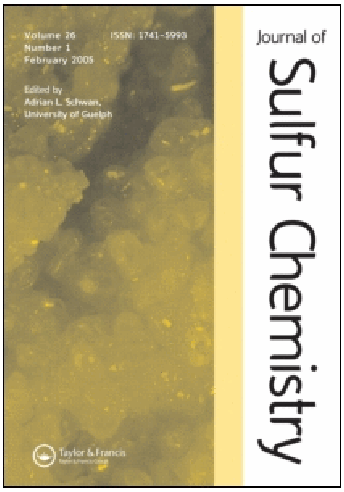

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Chalcogen-Centered Radicals

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CHALCOGEN-CENTERED RADICALS*

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The main types of radicals formed in initiated reactions of organic compounds of selenium and tellurium, detection methods, and their physico-chemical properties and reactivity are presented in this review.

Key words: Selenium, tellurium, radicals, organoselenium and -tellurium compounds, photolysis, thermolysis.

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1. GENERAL INTRODUCTION

Selenium- and tellurium-centered radicals are short-lived intermediates of many photolytical and thermal reactions of organoselenium and -tellurium compounds. They were first reported in the literature slightly more than two decades ago. However, their extensive investigation began only in the last years due to the discovery of the essential role of

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*Dedicated to Professor Shigeru Oae on the occasion of his 75th birthday in recognition of his great contribution to the chemistry of organic compounds of sulfur.

selenium as a trace element in living organisms, in human and animal food and in biochemical processes[1] as well as to their application in microelectronic systems engineering.[2,3] In the second half of this century eight new seleno proteins were discovered. It has been found that selenium-deficiency in food and soil may cause certain diseases in animals and anomalies in the growth and development of some types of plants.[1] Organoselenium and -tellurium compounds are used in the electronic industry, in xerography and photo-electronics, and in the production of glass, ceramics and pigments. Selenium-containing polymers possessing semiconductor properties and photosensitivity have been obtained.[2,3] On the basis of selenophene some neuro- and psychotropic drugs considerably less toxic than their sulfur analogs have been prepared.[4,5] In the chemistry of organoselenium compounds and, to a lesser extent, of their tellurium analogs, homolytic processes involving the generation of selenium- and tellurium-centered radicals are of great importance. This is due to the low energies of C-Se, Se-Se and Se-heteroatom bonds as well as of C-Te and Te-Te bonds, which are responsible for their ready heterolytic cleavage.[4-7]

The present review is concerned with the main types of radicals generated in initiated reaction of organic compounds of selenium and tellurium, with methods of radical detection, their properties and reactivity. All this information is compared with analogous data for sulfur-centered radicals.

Radical reactions of organosulfur compounds have been studied in much detail.[7-10] However, data on the rather closely related organoselenium compounds and their mainly photochemical radical reactions have only been summarized in short communications.[11,12] Reviews on radical reactions of organotellurium compounds are not available anywhere.

2. MAIN TYPES OF SELENIUM- AND TELLURIUM-CENTERED RADICALS

From organoselenium compounds the following types of selenium-centered radicals can be generated:

RSe - selenyl radicals
$RSeSe^{\cdot}$ - perselenyl radicals
$R_2Se\text{-}SeR^{\cdot}$ and $R_2Se\text{-}X^{\cdot}$ (X = Cl, Br, $OSiMe_3$, $COMe_2$, $SC(O)R'$) - selenuranyl radicals
$RSeO^{\cdot}$ - seleninyl radicals
$RSeO_2^{\cdot}$ - selenonyl radicals
From organotellurium compounds only $RTe^{\cdot}$ radicals are generated.

3. GENERATION, DETECTION AND PROPERTIES OF SELENIUM- AND TELLURIUM-CENTERED RADICALS

3.1. *Selenyl and Telluryl Radicals*

3.1.1. *Detection and physical properties* Selenyl radicals $RSe^{\cdot}$, the simplest selenium-centered radicals, have been discovered in the photolysis of diorganyl diselenides.[13] Hydroselenyl (HSe$^{\cdot}$) and hydrotelluryl (HTe$^{\cdot}$) radicals are generated when hydrogen is passed under silent discharge through a microwave absorption cell the walls of which are coated with selenium or tellurium, respectively (HS$^{\cdot}$ radicals are generated in a similar manner). The partial pressures are as follows (mm Hg): HSe$^{\cdot}$ 5, HTe$^{\cdot}$ 11, HS$^{\cdot}$ 10. The intensity of the microwave radiation of the radicals depends on the chalcogen: HSe$^{\cdot}$ 60, HTe$^{\cdot}$ 3, HS$^{\cdot}$ 240. DM values are 0.2 (10^{-8}), 0.1 and 0.3 esu for HSe$^{\cdot}$, HTe$^{\cdot}$ and HS$^{\cdot}$, respectively.

