butylammonium iodide. Typical of the behaviour of these three species is that of 3-hydroxy-3,3-diphenyl-1-propyne (45). A polarogram for this compound exhibits a single wave with a half-wave potential of −2.71 V vs SCE that appears to correspond to a two-electron transfer to yield the anion (46) (equation 22). However, the instability of the anion under the extant experimental conditions prompted the authors to investigate the reduction of 3-hydroxy-3,3-diphenyl-1-propyne in dimethylformamide containing an excess of phenol as well as the supporting electrolyte. Controlled-potential electrolysis of the starting material at −2.70 V vs SCE involved the addition of essentially six electrons, and 1,1-diphenylpropane (9) was formed in 95% yield. To account for this result, a mechanistic scheme implicating 1,1-diphenylallene (7) and 1,1-diphenyl-1-propene (8) was proposed (equation 23).



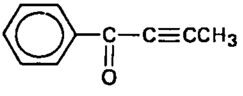
$$\underset{(45)}{Ph_2\underset{\displaystyle OH}{\underset{|}{C}}\text{—}C{\equiv}CH} \xrightarrow{2\,e^-} \underset{(46)}{Ph_2\bar{C}\text{—}C{\equiv}CH} + OH^- \qquad (22)$$



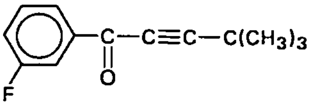
(23)

However, the allene (7) and olefin (8) are electroactive at potentials necessary to reduce the carbon—oxygen bond of the starting material, so that neither intermediate can be isolated.

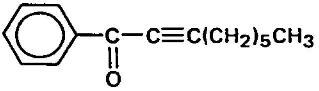
Finally, the polarographic and controlled-potential electrolytic behaviour of four acetylenic ketones – 1-phenyl-2-butyn-1-one (47), 1-(3-fluorophenyl)-4,4-dimethyl-2-pentyn-1-one (48), 1-phenyl-2-nonyn-1-one (49) and 1-phenyl-4-cyclohexyl-2-butyn-1-one (50) – in alcohol—water mixtures has been described by Degrand and Lacour[17]. Polarograms for the reduction of these species are unusually complicated in appearance; the number of polarographic waves depends on the pH of the medium. One of the mechanistic schemes proposed for the reduction of 1-phenyl-2-butyn-1-one (47) involves an allene intermediate (51) (equation 24),



(47)



(48)



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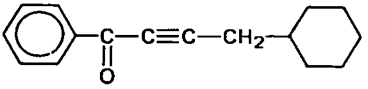

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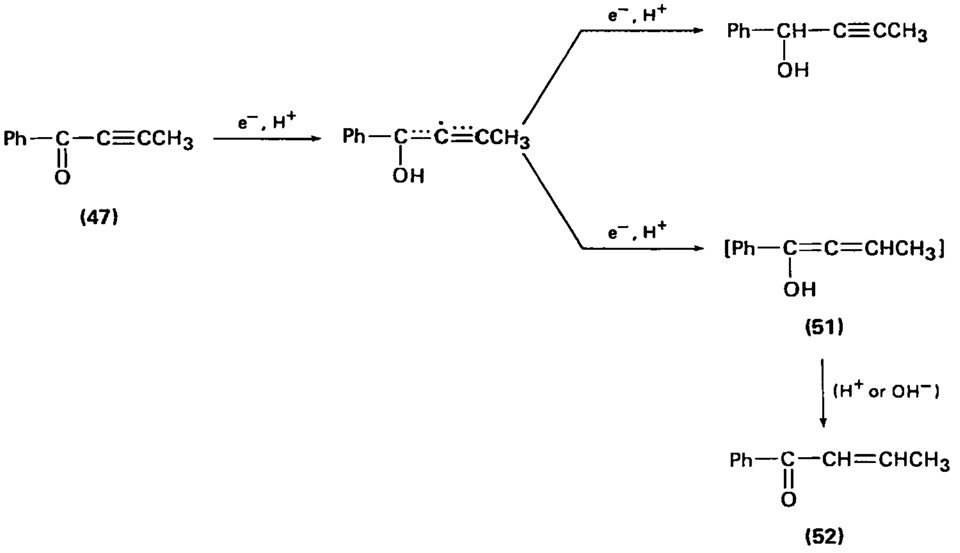


(24)

but, if the allene is formed transiently, it is quickly converted to 1-phenyl-2-buten-1-one (52) which undergoes further reduction to eventually yield 1-phenyl-2-buten-1-ol, 1-phenylbutan-1-ol and dimers, all of which can be isolated from the mixture of electrolysis products.

III. CUMULENES

A set of three papers by Kemula and Kornacki[18-20] comprises the only significant investigation of the electrochemistry of cumulenes. In dimethylformamide containing 0.2 M tetra-*n*-butylammonium iodide, a polarogram for 1,1,4,4-tetraphenylbutatriene (53) shows four diffusion-controlled waves[18] having half-wave potentials of −1.30, −1.63, −2.22 and −2.46 V vs SCE. Responsible for the first wave is a highly reversible one-electron process leading to generation of a radical anion (54) (equation 25). Cyclic voltammetry with a hanging mercury drop electrode was

$$\underset{(53)}{\mathrm{Ph_2C{=}C{=}C{=}CPh_2}} \xrightleftharpoons{e^-} \underset{(54)}{\mathrm{Ph_2C{=}C{=}\bar{C}{-}\dot{C}Ph_2}} \tag{25}$$

utilized to confirm the nature of this first electron-transfer step.

Addition of an electron to the radical anion (54) causes the second polarographic wave and results in the formation of the dianion (55) of the starting material (equation 26). If cyclic voltammograms are recorded at scan rates greater than

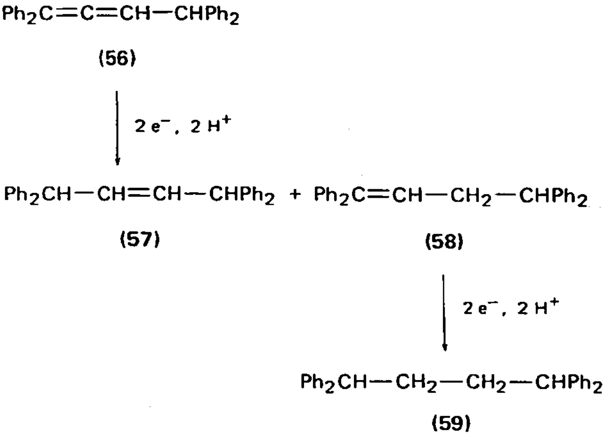
$$\underset{(54)}{\mathrm{Ph_2C{=}C{=}\bar{C}{-}\dot{C}Ph_2}} \xrightleftharpoons{e^-} \underset{(55)}{\mathrm{Ph_2C{=}C{=}\bar{C}{-}\bar{C}Ph_2}} \tag{26}$$

30V/s, the second stage of reduction exhibits a substantial degree of reversibility, and an anodic peak signalling oxidation of the dianion (55) back to the radical anion (54) can be seen. However, when the scan rate is decreased, dianions in the vicinity of the electrode are protonated (presumably by transfer of a hydrogen ion from the tetra-*n*-butylammonium cation) to yield 1,1,4,4-tetraphenyl-1,2-butadiene (56) (equation 27), and, at scan rates slower than 3 V/s, protonation of the dianion is

$$\underset{(55)}{\mathrm{Ph_2C{=}C{=}\bar{C}{-}\bar{C}Ph_2}} \xrightarrow{2\,H^+} \underset{(56)}{\mathrm{Ph_2C{=}C{=}CH{-}CHPh_2}} \tag{27}$$

virtually complete on the timescale of the experiment and reoxidation of the dianion is no longer observable. Another possible product, 1,1,4,4-tetraphenyl-2-butyne, which could be derived from the two-electron reduction of the starting material, is not formed.

Further reduction of 1,1,4,4-tetraphenyl-1,2-butadiene (56) at potentials corresponding to the third polarographic wave yields a mixture of 1,1,4,4-tetraphenyl-2-butene (57) and 1,1,4,4-tetraphenyl-1-butene (58); because the latter species is a phenyl-conjugated olefin, it is electroactive and undergoes reduction to the fully saturated 1,1,4,4-tetraphenylbutane (59), a process (equation 28) which causes the fourth polarographic wave. As stated above, for dimethylformamide containing



(28)

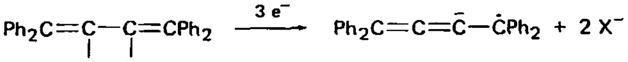
only tetra-*n*-butylammonium iodide, it is the supporting electrolyte cation which most probably serves as the source of protons for the various anionic species produced upon reduction of the starting material. On the other hand, in a dioxane–water solvent system, a polarogram for reduction of 1,1,4,4-tetraphenylbutatriene (**53**) shows only three waves, the half-wave potentials being −1.48, −2.24 and −2.53 V vs SCE. In a protic solvent the starting material undergoes in one step an irreversible two-electron, two-proton reduction directly to 1,1,4,4-tetraphenyl-1,2-butadiene (**56**); the second polarographic wave is attributable to the reduction of 1,1,4,4-tetraphenyl-1,2-butadiene (**56**) to a mixture of 1,1,4,4-tetraphenyl-2-butene (**57**) and 1,1,4,4-tetraphenyl-1-butene (**58**), and the third wave corresponds to conversion of the latter olefin (**58**) to 1,1,4,4-tetraphenylbutane (**59**).

Thus far, there have been no attempts to explore the possible synthetic usefulness of the preceding reactions. Obviously, by proper choice of potential (for example, −1.90 V vs SCE in either dimethylformamide, or dioxane–water), it should be feasible to prepare 1,1,4,4-tetraphenyl-1,2-butadiene (**56**) by means of the electrolytic reduction of the parent cumulene (**53**); interestingly, it is well established that chemical reduction of the cumulene gives a different olefin, 1,1,4,4-tetraphenyl-1,3-butadiene. Electrolysis of the parent cumulene at potentials close to −2.30 V vs SCE should result in a mixture of 1,1,4,4-tetraphenyl-2-butene (**57**) and 1,1,4,4-tetraphenyl-1-butene (**58**); in fact, from measurements of polarographic diffusion currents for the third and fourth waves for reduction of the cumulene in dimethylformamide, Kemula and Kornacki[18] estimated that the percentages of olefins 57 and 58 in the mixture are approximately 44% and 56%, respectively.

Studies have been made of the electrochemical behaviour of 1,4-diphenyl-1,4-di-*t*-butylbutatriene, 1,4-diphenyl-1,4-di-α-naphthylbutatriene, 1,4-diphenyl-1,4-dibiphenylbutatriene and 1,4-diphenyl-1,4-bis(*p*-chlorophenyl)butatriene in dimethylformamide containing 0.2 M tetra-*n*-butylammonium iodide, and the relationship between the polarographic half-wave potentials and absorption spectra for these compounds was probed[19]. Polarograms for *cis*- and *trans*-1,4-diphenyl-1,4-di-*t*-butylbutatriene exhibit only three waves with half-wave potentials of −1.77, −2.08 and −2.56 V vs SCE which are identical for each substance. Reduction of 1,4-diphenyl-1,4-di-α-naphthylbutatriene gives four polarographic waves having half-wave potentials (−1.34, −1.65, −2.14 and −2.45 V vs SCE) that agree closely with those for 1,1,4,4-tetraphenylbutatriene; this behaviour indicates that the electrochemistry of both species is very similar. For 1,4-diphenyl-1,4-dibiphenylylbutatriene, a polarogram with five waves is obtained and the half-wave potentials are –1.26, –1.58, –2.07, –2.33 and –2.55 V vs SCE; therefore, this compound also behaves much like 1,1,4,4-tetraphenylbutatriene except that the fifth wave is attributable to reduction of the biphenyl groups attached to the cumulene. Similarly, 1,4-diphenyl-1,4-bis(*p*-chlorophenyl)butatriene exhibits five polarographic waves with half-wave potentials of –1.21, –1.57, –2.13, –2.46 and –2.68 V vs SCE, and the fifth wave arises from reduction of the carbon–chlorine bonds of the *p*-chlorophenyl moieties.

In dimethylformamide containing 0.2 M tetra-*n*-butylammonium iodide, a polarogram for 1,1,4,4-tetraphenyl-2,3-dichloro-1,3-butadiene consists of four waves with half-wave potentials of –1.48, –1.68, –2.23 and –2.49 V vs SCE; under the same conditions, four polarographic waves are observed for the reduction of 1,1,4,4-tetraphenyl-2,3-dibromo-1,3-butadiene, and the half-wave potentials are –1.35, –1.65, –2.23 and –2.45 V vs SCE[20]. Note that the half-wave potentials for the second, third and fourth waves for each compound closely match those for 1,1,4,4-tetraphenylbutatriene (53). On the other hand, the half-wave potential for the first wave for each dihalobutadiene is more negative than the corresponding value for the cumulene (–1.30 V vs SCE) which indicates that the cumulene is somewhat easier to reduce than the dihalobutadienes. In addition, microcoulometric measurements have established that the first polarographic wave for each dihalobutadiene is caused by an electrochemical process involving the uptake of three electrons. However, the numbers of electrons associated with the reactions responsible for the second, third and fourth waves for the dihalobutadienes are exactly the same as those for the second, third and fourth waves for 1,1,4,4-tetraphenylbutatriene.

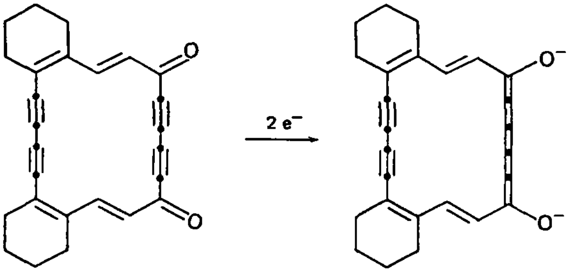
When the information in the preceding paragraph is scrutinized, it is evident that the first step in the reduction of each dihalobutadiene (60) is a three-electron process leading to formation of the radical anion (54) of 1,1,4,4-tetraphenylbutatriene (equation 29). Each of the two carbon–halogen bonds undergoes a one-electron scission to yield 1,1,4,4-tetraphenylbutatriene (53) which, being easier to reduce than the dihalobutadienes, immediately accepts one more electron to give radical anion (54). At potentials more negative than those of the first polarographic waves for the dihalobutadienes, the systems mimic the behaviour of 1,1,4,4-tetraphenylbutatriene described earlier.



$$\mathrm{Ph_2C{=}\underset{X}{C}{-}\underset{X}{C}{=}CPh_2} \xrightarrow{3\,e^-} \mathrm{Ph_2C{=}C{=}\overset{-}{C}{-}\overset{\cdot}{C}Ph_2} + 2\,X^- \qquad (29)$$

(60) (54)

More recently, a study of the electrochemical reduction of some tetradehydro-[18]annulene diones has been reported by Breslow, Murayama, Drury and Sondheimer[21]. Typical of the behaviour of these species is that shown by the dicyclohexenoannulene dione (61). Cyclic voltammetry of this compound at a platinum disk in dimethylformamide containing 1.0 M tetra-*n*-butylammonium perchlorate reveals a pair of reversible one-electron transfers; the first step in the reduction gives rise to a radical anion, and the overall reduction of the starting material results in the formation of a cumulene dianion (62) (equation 30). There has been no further exploration of the reduction of the cumulene dianions, but the possibility for additional study of these systems does exist.



(30)

(61) (62)

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The Chemistry of Ketenes, Allenes and Related Compounds
Edited by Saul Patai

CHAPTER **13**

Biological formation and reactions

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I. INTRODUCTION

The section on naturally occurring allenes in the first volume[1] of this series comprised less than one and a half pages, and encompassed ten compounds. Advances in chromatographic and spectroscopic methods have led, in the intervening fourteen years, to the isolation of numerous allenic natural products. These compounds are often of structural interest, they pose interesting biosynthetic questions, and they are in some cases endowed with significant physiological activity. Section II of this chapter will deal with the origins, structure and biosyntheses of allenic natural products, and will be subdivided in terms of plant, insect and animal origin.

In another context, enzymatically generated allenes (as well as ketenes and ketene imines) have recently assumed importance in the development of specific enzyme inactivators. Section III of this chapter will survey this area and the allene section will be partitioned on the basis of enzyme type. Section IV describes some allenes which appear to inhibit steroid transformations in insects.

II. ALLENIC NATURAL PRODUCTS

A. Fungal Allenes

The presence of the allene grouping in nature was first demonstrated in 1952 by Celmer and Solomons, who isolated and characterized the allenic fungal metabolite, mycomycin[2-4] Since that time a substantial number of other allenes have been found among the polyacetylenic metabolites of several fungi (see Table 1). Some of these allenes have antibiotic activity *in vitro*, but the compounds are too unstable to be of practical use[5-8].

It is helpful to discuss the biosynthesis of these allenic compounds in the larger context of the biosynthesis of fungal polyacetylenes. Like the common fatty acids, these polyacetylenes originate from the condensation of acetyl-CoA and subsequent Acyl-CoA derivatives with malonyl-CoA[17]. Two mechanisms have been suggested for the introduction of the acetylenic bonds. In the first mechanism an elimination from an enol phosphate or other suitably activated enol is proposed[18,19], whereas in the second mechanism the further dehydrogenation of an olefin to an acetylene has been suggested[17].

Bu'lock and Smith have demonstrated the conversion of $[10\text{-}^{14}C]$-oleic acid to dehyromatricarianol (7) by the fungus *Tricholoma grammopodium* and have suggested the sequence shown in Scheme 1 to explain this biotransformation[20]. Fungal polyacetylenes of various lengths would arise by oxidations of the postulated intermediate 5. Other structural modifications would be accomplished by related enzymatic processes, e.g. decarboxylation, hydroxylation, etc. The ubiquitous diyne–allene system can be viewed as a consequence of a propargyl rearrangement of the appropriate triyne precursor. Unpublished results have been cited that report a rearrangement of this type, accompanied by ester reduction and decarboxylation, for the conversion of triyne 8 to marasin (9) by the fungus *Marasmius ramealis*[17].

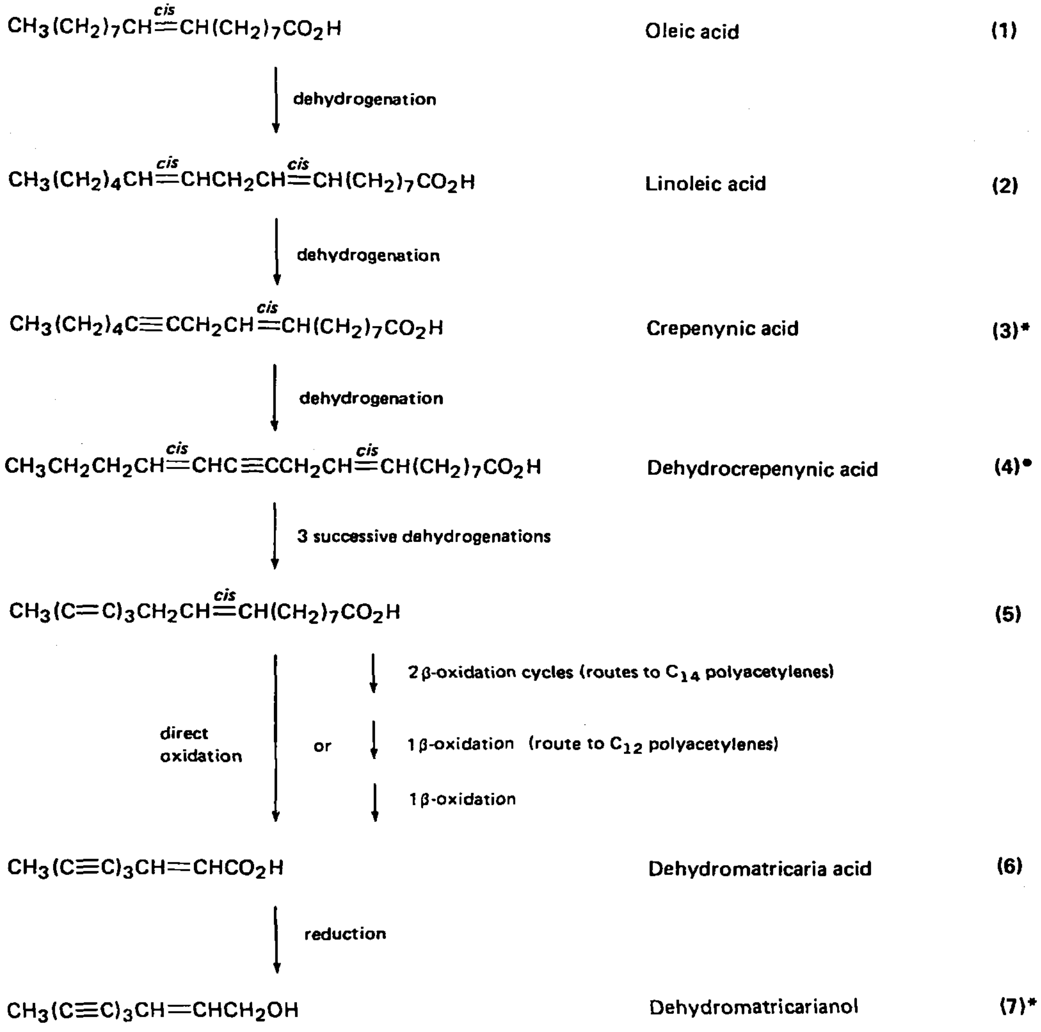
$HO_2C(C\equiv C)_3CH_2CH_2CO_2Et$

(8)

$HC\equiv C-C\equiv C-CH=C=CH-CH_2CH_2OH$

(9)

There are several earlier reviews that discuss the biosynthesis of polyacetylenes in greater detail[17,21-24], and several papers that describe the chemical synthesis of the diyne–allene system[25-28]. It is noteworthy that while polyacetylenes occur in higher plants, the allene grouping has not been found in these polyacetylenes. Speculation as to why this is the case is apparently lacking.



$CH_3(CH_2)_7CH\overset{cis}{=}CH(CH_2)_7CO_2H$ Oleic acid (1)

dehydrogenation

$CH_3(CH_2)_4CH\overset{cis}{=}CHCH_2CH\overset{cis}{=}CH(CH_2)_7CO_2H$ Linoleic acid (2)

dehydrogenation

$CH_3(CH_2)_4C{\equiv}CCH_2CH\overset{cis}{=}CH(CH_2)_7CO_2H$ Crepenynic acid (3)*

dehydrogenation

$CH_3CH_2CH_2CH\overset{cis}{=}CHC{\equiv}CCH_2CH\overset{cis}{=}CH(CH_2)_7CO_2H$ Dehydrocrepenynic acid (4)*

3 successive dehydrogenations

$CH_3(C{\equiv}C)_3CH_2CH\overset{cis}{=}CH(CH_2)_7CO_2H$ (5)

direct oxidation or 2 β-oxidation cycles (routes to C_{14} polyacetylenes) 1 β-oxidation (route to C_{12} polyacetylenes) 1 β-oxidation

$CH_3(C{\equiv}C)_3CH{=}CHCO_2H$ Dehydromatricaria acid (6)

reduction

$CH_3(C{\equiv}C)_3CH{=}CHCH_2OH$ Dehydromatricarianol (7)*

SCHEME 1.

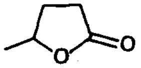
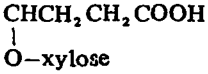
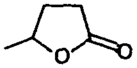
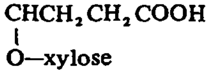
SCHEME 1. Scheme proposed by Bu'lock and Smith for the biosynthesis of ^{14}C-labelled dehydromatricarianol from [10-^{14}C]-oleic acid.[20] Compounds marked with an asterisk were isolated; compounds without an asterisk were postulated but not isolated.

B. Allenes from Higher Plants

1. *Unconjugated allenes*

In addition to the polyacetylenic allenes of fungal origin, four unconjugated allenes have been isolated from higher plants. These compounds are: laballenic acid (**10**) from *Leonotis nepetaefolia*[29], lamenallenic acid (**11**) from *Lamium pur-*

TABLE 1. Fungal allenic polyacetylenes

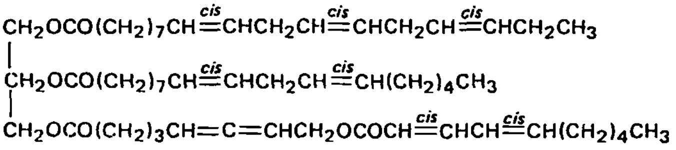
Compound		Reference
$HC\equiv C-C\equiv C-CH=C=CH-CH\overset{cis}{=}CH-CH\overset{trans}{=}CHCH_2CO_2H$	(Mycomycin)	2–4
$H_2C=C=CH-C\equiv C-C\equiv C-CH\overset{cis}{=}CHCH_2CO_2H$	(Drosophilin D)	9
$HC\equiv C-C\equiv C-CH=C=CH-X$		
X = CH_2OH		10
CH_2CH_2OH (Marasin)		11
$CH_2CH_2CH_2OH$		10
$CH_2CH_2CH_2CH_2OH$		10
$CH(OH)CH_2CH_2OH$		10
$CH(OH)CH_2CH_2CH_2OH$		10
$CH_2CH(OH)CH_2CH_2OH$		10
$CH_2COOR(R = H, R = CH_3)$		12–13
$CH(OH)CH_2CH_2COOR$ ($R = CH_3$; R = H, nemotinic acid)		14
	(Nemotin)	14
 $\underset{\displaystyle O-xylose}{\underset{\mid}{CH}}CH_2CH_2COOH$		15
$CH_3C\equiv C-C\equiv C-CH=C=CHX$		
X = CH_2CH_2OH		10
$CH(OH)CH_2CH_2COOH$ (Odyssic acid)		16
	(Odyssin)	16
 $\underset{\displaystyle O-xylose}{\underset{\mid}{CH}}CH_2CH_2COOH$		17

pureum[30], 8-hydroxy-5,6-octadienoic acid (12) from *Sapium japonicum*[31], and the allenic triglyceride tetraester 13 from *Sapium sebiferum*[32].

$$CH_3(CH_2)_{10}CH=C=CH(CH_2)_3COOH \tag{10}$$

$$CH_3CH\overset{trans}{=}CH(CH_2)_8CH=C=CH(CH_2)_3COOH \tag{11}$$

$$HOCH_2CH=C=CH(CH_2)_3COOH \tag{12}$$



(13)

$$\begin{array}{l} CH_2OCO(CH_2)_7CH\overset{cis}{=}CHCH_2CH\overset{cis}{=}CHCH_2CH\overset{cis}{=}CHCH_2CH_3 \\ \mid \\ CH_2OCO(CH_2)_7CH\overset{cis}{=}CHCH_2CH\overset{cis}{=}CH(CH_2)_4CH_3 \\ \mid \\ CH_2OCO(CH_2)_3CH=C=CHCH_2OCOCH\overset{cis}{=}CHCH\overset{cis}{=}CH(CH_2)_4CH_3 \end{array}$$

$$CH_3(CH_2)_{10}C\equiv C(CH_2)_4COOH \tag{14}$$

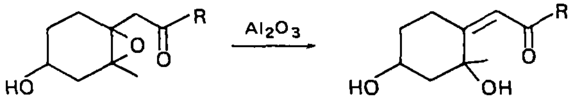
Both laballenic and lamenallenic acid have been shown to have the *R*-configuration, and both have been synthesized[33]. Bu'lock has suggested[22] that tariric acid (14) is the probable natural precursor of labellenic acid, and a similar acetylenic precursor for the allenic acid component of compound 13 has been suggested by Gunstone[34]. Further analysis of the seed oil from *Sapium sebiferum* has shown that the oil contains a number of allenic triglyceride tetraesters[35]. These compounds contain different fatty acids esterified at the $C_{(1)}$ and $C_{(2)}$ positions of the glycerol moiety. The seed oil from *Sebastiana ligustrina*[36] also contains these allenic triglyceride tetraesters, and it is quite likely that the seed oil from *Sapium japonicum* contains them as well[31]

2. *Allenic carotenoids*

Carotenoids are widely distributed in nature[37], and the development of modern chromatographic and spectroscopic methods during the last thirty years has led to an increased rate of isolation and structure elucidation of these pigments[38].