The spin-orbital constants of HSe$^{\cdot}$ and HTe$^{\cdot}$ (A_o = 1.600 ± 50 and 2250 ± 200 cm^{-1}) have been measured by EPR.[14] The adiabatic potential of HSe$^{\cdot}$ ionization has been determined as 9.845 – 0.003 eV and the dissociation energies, D_o (HSe-H) = 78.99 ± 0.18 and D_o (H-Se) = 74.27 ± 0.23 kcal/mol, respectively, in the photoionization of the HSe$^{\cdot}$ radical generated in a spectrometer cell by interaction of atomic hydrogen with hydrogen selenide.[15]

Organylselenyl radicals RSe$^{\cdot}$ are formed in the photolysis of diorganyl diselenides.[13] A direct EPR detection of these radicals (especially in the liquid phase) is hindered by the high value of the spin-orbital bond and, on some occasions, by specific interactions[16] which lead to orbitally degenerated ground states and to a high anisotropy of the g-factor.[17] Due to this fact the RSe$^{\cdot}$ radicals show short relaxation times and extremely broad lines in the EPR spectra.[9,16,17] Nevertheless, by use of EPR spectroscopy it has been possible to detect selenyl radicals generated in the photolysis of phenylmethaneselenol, didodecyl selenide, dioctadodecyl selenide and diphenyl selenide. Owing to the g-factor anisotropy selenyl radicals (as well as thiyl radicals[11]) possess asymmetric spectra with a g-factor greatly different from that characteristic of the free electron and of carbon-centered radicals.[18,19]

Radical	$g_{\perp}$	$g_{\parallel}$
$PhS\dot{e}$	2.003	2.016
$PhCH_2S\dot{e}$	2.091	2.124
$Me(CH_2)_{11}S\dot{e}$	2.088	2.122
$Me(CH_2)_{17}S\dot{e}$	2.083	2.115

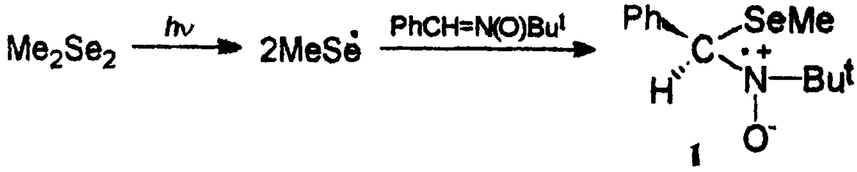
SCHEME 1

It was not possible to detect by EPR spectroscopy the methylselenyl radical MeSe$^{\cdot}$,[18] whereas the available data concerning the EPR detection of the PhSe$^{\cdot}$ radical are rather contradictory.[18,20] No information on EPR detection of RTe$^{\cdot}$ radicals is available.

Arylselenyl radicals can be detected by UV spectroscopy.[21,22] The absorption band of the PhSe$^{\cdot}$ radical (as well as that of PhS$^{\cdot}$) occurs in the 490 nm region, while those of 4-$MeOC_6H_4Se^{\cdot}$, 4-$MeOC_6H_4S^{\cdot}$, and 4-$MeOC_6H_4Te^{\cdot}$ are observed in the 535 (methanol), 525 and 508 nm region, respectively.[22,23]

Analogous to thiyl radicals,[9] selenyl radicals RSe˙ are readily identified by EPR spectroscopy as adducts with spin traps.[24] 2-Nitrosopropane, 2-methyl-2-nitrosopropane, nitrosodurene, *tert*-butyl-phenylnitrone, etc. have been used as traps.

Methylselenyl radicals, generated in the pyrolysis of dimethyl diselenide, do not react with 2-methyl-2-nitrosopropane, but readily react with *tert*-butyl-phenylnitrone:[17]



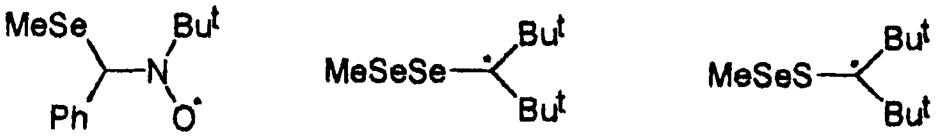
1

SCHEME 2

Adduct 1 is characterized by a high g-factor (2.0097). Its structure is proved by the STC constants: $a^N = 13.5$ Gs, a^H (1H) = 2.06 Gs, a^H(3H) = 0.85 Gs.[17]