It was not until 1966 that the first allenic carotenoid structure was established[39-41]. This compound, fucoxanthin (found in brown algae and diatoms) is considered to be the most abundant of the carotenoids, and had first been isolated some 40 years previously. Rigorous chemical and spectroscopic studies, detailed in an extensive paper by Weedon and coworkers[42], firmly established structure 15 (Table 2) for fucoxanthin. A number of other allenic carotenoids have since been identified, and their structures are also shown in Table 2.

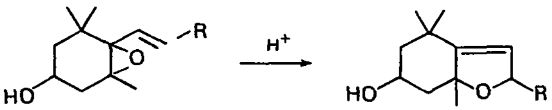
Two close relatives of fucoxanthin were secured during the isolation of fucoxanthin from *Fucus vesiculosus*[42]. These compounds, isofucoxanthin (16) and isofucoxanthinol (17) may well be artefacts, formed from fucoxanthin during chromatography on alumina. Indeed, it was shown that treatment of fucoxanthin with basic alumina could generate 16 and 17 (equation 1). Base-catalysed conversion of the β,γ-epoxyketone system in fucoxanthin to the γ-hydroxy-α,β-unsaturated ketone system of 16 and 17, via proton abstraction at $C_{(7)}$, is not unexpected. It has been suggested[41] that a pigment found in the yolks of eggs from chickens fed on seaweed meal is isofucoxanthin (16). It is not clear if this compound is an artefact from the isolation procedure, or if indeed isofucoxanthin is originally present in the egg yolks.



(1)

A more complex variant of fucoxanthin itself, considered to be the 19'-hexanoyloxy derivative (18), has been isolated[43] from algae.

Two more allenic carotenoids, isolated from green leaves, are the closely related foliaxanthin (19) and foliachrome (20)[44]. The latter compound can be obtained directly from foliaxanthin (19) by mild acid treatment, which transforms the allylic epoxide system of (19) to the dihydrofuran system of foliachrome (20) (equation 2). It was subsequently established[45] that foliaxanthin is, in fact, identical with the



(2)

TABLE 2. Allenic carotenoids

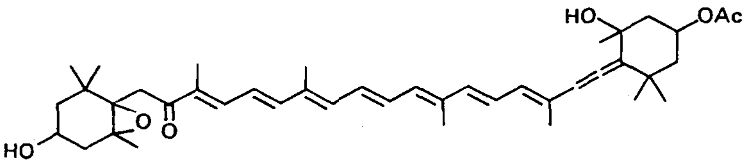
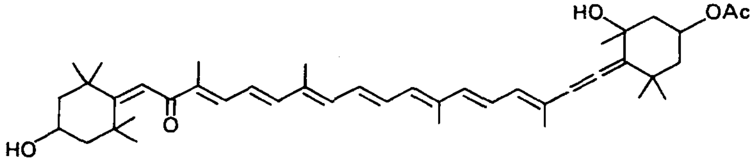
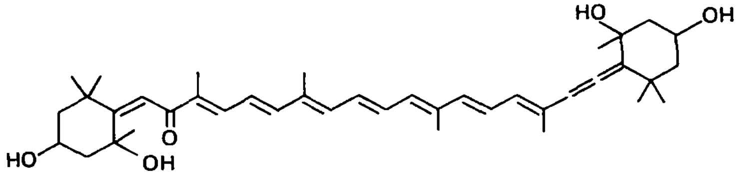
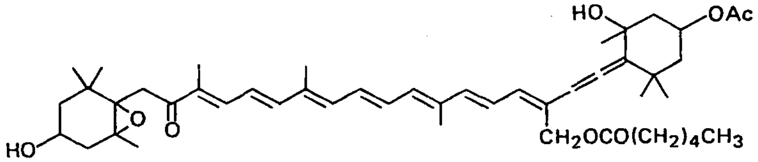
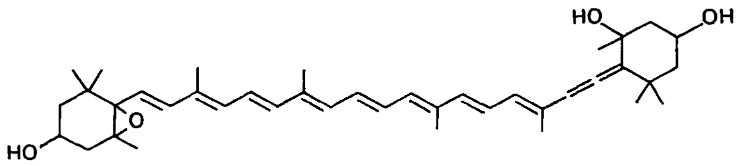
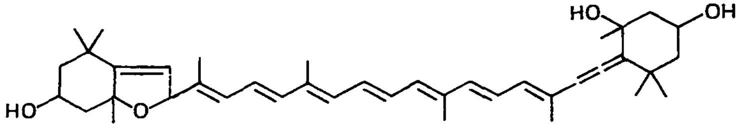
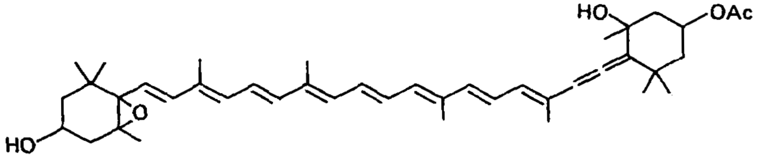
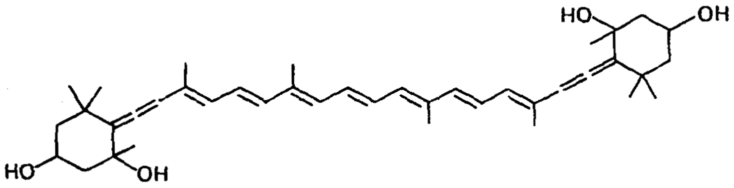
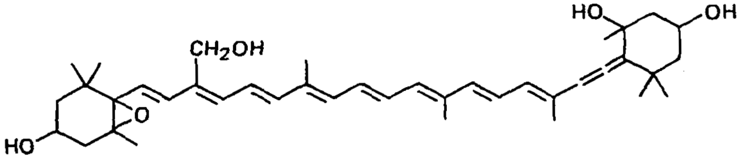
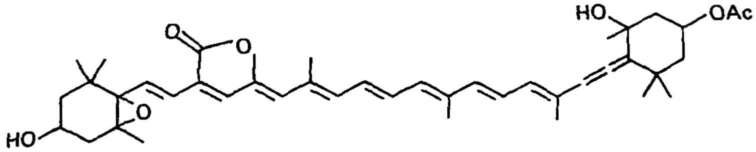
Compounds	Reference
 Fucoxanthin (15)	39–42
 Isofucoxanthin (16)	42
 Isofucoxanthinol (17)	42
 19′-Hexanoyloxyfucoxanthin (18)	43
 Neoxanthin≡Foliaxanthin (19)	44, 45
 Neochrome≡Foliachrome (20)	44, 45

TABLE 2. Continued

Compound	Reference
 Dinoxanthin (21)	47
 Mimulaxanthin (22)	48
 Vaucheriaxanthin (23)	49
 Peridinin (24)	50

very widespread pigment neoxanthin, while foliachrome is identical with the neoxanthin-derived pigment neochrome. The pigments trollixanthin and trolliflor have also been reported[46] recently to be identical with neoxanthin, in line with an earlier suggestion [42] that they might well be allenic and closely related to neoxanthin. Finally, the compound dinoxanthin (21) has been found[47] to be simply the 3′-acetate of neoxanthin.

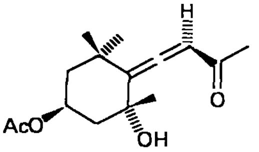
Other allenic carotenoids include mimulaxanthin[48] (22; from *Mimulus guttatus*), and vaucheriaxanthin (isolated from *Xanthophyceae*) for which the revised structure 23 has been recently suggested[49].

Finally, peridinin, the principal carotenoid pigment of dinoflagellates and known since 1890, has been shown recently to have the interesting structure 24[50].

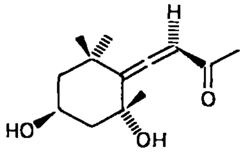
The absolute configuration of the allenic end-group in fucoxanthin (15) and in neoxanthin (19) has been established by Weedon and coworkers[51]. Thus, the allenic ketone 25 was obtained by oxidative degradation of fucoxanthin (15) by methods which did not affect the stereochemical integrity of the original system. Compound 25 was then converted to the corresponding optically active 3-hydroxy compound 26, whose absolute configuration was shown to be 3*S*,5*R*,6*R* by X-ray crystallography, using the 3-*p*-bromobenzoate ester 27. Hence the absolute configuration of the fucoxanthin-derived compound 25 is also 3*S*,5*R*,6*R*.

The allenic carotenoid neoxanthin (19) has previously been correlated with fucoxanthin (15) and consequently also possesses the 3*S*,5*R*,6*R* configuration in its allenic end-group[51].

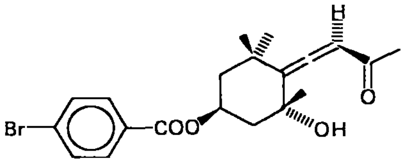
Compound 26 has also been isolated and characterized by Meinwald and coworkers[52] from the defensive secretion of the flightless grasshopper *Romalea microptera* (see Section II.C). The findings outlined above are also in accord with the suggestion[52] that the 'grasshopper ketone' (26) may be produced in the insect by degradation of a dietary allenic carotenoid such as neoxanthin.



(25)

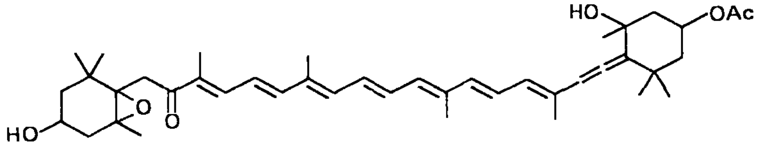


(26)

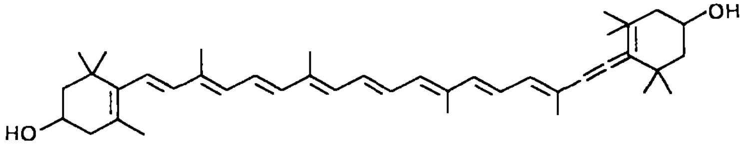


(27)

Finally, the biogenesis of the allenic carotenoids will be discussed. It has been speculated[42] that there is a biogenetic connection between acetylenic carotenoids and allenic carotenoids. A number of acetylenic carotenoids are known[38], and indeed fucoxanthin (15) and the acetylenic carotenoid diatoxanthin (28) cooccur in diatoms[53].

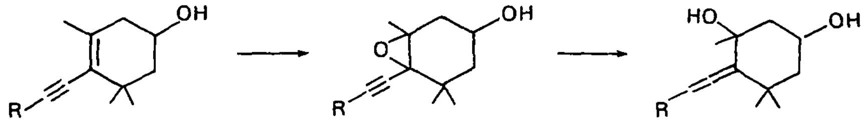


(15)



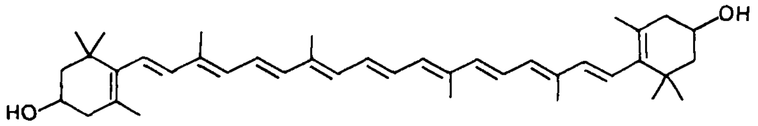
(28)

It has been pointed out[42] that ring-epoxidation of an acetylenic end-group, followed by a reductive process could, in principle, generate the allenic system (29 → 31).



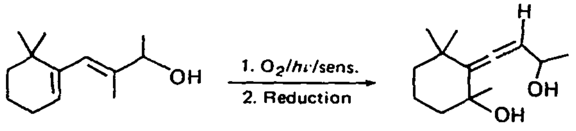
(29) (30) (31)

More recently, the carotenoid zeaxanthin (32), or a related compound, has been proposed as a biosynthetic precursor for the allenic carotenoids fucoxanthin and neoxanthin.



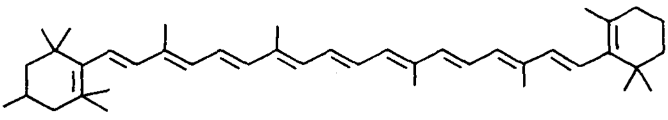
(32)

The proposal stems from studies, made independently by three groups, on the photosensitized oxygenation of β-ionol (33) and similar systems[54–56]. The process generates, *inter alia*, allenic hydroperoxides which can be reduced to allenic alcohols (e.g. 34).



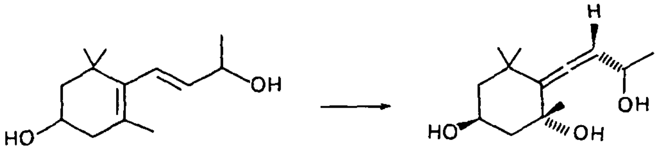
(33) (34) (3)

These results have led to the suggestion[54–56] that analogous processes in nature might convert zeaxanthin to allenic carotenoids such as fucoxanthin and neoxanthin. Indeed, in a model study with all-*trans* β-carotene 35, it has been reported[57] that photosensitized oxygenation leads to a complex mixture containing an allenic carotenoid.



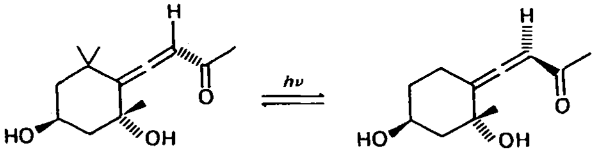
(35)

This biosynthetic proposal was thrown into disarray when it was found[58] that the photosensitized oxidation of the β-ionol derivative 36 produces an allene 37 whose relative configuration is *opposite* to that found in fucoxanthin and neoxanthin.



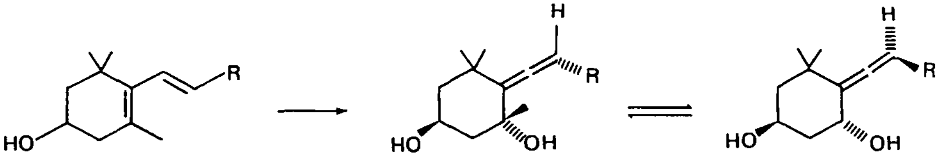
(36) (37) (4)

The suggestion was then made[59] that allenic systems initially formed in nature might undergo photoisomerization. Indeed, irradiation of the allenic ketone 38 using a high-pressure mercury lamp, induced photo equilibration giving an approximately 1:1 mixture of 38 and 26.



(38) (26) (5)

This stereomutation might then be incorporated into a scheme in which photooxidation of a diene precursor (e.g. 39) generates an *S*-allenic carotenoid (40) which then isomerizes to the natural *R*-allene (41).



(39) (40) (41) (6)

This proposal was tested[60], using fucoxanthin, and it was found that stereomutation occurred readily in benzene with iodine catalysis and diffuse light. A number of isomers were obtained, and one proved to be the unfamiliar *S*-allene, which can be very readily converted back to the *R*-allene. Furthermore, a small quantity of this common *S*-allenic isomer of fucoxanthin was then found in a fresh seaweed sample, lending some support to this biosynthetic hypothesis. It is worth pointing out that the postulated diene oxidation and stereomutation processes need not necessarily be light-catalysed in the plant.

C. Allenes from Insects

The male dried-bean beetle, *Acanthoscelides obtectus* (Say), has the distinction of being the only insect so far known to use an allenic compound, (—)-methyl *n*-tetradeca-*trans*-2,4,5-trienoate (42), for a sex pheromone[61,62]. The biosynthesis of this pheromone has not been investigated, but several synthetic routes to the compound have been developed[63-67].

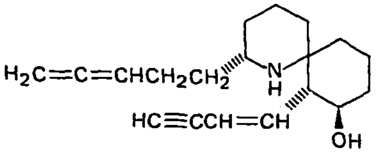
$$CH_3(CH_2)_6CH_2CH{=}C{=}CHCH\overset{trans}{=}CHCOOCH_3$$

(42)

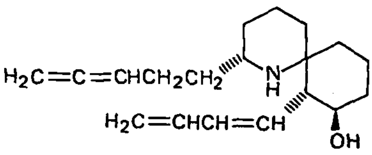
The flightless grasshopper *Romalea microptera* uses the allenic ketone 26 as an ant-repellant[52]. This compound has already been described in the section on allenic carotenoids (Section II.B.2). As noted there, it seems quite likely that the grasshopper generates this compound by oxidative degradation of a dietary allenic carotenoid[52]. This suggestion is consistent with the fact that the allenic end-groups of the carotenoids fucoxanthin and neoxanthin both have the same absolute configuration as allenic ketone 26[51]. Several synthetic routes to the 'grasshopper ketone' have been developed[51,59,68,69].

D. Allenic Alkaloids from Neotropical Frogs

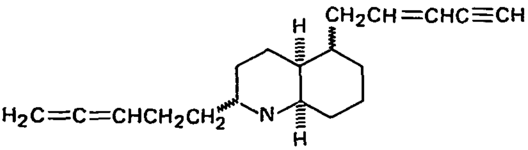
Many members of the *Dendrobatidae*, a family of small neotropical frogs, secrete toxic skin alkaloids some of which are used as dart poisons by certain South American Indians. An impressive series of studies has led to the isolation and structure elucidation of many of these neurotoxins (recently classified by Daly and coworkers[70]) which are used by the frogs as defences against predators. At least six classes of alkaloids have been recognized[70]. These comprise the steroidal batrachotoxins[71] as well as at least five classes of non-steroidal alkaloids. The latter include the histrionicotoxins[70,73] (1-azaspiro-[5.5]-undecanes) and the pumiliotoxin C class[74] (decahydroquinolines), and allenic groupings have been found in both these classes. Thus, isodihydrohistrionicotoxin (43) and isotetrahydrohistrionicotoxin (44) each contains a terminal allene grouping, as does the pumiliotoxin C representative (45).



(43)



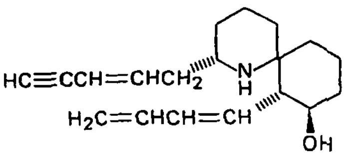
(44)



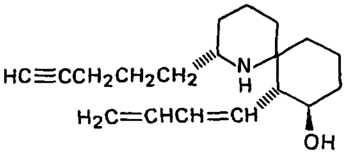
(45)

The histrionicotoxin structures (43 and 44) are firmly established, and these compounds are the first reported examples of naturally occurring allenic alkaloids, The positions and configurations of the side-chains are not yet rigorously defined in the case of the allenic pumiliotoxin C (45).

The biogenesis of these alkaloids still remains to be determined. However, a plausible biosynthetic pathway, stemming from a piperidine precursor, has been proposed[70] to account for the ring-systems in the non-steroidal dendrobatid alkaloids. The genesis of the allene system in these compounds is unknown, but the cooccurrence of the allenic histrionicotoxins (43 and 44) with the acetylenic analogues 46 and 47 is interesting. The allene system could, in principle, arise by enzymatic 1,4-reduction of the conjugated ene–yne side-chain or via propargylic rearrangement of the $CH_2CH_2CH_2C{\equiv}CH$ system.



(46)



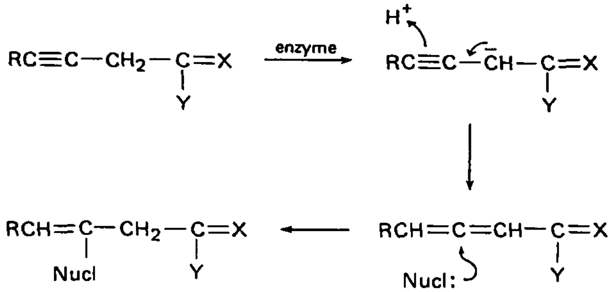
(47)

Since complete reduction of the unsaturated side-chains yields a compound with substantially unchanged biological activity, the allenic grouping is not essential for the physiological action[75] of the histrionicotoxins.

III. ALLENES, KETENES AND KETENE IMINES AS ENZYME-GENERATED INACTIVATORS

Much of the current interest in the biological formation and reactions of allenes and, to a lesser degree, of ketenes and ketene imines is related to the development of enzyme-generated irreversible inhibitors. Such inactivators, termed k_{cat} inhibitors or suicide substrates, contain a potential reactive grouping, which is unmasked by the normal catalytic action of the target enzyme. This latent reactive grouping is usually electrophilic, and its formation at the active site of the target enzyme should lead to covalent bond formation with an adjacent enzyme nucleophile. The general area has been the subject of several reviews[76-79], the most recent being the excellent survey by Walsh[79].

The principle of suicide inactivation, stemming from Bloch's original studies[80], has been applied to numerous enzymes which catalyse carbanion formation. Such enzymes can, in principle, generate the propargylic anion from a suitable acetylenic substrate analogue leading to an allene (equation 7). The latter, when part of a conjugated system, is susceptible to Michael addition at the sp-hybridized carbon by an enzyme nucleophile. Similar reasoning has been followed for the enzymatic generation of ketenes and ketene imines. Other enzymatically generated electrophiles have been employed as enzyme inactivators, but these fall outside the scope of this chapter.

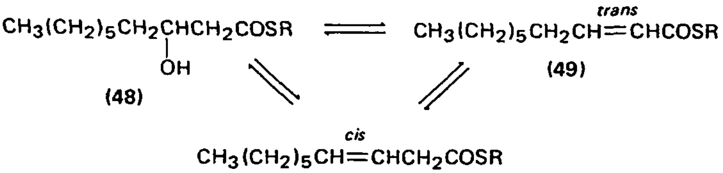


(7)

A. Allenes

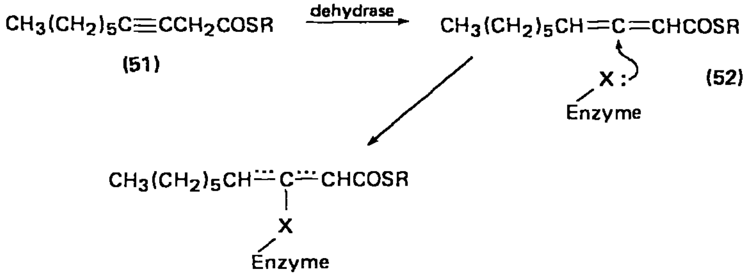
1. *Isomerases*

The original work with allenes in this area was done by Bloch and his colleagues in studies of the inhibition of the *Escherichia coli* enzyme, β-hydroxydecanoyl thiol ester dehydrase[80]. This dehydrase reversibly interconverts D(—)-β-hydroxydecanoyl thiol ester 48, α,β-decenoyl thiol ester 49 and β,γ-decenoyl thiol ester 50.



(50)

When the enzyme was incubated with acetylenic substrate analogue 51, potent time-dependent irreversible inactivation of the dehydrase was observed[81–83]. Further investigation of the mechanism of this inactivation showed[84,85] that acetylenic thiol ester 51 was enzymatically converted to (+)-2,3-decadienoyl thiol ester 52. Thiol ester 52 is a good electrophile because its allene group is activated by conjugation with the thiol ester group. Consequently, allene 52 is readily attacked by a nucleophilic amino acid residue (thought to be histidine) at the active site of dehydrase, leading to an inactive covalently-modified enzyme (equation 8)[83]



(8)

Model studies, involving the reaction of 2,3-decadienoic acid and its derivatives with histidine and several of its derivatives, have been performed to elucidate the structure of the allene–enzyme adduct[85], Adducts containing the double bond of the decenoyl moiety in either the α,β- or the β,γ-position were isolated, depending on the particular histidine derivative used as a nucleophile (see Table 3).

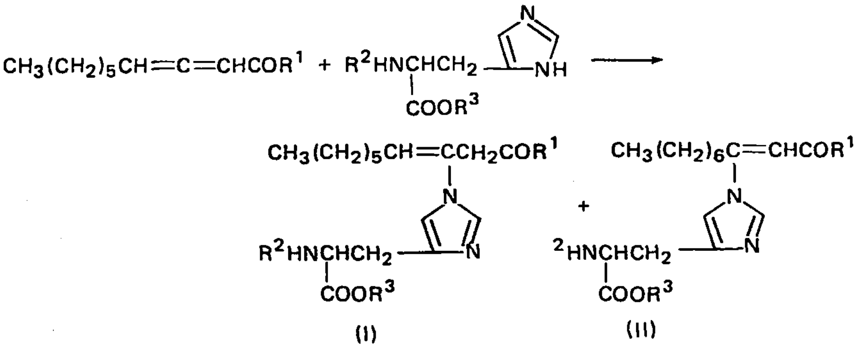
The formation of a conjugated allene from a non-conjugated acetylenic substrate at the active site of an enzyme does not necessarily mean that the enzyme will be inactivated via nucleophilic reaction with the activated allene. It is possible, for example, that the allene may leave the active site before nucleophilic addition can occur. Alternatively, the enzyme may not have a nucleophilic residue appropriately placed for such an addition reaction. It may be for these reasons that an acetylene–allene acyl thiol ester isomerase from hog liver can isomerize 3-decynoyl-*N*-acetylcysteamine to (+)-2,3-decadienoyl-*N*-acetylcysteamine without being inactivated by the allenic product[86]. Beef-liver crotonase is also able to hydrate 2,3-decadienoyl-*N*-acetylcysteamine to the enol form of β-ketodecanoyl-*N*-acetylcysteamine without being inactivated by the allene[87].

Although pig-heart thiolase is not an isomerase, its inhibition by 3-butynoyl-CoA (53) and 3-pentynoyl-CoA (54)[88] is noted here because of the close similarity of these CoA esters to the thiol ester compounds used by Bloch[80] in his studies. Apparently this thiolase has, at the active site, a properly placed basic group which facilitates propargylic anion formation, and subsequent allene formation. In agreement with this proposal, buta-2,3-dienoyl-CoA (55) has been shown to inactivate thiolase[89]. Presumably penta-2,3-dienoyl-CoA (56) would also inhibit thiolase[89]. The same compounds have also been shown to inactivate rat hepatic cytoplasmic thiolase[90].