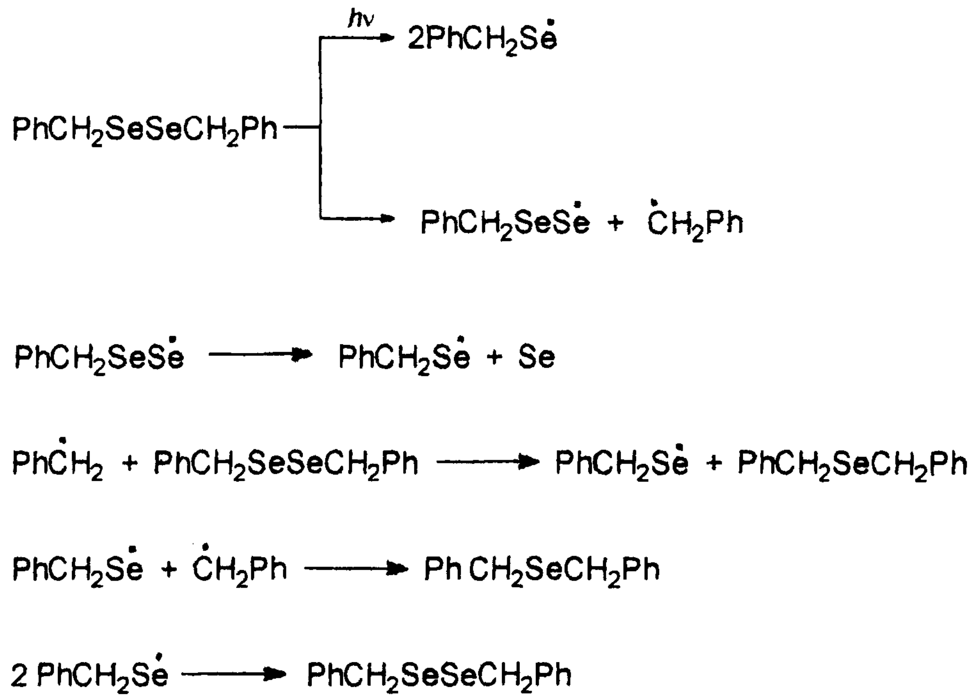
The arylselenyl radicals PhSe˙ and 4-$O_2NC_6H_4Se$˙ have been trapped with nitrosodurene.[17,25] EPR spectroscopy is also of help in detecting complex radicals $RSeMX_3$ formed from selenides and diselenides reacting with aluminum and gallium halides (X = Cl, Br). The EPR spectra of the Ar_2Se_2-$AlBr_3$-C_6H_6 system contain three singlets (g = ~2.07, ~2.03 and ~2.0025). These were assigned to the complex radicals Ar˙, ArSe˙ and ArSeSe˙.[26]

3.1.2. *Generation and reactions of organoselenium and -tellurium compounds under photolysis and radiolysis* The selenyl radicals generated in the photolysis of diorganyl diselenides readily add to C=C, C=S, and C=Se multiple bonds, etc. The methylselenyl radicals formed in the photolysis of dimethyl diselenide form adducts of the type:



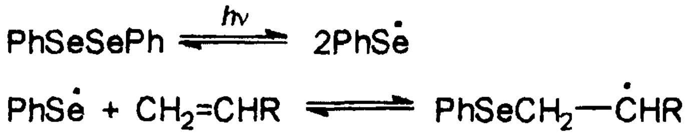
SCHEME 3

by addition to the multiple bonds of the corresponding spin traps.[17] The photolysis of dibenzyl diselenide occurs quite differently, starting with breakage of the Se-C bond and the formation of dibenzyl selenide and selenium. In this case the benzylselenyl radical is generated from the previously formed benzylperselenyl radical and instantly reacts with the benzyl radical:[27]



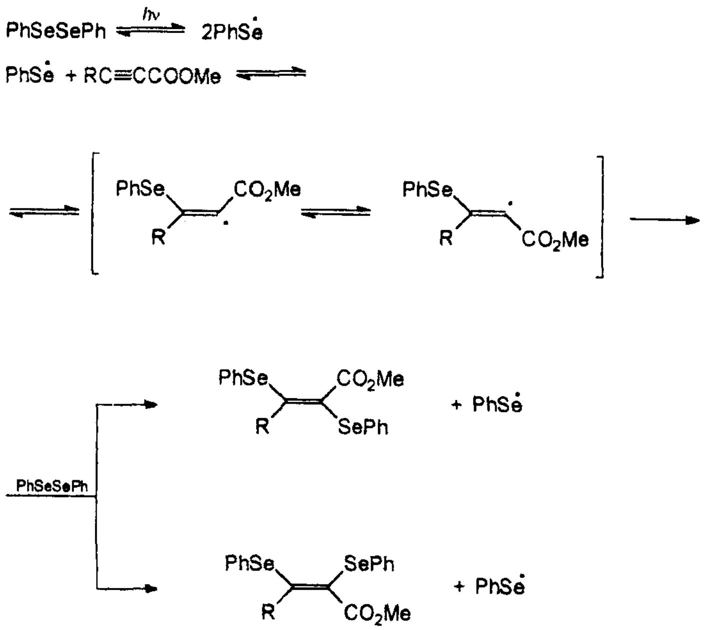
SCHEME 4

When exposed to irradiation in benzene solution either in the presence of air or of acetonitrile, dibenzyl diselenide forms benzaldehyde, benzyl alcohol and elemental selenium,[23] whereas in carbon tetrachloride benzyl chloride is formed.[29] This is supported by the predominant cleavage of the C-Se bond in the photolysis of dibenzyl diselenide. The photolysis of diphenyl diselenide leads to phenylselenyl radicals $PhSe^{\bullet}$. The latter differ by their low reactivity towards hydrogen, oxygen or halogen donors: however, they easily add to activated olefins:[23,30,31]