$RC{\equiv}CCH_2COSCoA$	$RCH{=}C{=}CHCOSCoA$
(53) $R = H$	(55) $R = H$
(54) $R = CH_3$	(56) $R = CH_3$

Another example of suicide inactivation of an isomerase has been described recently. The enzyme in question, Δ^5-3-ketosteroid isomerase from *Pseudomonas*

TABLE 3. Reaction[a] of 2,3-decadienoyl systems with histidine derivatives[85]



			Isolated yield (%)	
R^1	R^2	R^3	I	II
OH	CH_3CO	H	–[b]	–[b]
OCH_3	CH_3CO	H	40	–
SCH_2CH_3	CH_3CO	H	70[c]	–
SCH_2CH_3	H,	CH_3	–	40[d]
SCH_2CH_3	CH_3CO	CH_3	33	–[e]

[a] In all experiments the molar ratio of allene to histidine derivative was 1:2.

[b] No adducts were found. The allene appeared to polymerize.

[c] The product appeared to be a mixture of *cis* and *trans* olefinic adducts.

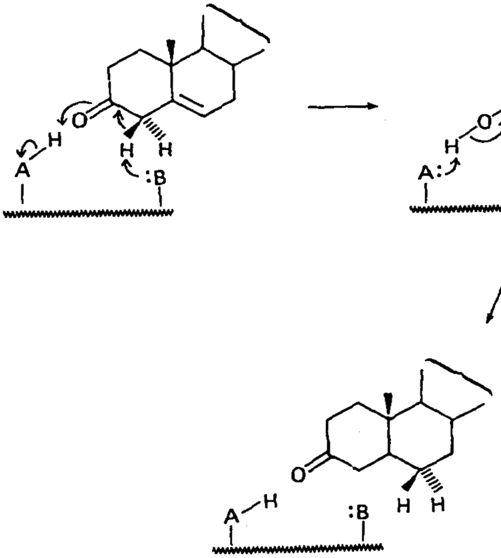
[d] The possibility that the histidine methyl ester was attached by the α-amino group instead of an imidazole nitrogen was not ruled out.

[e] The crude product was reported to contain this isomer. The ratio between the major isomer (the only isomer purified) and the minor isomer was reported as 30:1 respectively.

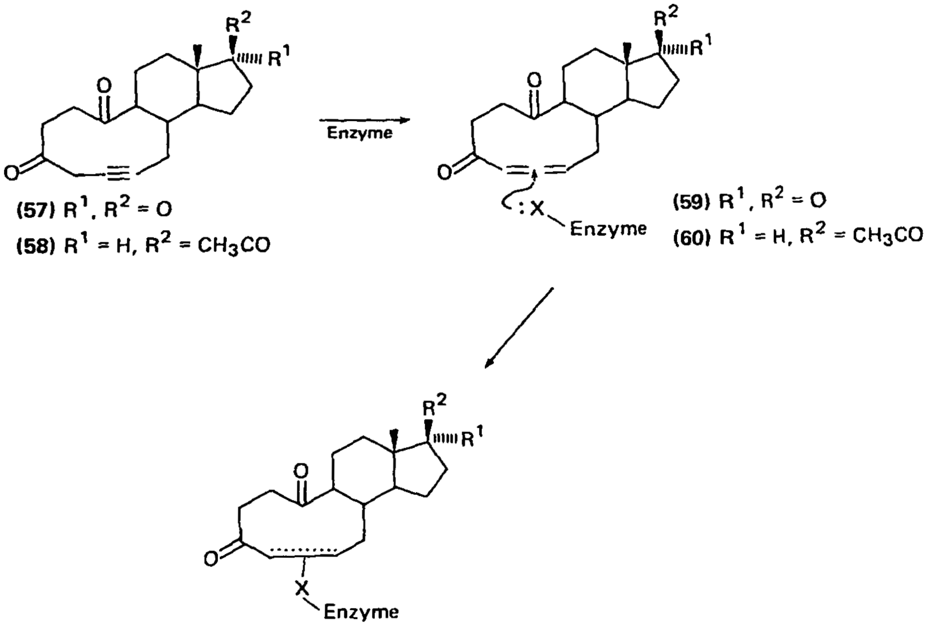
testosteroni, catalyzes the conversion of Δ^5-3-keto steroids to the corresponding Δ^4-3-keto steroids[91,92]. The proposed mechanism[91,93] involves abstraction of the 4β-axial proton, which is transferred intramoleculary to the 6β-position via a dienol intermediate (Scheme 2).

The acetylenic secosteroids 57 and 58 have been designed and synthesized as substrates for Δ^5-3-keto steroid isomerase[94]. It was hoped that the enzyme, through its normal catalytic action, would convert the β,γ-acetylenic ketones 57 and 58 to the corresponding conjugated allenic ketones 59 and 60. The latter should then react with an enzyme nucleophile (Scheme 3).

Indeed, incubation of the enzyme with compound 57 or 58 results in rapid, time-dependent irreversible inhibition of the enzyme[95]. A single inactivator molecule is bound per subunit of enzyme after inactivation[96]. The allenic ketones derived from these acetylenic suicide substrates have been synthesized non-enzymatically, and characterized, and their inhibitory effects have been studied[97]. Thus



SCHEME 2.

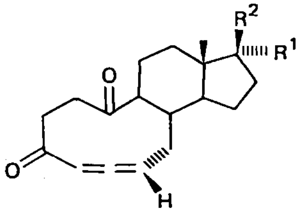


(57) $R^1, R^2 = O$
(58) $R^1 = H, R^2 = CH_3CO$

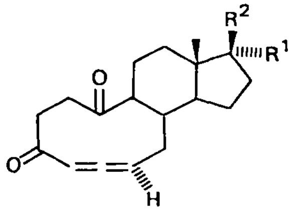
(59) $R^1, R^2 = O$
(60) $R^1 = H, R^2 = CH_3CO$

SCHEME 3.

acetylenic ketone 57 gave allenic ketones 61 and 62. Similarly, 58 gave the corresponding allenic ketones 63 and 64. The (4*R*)-allenes 61 and 63 each proved to irreversibly inactivate the enzyme in a manner identical to that of their acetylenic ketone precursors, indicating that the rate of isomerization is faster than the rate of inactivation. The (4*S*)-allenes 62 and 64 also inhibit the enzyme, but at slightly slower rates. However, since these allenes are somewhat unstable in solution, precise rates of inactivation are difficult to obtain[97].



(61) $R^1, R^2 = O$
(63) $R^1 = H, R^2 = CH_3CO$



(62) $R^1, R^2 = O$
(64) $R^1 = H, R^2 = CH_3CO$

It has also been shown[97] that incubation of the enzyme with the acetylenic ketones 57 or 58 generates the corresponding *pair* of allenic ketones in each case. Furthermore, prior to inactivation by the allenic ketones, the enzyme has been shown[97] to interconvert the (4*R*)- and (4*S*)-allenes. This interesting result no doubt stems from the principle of microscopic reversibility. However, it raises some question about the supposed complete β-face stereospecificity of the enzyme.

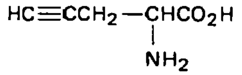
The (4*R*)-allenic ketone 61 has been subjected to X-ray crystallographic study, as has the acetylenic precursor 57. These studies[98] show that 61 is conformationally very similar to a normal Δ^4-3-keto steroid product of the enzyme. The acetylenic ketone 57 has a solid-state conformation which requires ring-inversion to resemble the solid-state conformation of the normal Δ^5-3-keto steroid substrate. It is not yet clear whether such a conformational change in 57 occurs in solution, or on binding to the enzyme.

Model studies have been carried out with (4*R*)-allenic ketone 61 and a variety of nucleophiles[99]. These reactions are summarized in Table 4. The factors which dictate Michael addition of XH giving the system 65 versus Michael addition with transannular bond formation to yield 66 are still not determined.

Finally, the acetylenic ketones 57 and 58, as well as allenic ketone 53 have been shown[100] to cause significant dose-dependent decreases in prostatic weight in normal intact male rats. The mechanism for this *in vivo* effect has not been established.

2. *Pyridoxal-linked enzymes*

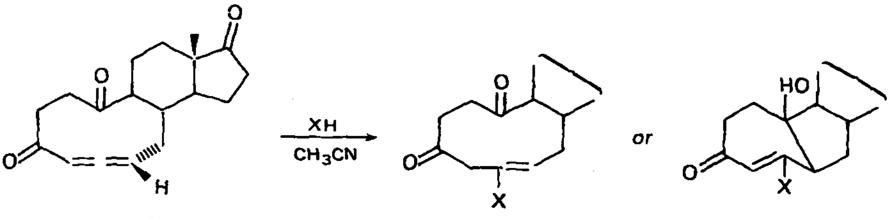
The natural product 2-amino-4-pentynoic acid (propargyl glycine) (67) inactivates a number of pyridoxal-dependent enzymes which generate β-carbanions from substrates. These enzymes are γ-cystathionase[101], cystathionine γ-synthetase[102], glutamic–pyruvic transaminase[102] and L-aspartate aminotransferase[103].



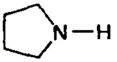
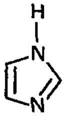
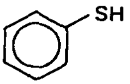
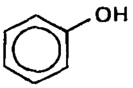
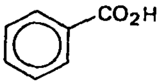
$$HC{\equiv}CCH_2{-}\underset{\displaystyle NH_2}{\underset{|}{C}}HCO_2H$$

(67)

TABLE 4. Addition of nucleophiles to (4*R*)-allenic ketone 61



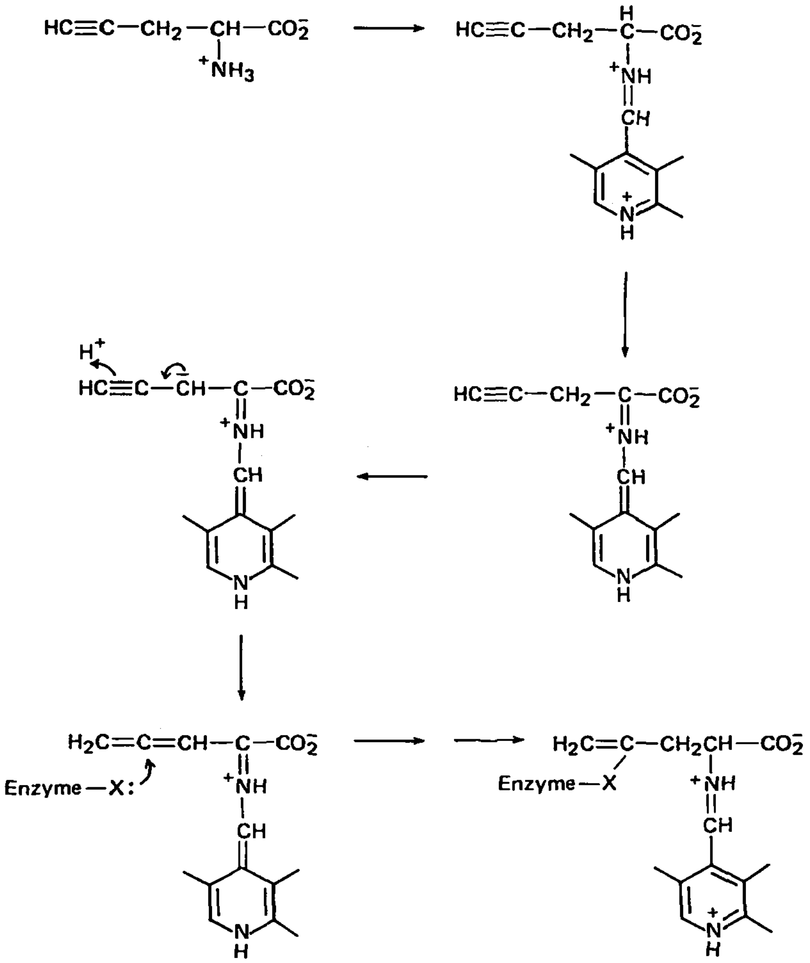
(61) (65) (66)

XH	Product
	66
CH_3OH	66
H_2O	66[a]
	65
	65
	65[b]
	65[b]
CH_3CO_2H	65[b]

[a] Isolated as the 3,5-diketone.
[b] Reaction carried out in the presence of triethylamine.

In all these cases, the mechanism of action is thought to involve enzymatic formation of a propargylic anion, and its rearrangement to an electrophilic conjugated allenic system. The postulated process is illustrated in Scheme 4 for the inactivation of γ-cystathionase by propargylglycine, a process first described by Abeles and Walsh[101] and recently the subject of a detailed paper by Washtien and Abeles[104].

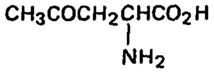
The inactivation process is time-dependent and irreversible and one mole of labelled propargyl glycine is incorporated per mole of enzyme. The proposed mechanism (Scheme 4) involves reaction of an enzyme-generated conjugated allene



SCHEME 4.

with a nucleophilic amino-acid residue at the active site. Experiments with α-deuteropropargylglycine indicated that the inactivation rate shows a kinetic isotope effect of 2·2. This is closely similar to the isotope effect for an α-deuterated substrate, and is consistent with the proposed scheme.

Attempts to isolate a labelled peptide from enzyme which had been inactivated with ^{14}C-labelled propargylglycine were unsuccessful. Vigorous acid hydrolysis of the inhibitor–enzyme adduct gave 2-amino-4-ketopentanoic acid 68. This is consistent with, although it does not establish, the formation of an allenic system which undergoes a Michael reaction with a nucleophilic amino-acid residue. On the basis of comparison of the rates of acid-catalysed hydrolysis of the inhibitor–enzyme adduct with those of enol ethers, a thioenol ether and enamines, it is speculated that the hydroxyl group of a tyrosine or the thiol group of a cysteine residue may be the nucleophile.



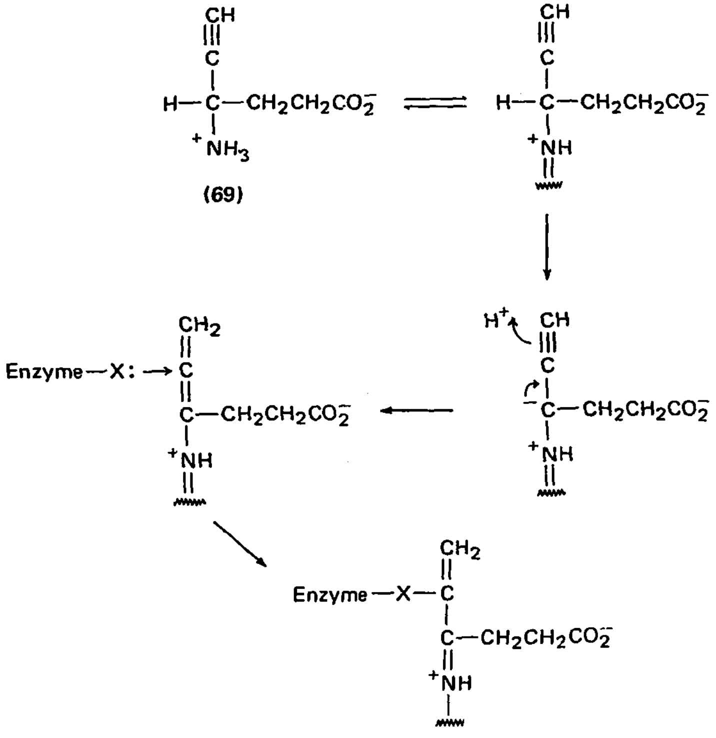
$\mathrm{CH_3COCH_2\underset{\displaystyle NH_2}{\underset{|}{C}}HCO_2H}$

(68)

Another example of this approach is found in studies of the irreversible inhibition of the pyridoxal phosphate-dependent γ-aminobutyric acid (GABA) transaminase. This important enzyme reversibly transaminates γ-aminobutyric acid with α-ketoglutarate to give succinic semialdehyde and glutamic acid (equation 9). Pyridoxal phosphate is involved in Schiff-base formation with the requisite intermediates.

$$\begin{array}{c}\mathrm{HO_2CCH_2CH_2CH_2NH_2 + HO_2CCH_2CH_2COCO_2H}\\ \uparrow\!\downarrow\\ \mathrm{HO_2CCH_2CH_2CHO + HO_2CCH_2CH_2CHNH_2CO_2H}\end{array} \qquad (9)$$

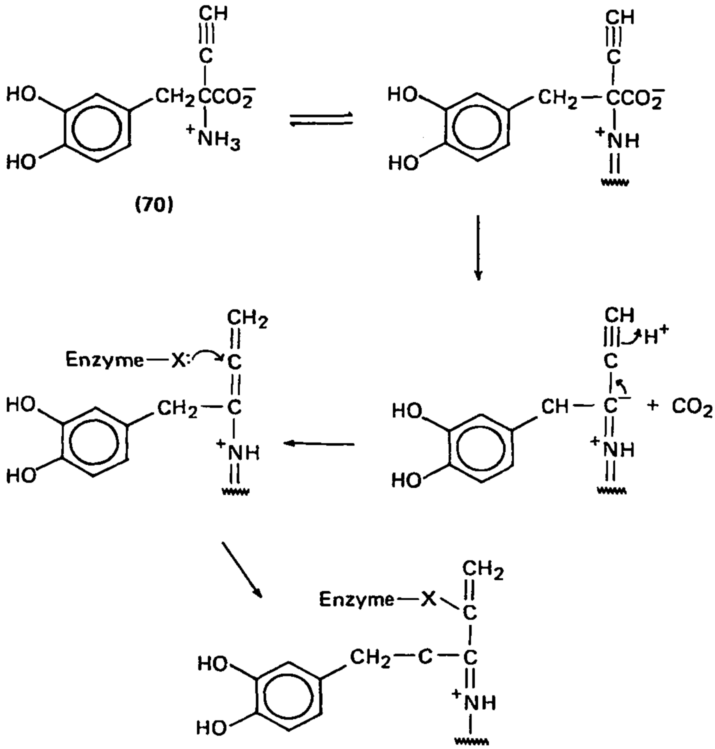
4-Aminohex-5-ynoic acid (69) was designed as a suicide substrate for this enzymatic reaction[105]. It has been proposed that compound 69 first forms the Schiff base with pyridoxal phosphate, and that the acetylene group is then isomerized enzymatically to an allene. This allene is reactive because it is conjugated to the Schiff base and is therefore susceptible to nucleophilic addition by an enzyme amino acid residue (see Scheme 5).



SCHEME 5.

As in the previous case, allene formation has not been experimentally demonstrated. Nevertheless, the use of the acetylenic acid **69** leads to potent time--dependent irreversible inhibition of γ-aminobutyric acid transaminase both *in vitro*[106] and *in vivo*[107]. This compound is now being used as a tool to study the role of brain γ-aminobutyric acid levels in various seizure model systems[108,109].

Another acetylenic amino acid (**70**), an analogue of 3,4-dihydroxyphenylalanine (DOPA), has recently been synthesized by two different groups of investigators[110,111] as a potential irreversible inhibitor of the pyridoxal phosphate-dependent DOPA decarboxylase. Schiff-base formation is again involved in this catalytic conversion, and a possible mechanism to explain irreversible inhibition of DOPA decarboxylase by compound **70** is shown in Scheme 6. The compound is stated to be a potent enzyme inhibitor, but the relevant data have not yet been published.

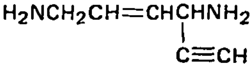


SCHEME 6.

A very recent study[112] concerns the pyridoxal-dependent enzyme L-ornithine decarboxylase, which catalyses the transformation of L-ornithine (**71**) to putrescine (**72**) (equation 10) and plays an important role in polyamine biosynthesis. Two acetylenic analogues of putrescine have recently been shown to cause powerful inhibition of ornithine decarboxylase. These compounds **73** and **74** each effect time-dependent inactivation of the enzyme, and meet the criteria for active site-directed irreversible inhibition. In each case, also, one optical isomer is an inhibitor whilst the other isomer is inert.

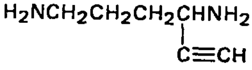
$$H_2NCH_2CH_2CH_2\underset{CO_2H}{\underset{|}{C}}HNH_2 \rightleftharpoons H_2NCH_2CH_2CH_2CH_2NH_2 \qquad (10)$$

(71) (72)



$$H_2NCH_2CH{=}CH\underset{C\equiv CH}{\underset{|}{C}}HNH_2$$

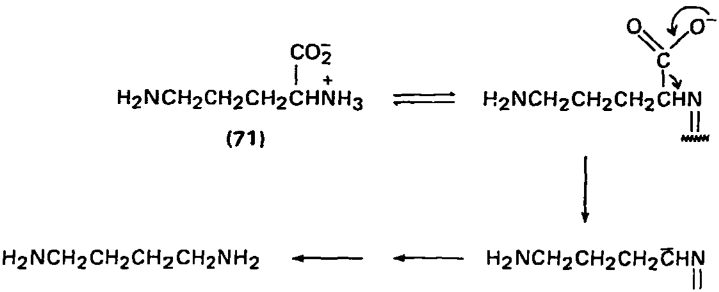
(73)



$$H_2NCH_2CH_2CH_2\underset{C\equiv CH}{\underset{|}{C}}HNH_2$$

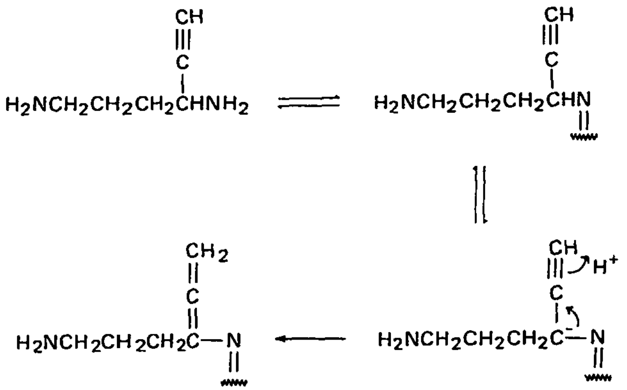
(74)

The design of these inhibitors is based on the principle of microscopic reversibility. Thus, the normal enzymatic decarboxylation of ornithine (71) is envisaged to proceed via the pyridoxal phosphate Schiff base, with subsequent steps leading to product, after carbanion protonation and regeneration of pyridoxal phosphate (equation 11). In the case of the product analogue 74, for example, it is postulated



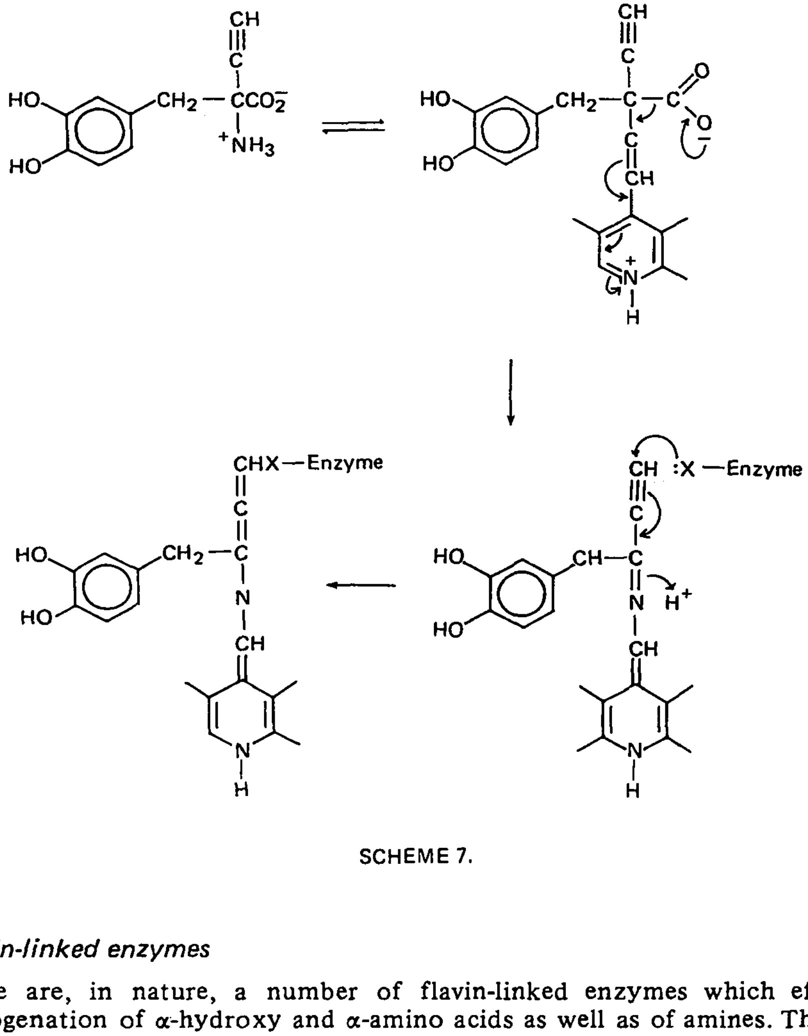
(11)

that binding to the active site of the enzyme is followed by Schiff-base formation with pyridoxal phosphate. Proton abstraction as shown (an inherent part of the reverse reaction) results in a propargylic anion which can generate the allene on protonation (equation 12). The resulting electrophilic conjugated allene is then expected to react with a nucleophilic amino-acid residue at the active site. Similar reasoning applies to product analogue 73. Studies were also made with 4-deutero-5-hexyne-1,4-diamine. These studies revealed an unaltered inactivation rate constant, but demonstrated a primary kinetic isotope effect of 1·9 on the apparent K_I. Although proton abstraction is therefore taking place, it is presumed that covalent binding of the electrophilic allenic system to the enzyme is the rate-determing step.



(12)

Before leaving this section, it should be pointed out that there is at least one other plausible mechanism to explain the suicide inactivation of γ-aminobutyrate transaminase, ornithine decarboxylase and DOPA decarboxylase. This mechanism is illustrated in Scheme 7. Although the example used is the DOPA decarboxylase inhibition, the principle applies equally to the other two systems mentioned above.

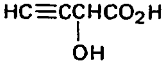


SCHEME 7.

3. *Flavin-linked enzymes*

There are, in nature, a number of flavin-linked enzymes which effect the dehydrogenation of α-hydroxy and α-amino acids as well as of amines. There is no universally accepted detailed mechanism for these reactions. However, it seems likely that dehydrogenation is preceded by enzymatic abstraction of the α-hydrogen from the substrate[113]. Consequently, these enzymes offer possibilities for suicide inactivation by appropriate acetylenic substrate analogues. Indeed, some of these dehydrogenases and oxidases are inactivated by acetylenic compounds, possibly via enzyme-generated allenic intermediates.

a. α-Hydroxy acid oxidases and dehydrogenases. The compound 2-hydroxy-3-butynoate (75) has been shown to produce inactivation of a number of α-hydroxy acid oxidases and dehydrogenases[113-118], which catalyse the conversion of α-hydroxy acids to α-keto acids. In all these cases, the acetylenic α-hydroxy acid **75** serves as a substrate, with formation of the corresponding α-keto acid **76**.