SCHEME 5

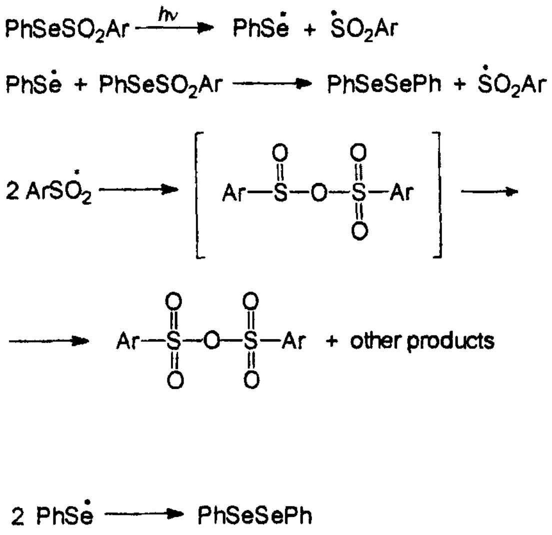
The rate constant of the addition is from $2.9 \cdot 10^6$ $mol^{-1} \cdot c^{-1}$ for α-methylstyrene to $\sim 10^3$ $mol^{-1} \cdot c^{-1}$ for vinyl acetate. These values are smaller by a factor of 10–50 than those for reactions with the $PhS^{\bullet}$radical which indicates a greater stability of the phenylselenyl radical. UV-Generated phenylselenyl radicals effectively add to activated acetylenes, but are very reluctant to react with inactivated acetylenes such as 1-decyne, for example:[32]



SCHEME 6

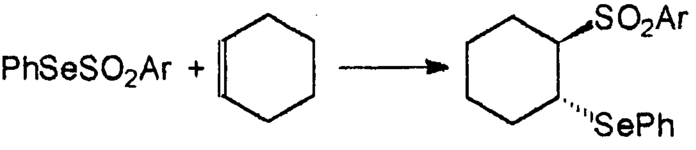
In the mixture of bis(phenylseleno)ethenes formed the E-isomers prevail. Dimesityl diselenide reacts with activated alkynes very slowly due to steric factors.

Phenylselenyl radicals are also generated by photolysis of *Se*-phenyl areneselenosulfonates, thus inducing chain decomposition of the latter leading to diphenyl diselenide and arenesulfonic acid anhydride:[33]



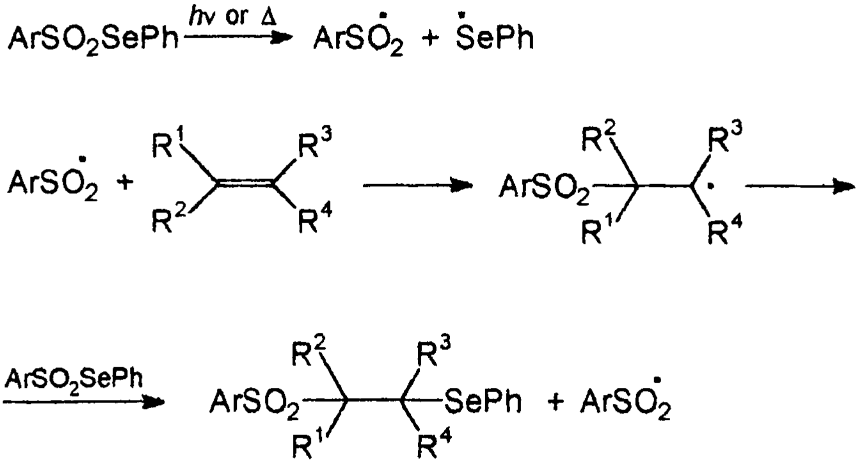
SCHEME 7

In the presence of alkenes the photolysis of *Se*-phenyl areneselenosulfonates gives 1-(arylsulfonyl)-2-(phenylseleno)alkanes. The reaction occurs strictly steroselectively and gives *trans*-adducts:[34])



SCHEME 8

The photolytic addition of selenosulfonates to alkenes is a faster process than the thermal addition (in boiling chloroform or benzene). In the two cases the reaction follows a radical chain mechanism. The reaction is accelerated by AIBN initiation and slows down in the presence of 2,6-di-*tert*-butyl-4-cresol:[35]



SCHEME 9

In the presence of *m*-chloroperbenzoic acid or hydrogen peroxide the spontaneously formed 1-(arylsulfonyl)-2-(phenylseleno)alkanes eliminate selenophenol with formation of the corresponding vinyl sulfones.

The photolysis of diorganyl diselenides is accelerated by tertiary phosphines and chiefly consists of cleavage of the Se-Se bond in both diphenyl diselenide and dibenzyl diselenide:[36–38]

$$\mathrm{RSeSeR} \xrightleftharpoons{h\nu} 2\,\mathrm{RS\dot{e}}$$

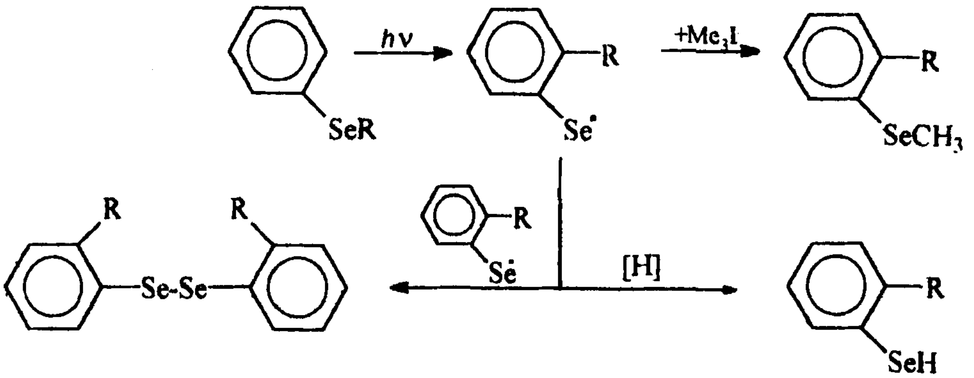
$$\mathrm{RS\dot{e}} + \mathrm{R'_3P} \longrightarrow \mathrm{RSe{-}\dot{P}R'_3}$$

$$\mathrm{RSe{-}\dot{P}R'_3} \longrightarrow \mathrm{\dot{R}} + \mathrm{Se{=}PR'_3}$$

$$\mathrm{\dot{R}} + \mathrm{RSeSeR} \longrightarrow \mathrm{RSeR} + \mathrm{\dot{S}eR}$$

SCHEME 10

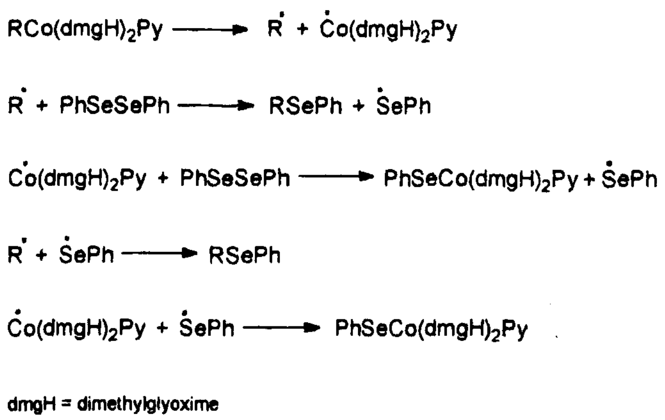
Phenylselenyl radicals are also generated in the photoinduced rearrangement of aryl benzyl selenides containing a weakened Se-C bond:[39]



R = CH$_2$Ph

SCHEME 11

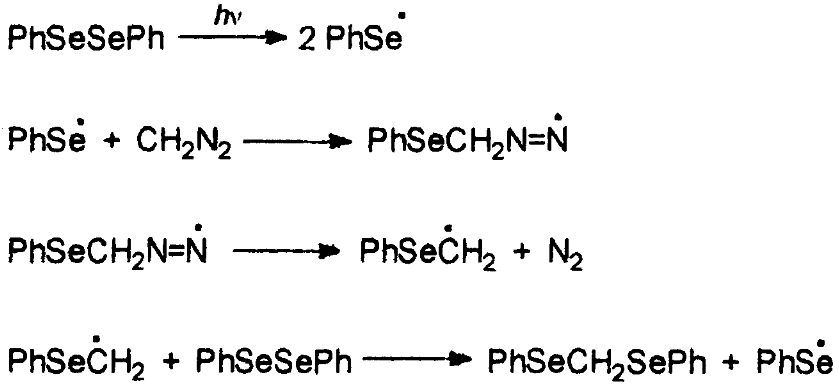
Phenylselenyl radicals are intermediates of the photoinduced reaction of organocobaloximes with diphenyl diselenide:[40]



SCHEME 12

Diphenyl diselenide reacts with zirconiumorganic complexes,[11] metal carbonyls[42,43] and adamantyl radicals by an analogous scheme.[44,45]