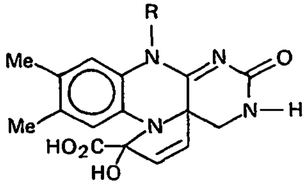
$$HC{\equiv}C\underset{\displaystyle OH}{\underset{|}{C}}HCO_2H$$

(75)

$HC{\equiv}CCOCO_2H$

(76)

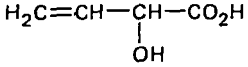
The inactivation is irreversible in all cases, and involves covalent attachment of inactivator to the flavin cofactor. Detailed studies[119,120] with the L-lactate dehydrogenase from *Mycobacterium smegmatis* have led to structure **77** for the adduct formed from the flavin cofactor and the inactivator.



(77)

Two plausible pathways (Schemes 8 and 9) have been suggested for the irreversible inactivation of these flavoenzymes by the acetylenic substrate **75**. These proposals are based, respectively, on the electrophilic character of the flavin in its initial oxidized state, and on the nucleophilic character of reduced flavin after substrate oxidation. In path A (Scheme 8), the allenic carbanion **78**, derived from the initially formed acetylenic carbanion carries out a nucleophilic attack on the oxidized flavin. Path B (Scheme 9) requires formation of an enzyme-bound oxidation product (**79**) which is electrophilic and is attacked in the Michael sense by reduced nucleophilic flavin **80**. Both of these paths lead to the same 4a-substituted flavin **81** which can give the carbinolamine **77**.

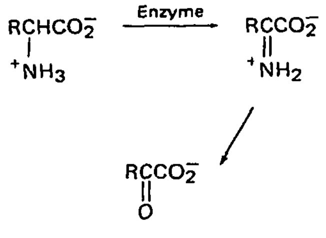
At present, there is no clear differentation between proposals A and B which involve, respectively, flavin modification before and after flavin reduction. It should be noted, however, that the olefinic acid 2-hydroxy-3-butenoic acid (**82**) is a substrate for, but not an inactivator of, the flavoenzymes which are inactivated by 2-hydroxy-3-butynoic acid[113]. This casts some doubt on, but no means rules out the Michael addition pathway B.



$$H_2C{=}CH{-}\underset{\displaystyle OH}{\underset{|}{C}}H{-}CO_2H$$

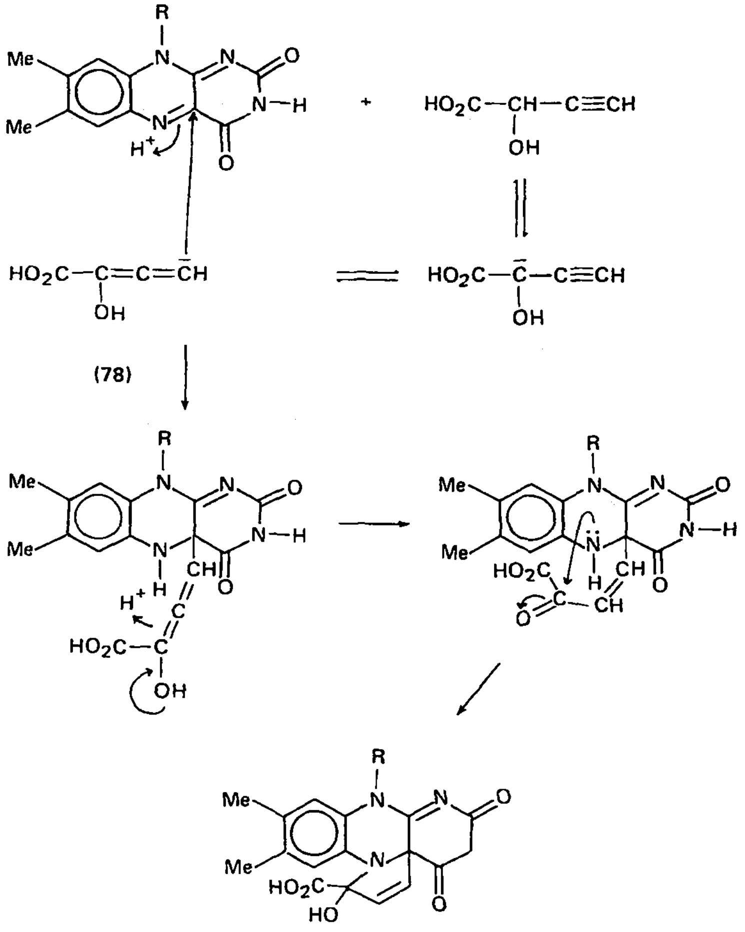
(82)

b. α-Amino acid oxidases. The flavoenzyme D-amino acid oxidase from hog kidney catalyses the conversion of α-amino acids to α-keto acids via dehydrogenation to the α-imino acid (equation 13).



$$R\underset{{}^{+}NH_3}{\underset{|}{C}}HCO_2^- \xrightarrow{\text{Enzyme}} R\underset{{}^{+}NH_2}{\underset{\|}{C}}CO_2^- \longrightarrow R\underset{O}{\underset{\|}{C}}CO_2^- \qquad (13)$$

Path A



(78)

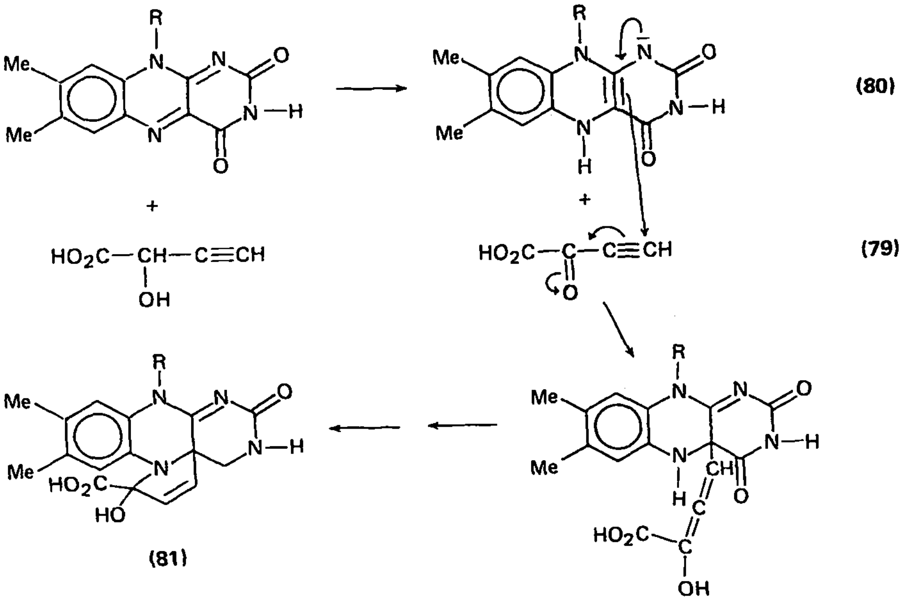
(81)

SCHEME 8.

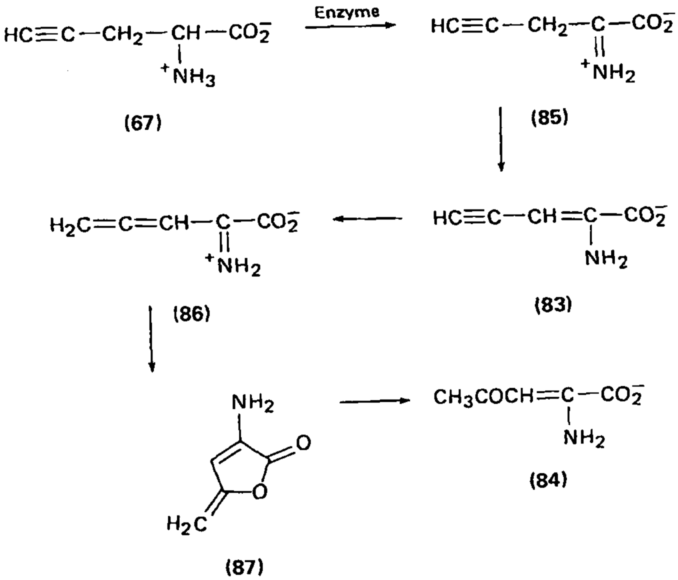
This enzyme has been reported[121] to be irreversibly inactivated by propargyl glycine (67). Subsequent work by Marcotte and Walsh[122] has shown that the process involves modification of the apoprotein rather than of the flavin moiety. They have also shown[123] that the enzyme, although alkylated, is not inactivated. It has instead been modified so as to show quite different substrate specificity and kinetic properties.

The inactivation involves a considerable number of substrate turnovers per alkylation, and results in at least five modified enzyme species. Two noncovalently bound inhibitors 83 and 84 are also formed during the inactivation process. Scheme 10 has been proposed[124] for the nonenzymatic formation of 83 and 84, following the initial enzymatic oxidation of propargyl glycine to give imine 85. On release from the enzyme, 85 is considered to rearrange rapidly to the acetylenic enamine

Path B



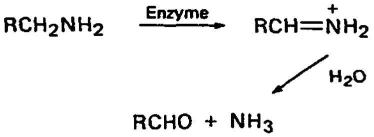
SCHEME 9.



SCHEME 10.

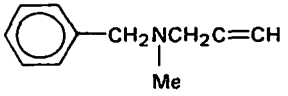
83, which protonates to give conjugated allene 86. The latter undergoes cyclization via intramolecular carboxylate addition to lactone 87 which accumulates in solution. The lactone 87 can also give rise to 2-amino-4-keto-2-pentenoate (84). The actual alkylation of the enzyme may involve allenic imine or the corresponding allenic ketone.

c. Amine oxidases. The pharmacologically important monoamine oxidases catalyse[125] the oxidative deamination of amines to aldehydes (equation 14).



$$RCH_2NH_2 \xrightarrow{\text{Enzyme}} RCH{=}\overset{+}{N}H_2 \xrightarrow{H_2O} RCHO + NH_3 \qquad (14)$$

Mitochondrial monoamine oxidase contains covalently linked flavin cofactor, and is irreversibly inhibited[126,127] by acetylenic amines such as the drug pargyline (88). This inhibition involves a 1:1 covalent adduct between enzyme and inactivator, with attack specifically on the flavin cofactor.

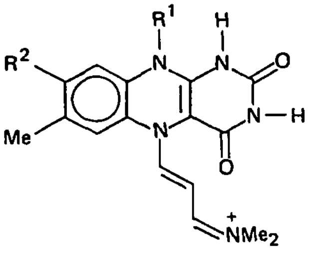


(88)

$Me_2NCH_2C{\equiv}CH$

(89)

Recent work[128] with bovine-liver mitochondrial monoamine oxidase has shown that this enzyme is similarly inhibited by 3-dimethylamino-1-propyne (89). Furthermore, the flavin-inactivator adduct has been assigned structure **90** on the basis of extensive chemical and spectroscopic studies.

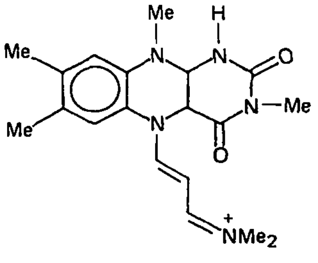


R^1 = Ribityl phosphate

R^2 = CH_2—S—Enzyme

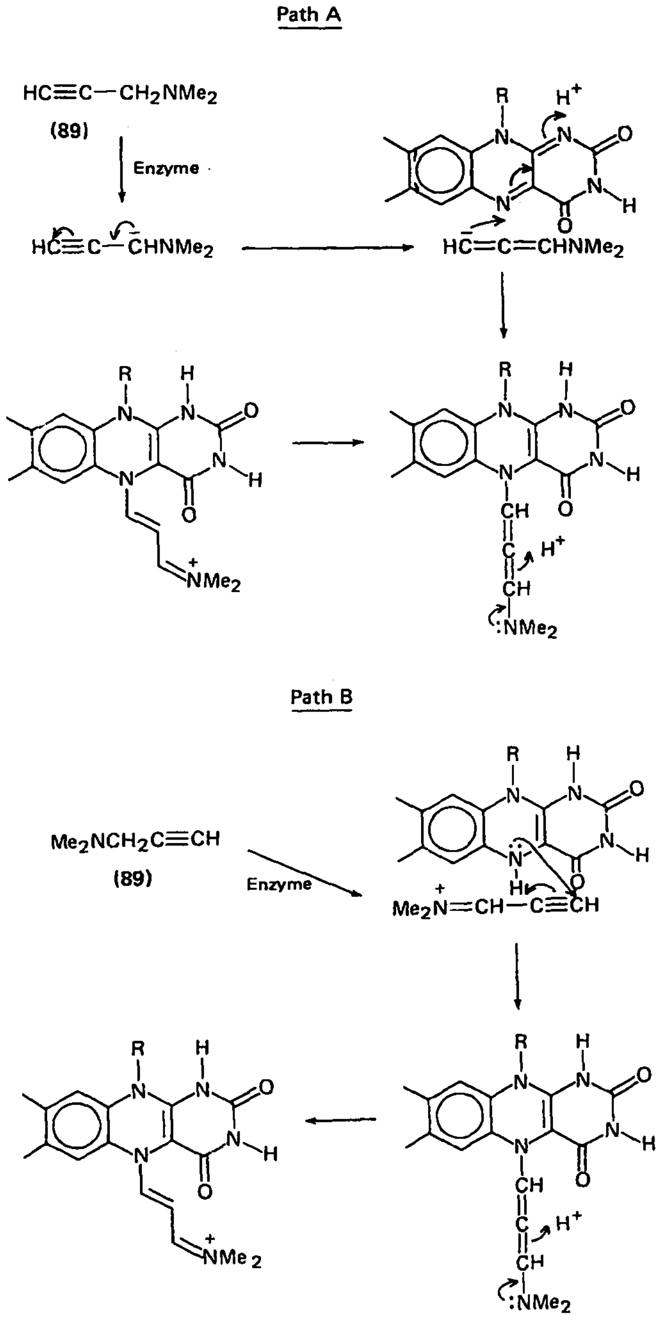
(90)

A closely similar structure, **91**, has been proposed[129-131] for an adduct generated photochemically from 3-methyllumiflavin and 3-dimethylamino-1-propyne (89).



(91)

To account for the formation of adduct **90**, three possible mechanisms have been suggested[128] (Scheme 11). The first, path A, involves initial enzyme-catalysed



SCHEME 11.

abstraction of an α-proton from the acetylenic inactivator **89**. The derived allenic carbanion could then react with the coenzyme as shown. An alternative mechanism, path B, involves oxidation of **89** followed by Michael addition of the reduced flavin. Formation of a radical-pair complex has also been suggested[128].

Another recent study, again using bovine-liver mitochondrial monoamine oxidase has revealed[132] that the allenic amine **92**, while a potent irreversible inhibitor, does not produce the absorption at 391 nm characteristic of adduct **90**, although the 455 nm absorption of the native flavoenzyme is lost.

In the same study[132], the closely related acetylenic amine **93** inhibits the enzyme, with the expected generation of the 391 nm absorption characteristic of adduct **90**. Furthermore, the homologous allenic amine **94** is not an inactivator of the enzyme, nor is the related dienamine **95** an inhibitor. Substitution of a methyl group for any one of the allene hydrogen atoms in **92** results in loss of inhibitory activity. The nature of the modified flavin following inactivation by **92**, although not known, is clearly different from that obtained using acetylenic amines. At present there is no mechanistic evidence available, but the speculation[132] of cycloaddition to the flavin by enzyme-activated allene is interesting.

$H_2C{=}C{=}CHCH_2NMe_2$

(92)

$CH_3C{\equiv}CCH_2NMe_2$

(93)

$H_2C{=}C{=}CHCH_2CH_2NMe_2$

(94)

$H_2C{=}CHCH{=}CHNMe_2$

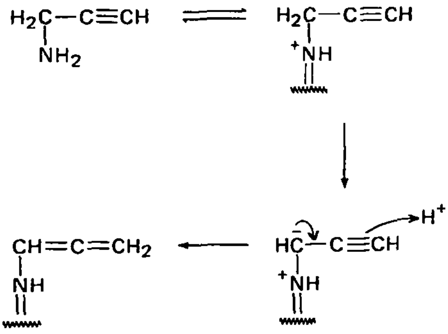
(95)

4. *Non-flavin monoamine oxidase*

Plasma monoamine oxidase, which is not a flavin-linked enzyme, is irreversibly inactivated by propargylamine (**96**), although it is not affected by pargyline (**88**)[133,134]. The enzyme, which is copper-dependent, generates a Schiff base with substrate. Consequently, a plausible mechanism has been suggested[133,134], involving removal of the α-proton from the Schiff-base intermediate (Scheme 12). The resulting conjugated allene is then expected to react with an enzyme nucleophile. The specific nature of the resulting adduct has not yet been described.

$HC{\equiv}CCH_2NH_2$

(96)

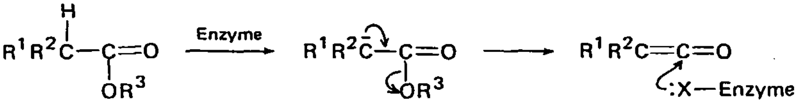


SCHEME 12.

B. Ketenes and Ketene Imines

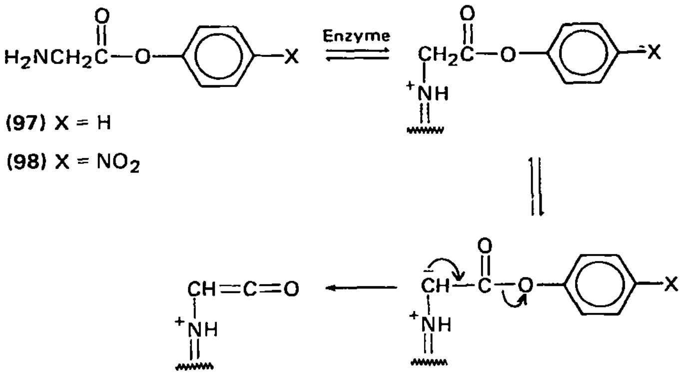
1. *Ketenes*

An example of enzyme-generated inhibition postulated to involve a ketene intermediate has been described by Abeles and coworkers[135,136]. In earlier work by this group on plasma amine oxidase, the proton-abstracting ability of the enzyme has been used to advantage in connection with suicide inactivators. In the present case, it was proposed that carbanion formation α to an ester grouping containing a good leaving group might generate a highly reactive ketene, through an elimination reaction (equation 15).



(15)

In the event, it was found that the *p*-nitrophenyl and phenyl esters of glycine (97 and 98) are good substrates for, and inactivators of, the enzyme. The inactivation appears to involve irreversible modification of the enzyme by covalent bonding. These results are consistent with α-proton abstraction from an enzyme-bound Schiff-base intermediate, followed by elimination of *p*-nitrophenolate to give a ketene-like intermediate (equation 16). The latter can react covalently with a nucleophilic amino-acid residue on the enzyme, or it can undergo reaction with water to give glycine.



(97) $X = H$

(98) $X = NO_2$

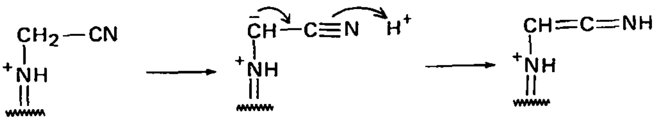
(16)

2. *Ketene imines*

In studies with plasma monoamine oxidase, Abeles and coworkers found[135,136] that 2-aminoacetonitrile (99) caused inactivation of the enzyme, in a manner similar to that described for the glycine esters described above. A possible pathway involves proton abstraction from $C_{(2)}$ of an enzyme-bound Schiff-base intermediate giving a conjugated ketene imine (equation 17). The latter should be susceptible to attack by a nucleophilic enzyme residue.

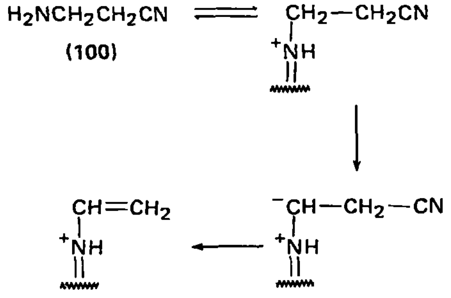
H_2NCH_2CN

(99)



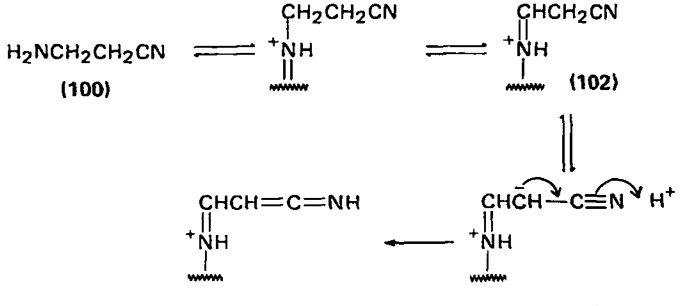
(17)

The homologue of 99 is 3-aminopropionitrile (**100**), a naturally occurring plant toxin found as 3-*N*-(γ-L-glutamyl)propionitrile[137]. Administration of 3-aminopropionitrile (**100**) to animals produces osteolathyrism, a disease considered[138] to result principally from interference with normal collagen cross-linking. Rando has suggested[77] that the lathyrogenic action of **100** may stem from irreversible inhibition of a monoamine oxidase which normally oxidizes *C*-amino groups of lysine residues during the cross-linking process. The proposed mechanism involves the elimination of cyanide ion from the Schiff base derived from **100** and pyridoxal phosphate, generating a reactive conjugated imine (**101**) (equation 18). Walsh has suggested[79] the use of ^{14}C-[cyano] 3-propionitrile to test this proposal.



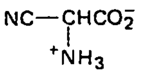
(18)

Another possibility is that the intermediate Schiff base first undergoes enzyme-induced proton loss to give **102** followed by abstraction of the proton at $C_{(2)}$ to give β-carbanion **103**. The latter could then generate the electrophilic ketene imine **104** (equation 19).



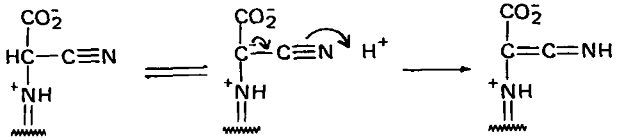
(19)

Finally, the inactivation of the β_2 subunit of tryptophan synthetase by cyanoglycine (**105**) has been suggested[139] to involve ketene imine formation via enzymatic formation of an α-cyano carbanion (equation 20).



$$NC{-}\underset{^{+}NH_3}{\underset{|}{C}}HCO_2^-$$

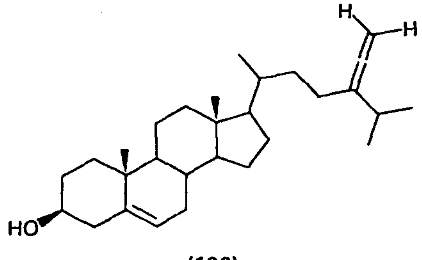
(105)



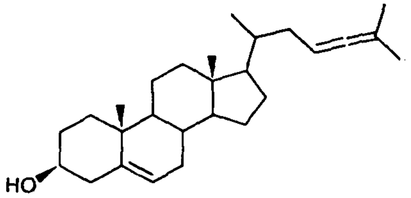
(20)

IV. ALLENES WHICH AFFECT INSECT STEROID TRANSFORMATIONS

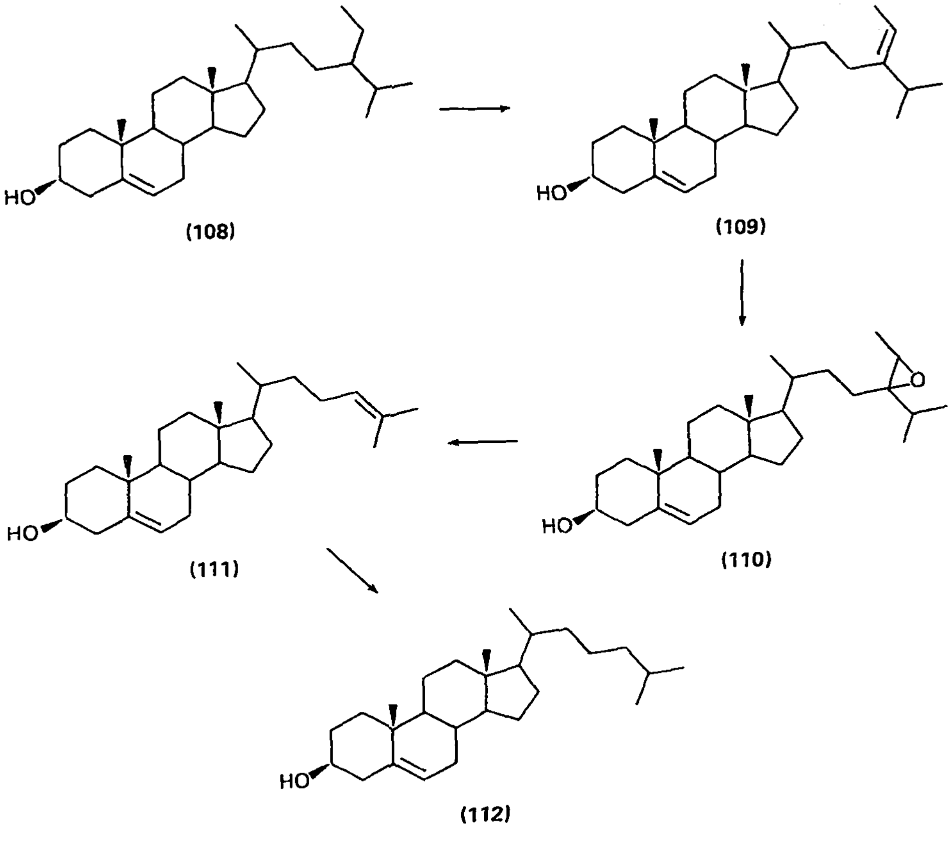
Two steroidal allenes, stigmasta-5,24(28),28-trien-3β-ol (**106**) and cholesta-5,23,24-trien-3β-ol (**107**), have been synthesized and tested as inhibitors of the conversion of sitosterol **108** to cholesterol **112** in the phytophagous silkworm, *Bombyx mori*[140,141]. Such insects are incapable of *de novo* cholesterol biosynthesis and must obtain their cholesterol from phytosterols such as sitosterol. Scheme 13 has been proposed for the biosynthetic transformation of sitosterol (**108**) to cholesterol (**112**)[142].



(106)



(107)



SCHEME 13.

Allene **106** was designed as a structural analogue of fucosterol (**109**) and allene **107** as a structural analogue of desmosterol (**111**). When the compounds were tested for their inhibitory effects on the growth and development of, and steroid transforming reactions in, the silkworm, allene **106** was found to inhibit the conversion of steroids **108** → **109** and/or **109** → **110**. The larvae remained in the second instar for more than 20 days without progressing to the third instar. The allene **106** was not readily metabolized. In contrast, allene **107** was readily metabolized. All of the larvae died when allene **107** was incorporated in the diet in the amount of 0·1%. Even when the diet included cholesterol the larvae died. As an explanation, it has been suggested that the metabolite(s) of allene **107** might be inhibiting the formation of ecdysone from cholesterol[143].

V. ACKNOWLEDGEMENT

Support by U.S.P.H.S. Grants AM 15918 and CA 23582 is gratefully acknowledged.

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