The photolytic reaction of diphenyl diselenide with diazomethane occurs by a radical chain mechanism:[45]



SCHEME 13

The photochemical reaction of diphenyl diselenide or *Se*-phenyl areneselenosulfonates with alkylmercury(II) halides is initiated by generation of selenyl radicals:[46]

$$\mathrm{PhSeY} \xrightarrow{h\nu} \mathrm{Ph\dot{S}e} + \mathrm{Y}^{\bullet}$$

$$\mathrm{Y}^{\bullet} + \mathrm{RHgCl} \longrightarrow \mathrm{R}^{\bullet} + \mathrm{YHgCl}$$

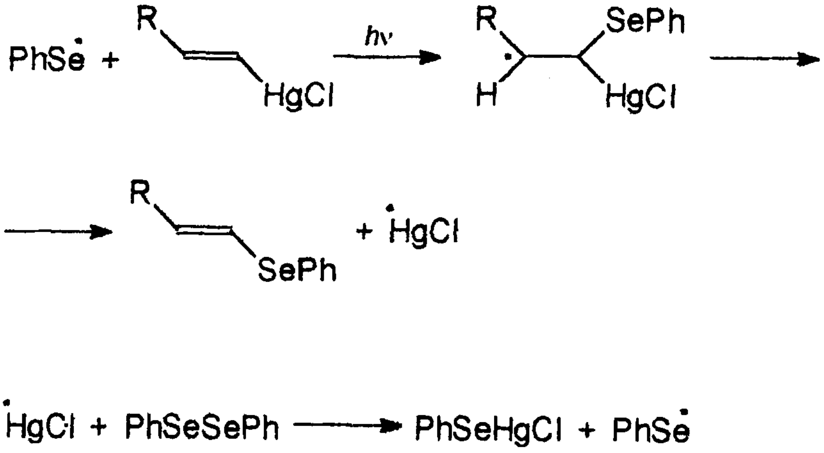
$$\mathrm{R}^{\bullet} + \mathrm{PhSeY} \longrightarrow \mathrm{RSePh} + \mathrm{Y}^{\bullet}$$

$$\mathrm{Ph\dot{S}e} + \mathrm{R}^{\bullet} \longrightarrow \mathrm{PhSeR}$$

$$\mathrm{Y} = \mathrm{SePh} \text{ or } \mathrm{SO_2Ar}$$

SCHEME 14

Analogously, vinyl selenides are formed from vinylmercury(II) halides.[47] The reaction mechanism involves addition of the phenylselenyl radical to the double bond:



SCHEME 15

Pulse radiolysis of bis(4-methoxyphenyl) diselenide in methanol generates two radicals, $ArSe^{\cdot}$ and $ArSeSe^{\cdot}$.[48]

From ditellurides only the radical $ArTe^{\cdot}$ is formed under analogous conditions.

Upon irradiation selenophenol reduces α,β-unsaturated carboxylic acid derivatives, activated olefins, β-phenylseleno ketones, as well as hydrazones, oximes and anilides to the corresponding saturated ketones, alkanes and to hydrazines, hydroxylamines and anilides by a radical mechanism:[49]

SCHEME 16

Under similar conditions benzyl phenyl selenide generates benzyl radicals which react with selenophenol to form toluene:[50]

$$\mathrm{PhCH_2SePh} \xrightarrow{h\nu} \mathrm{PhMe} + \mathrm{PhSeSePh}$$

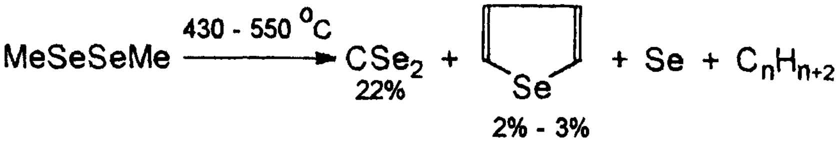
SCHEME 17

3.1.3 *Generation and conversions of organoselenium and -tellurium compounds in thermal reactions* At 450–600 °C diorganyl selenides and diselenides decompose to give elemental selenium, hydrogen selenide and a mixture of lower hydrocarbons C_1–C_2. Pulse thermolysis of dimethyl diselenide *in vacuo* (0.1 mm Hg) at 550 °C leads to dimethyl selenide, methaneselenol, methane and selenium as well as to selenoformaldehyde:[51]

$$\mathrm{MeSeSeMe} \xrightarrow{550\ ^{\circ}\mathrm{C}} \mathrm{MeSeMe} + \mathrm{MeSeH} + \mathrm{CH_4} + \mathrm{Se}$$

SCHEME 18

Thermolysis of Me_2Se_2 at 430–500 °C and under atmospheric pressure on the other hand forms carbon diselenide as the main product.[52] Along with carbon diselenide, 2–3% selenophene, a mixture of gasous hydrocarbons and selenium are formed:



SCHEME 19

The liquid products of the thermolysis of dialkyl diselenides (n = 2–4) at 300–500 °C are mainly the corresponding alkaneselenols and dialkyl selenides. The formation of these products is accompanied by the liberation of solid selenium and gaseous hydrogen selenide and alkenes as well as of traces of selenophene:[15]

$$\mathrm{Pr^iSeSePr^i} \longrightarrow \mathrm{CH_2{=}CHMe} + \mathrm{Pr^iSeH} + \mathrm{H_2Se} + \mathrm{Se}$$

SCHEME 20

Pulse thermolysis *in vacuo* (20 mm Hg, 600 °C) of dihexyl, didodecyl and bis(2-phenylethyl) diselenide gives only the corresponding alkene and selenium:[53]

$$\mathrm{RCH_2CH_2SeSeCH_2CH_2R} \longrightarrow \underset{90-95\%}{\mathrm{RCH{=}CH_2}} + \mathrm{Se}$$

$\mathrm{R = Ph, Bu, C_6H_{13}}$

SCHEME 21

Pulse thermolysis *in vacuo* converts dibenzyl selenides and diselenides to dibenzyls and selenium:[54,55]

$$\mathrm{ArCH_2SeCH_2Ar} \xrightarrow{600\,^\circ\mathrm{C}} \underset{63-89\%}{\mathrm{ArCH_2CH_2Ar}} + \mathrm{Se}$$

$$\mathrm{PhCH_2SeCH_2Ar} \xrightarrow{600\,^\circ\mathrm{C}} \underset{13\%}{\mathrm{PhCH_2CH_2Ph}} + \underset{24\%}{\mathrm{PhCH_2CH_2Ar}} +$$

$$+ \underset{8\%}{\mathrm{ArCH_2CH_2Ar}} + \mathrm{Se}$$

$$\mathrm{PhCH_2SeSeCH_2Ph} \xrightarrow{210\,^\circ\mathrm{C}} \underset{99.4\%}{\mathrm{PhCH_2CH_2Ph}} + \mathrm{Se}$$

SCHEME 22

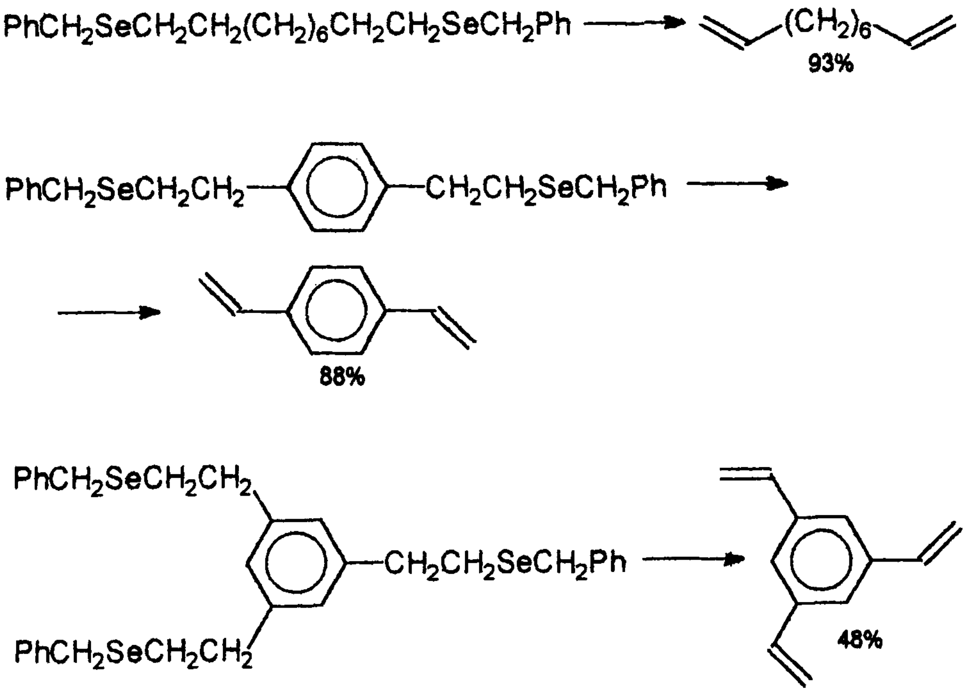
Pulse pyrolysis *in vacuo* of alkyl benzyl selenides affords, together with dibenzyl and selenium, the corresponding alkene and methane:[53]

$$\mathrm{PhCH_2SeCH_2CH_2Ph} \xrightarrow{600\,^\circ\mathrm{C}} (\mathrm{PhC\dot{H}_2} + \mathrm{\dot{S}eCH_2CH_2Ph}) \longrightarrow$$

$$\longrightarrow \underset{49\%}{\mathrm{PhMe}} + \underset{37\%}{\mathrm{PhCH_2CH_2Ph}} + \underset{96\%}{\mathrm{PhCH{=}CH_2}} + \mathrm{Se}$$

SCHEME 23

From bis- or tris(benzyl selenides) the following alkenes have been obtained, respectively, following a similar pathway:[53]



SCHEME 24

At moderate temperatures (150–170 °C) the thermolysis of dibenzyl diselenides leads to mixtures of dibenzyl polyselenides and selenium:[56]

$$\mathrm{PhCH_2SeSeCH_2Ph} \longrightarrow \mathrm{PhCH_2Se_nCH_2Ph} + \mathrm{Se}$$

$$\mathrm{PhCH_2Se_nCH_2Ph} + m\,\mathrm{Se} \longrightarrow \mathrm{PhCH_2Se_{n+m}CH_2Ph}$$

$n = 1 - 3$

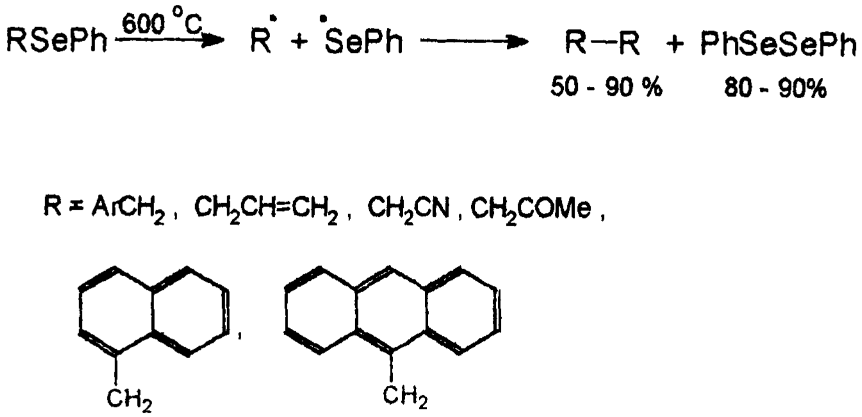
SCHEME 25

Bis(diphenylmethyl) selenide is converted in an analogous way:[55]

$$\mathrm{Ph_2CHSeCHPh_2} \xrightarrow{140\,^{\circ}\mathrm{C}} \mathrm{Ph_2CHSe_nCHPh_2} + \mathrm{Se}$$

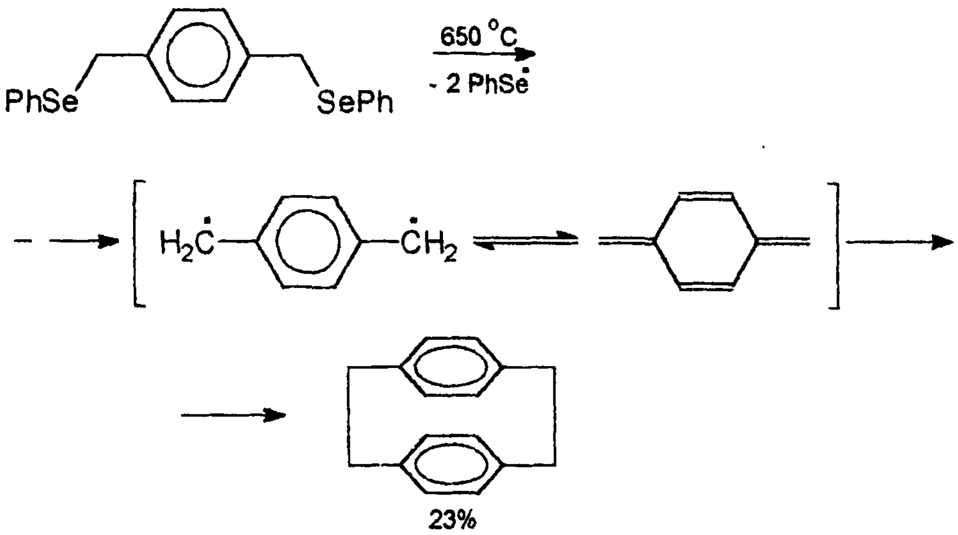
SCHEME 26

Upon thermolysis phenyl organyl selenides RSePh where R is a relatively stable radical, dissociate with rupture of the R-Se˙ bond which leads to the generation of phenylselenyl radicals.[53,57] The two radicals further dimerize as follows:



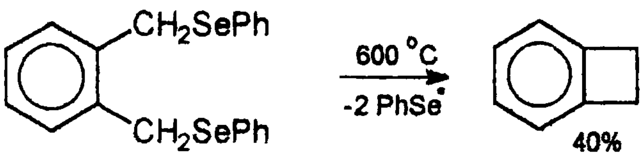
SCHEME 27

This kind of thermodecomposition of phenyl selenides allows the thermolysis of 1,4-bis(phenylselenomethyl)benzene to be used for the preparation of [2,2]paracyclophane:[53,57]



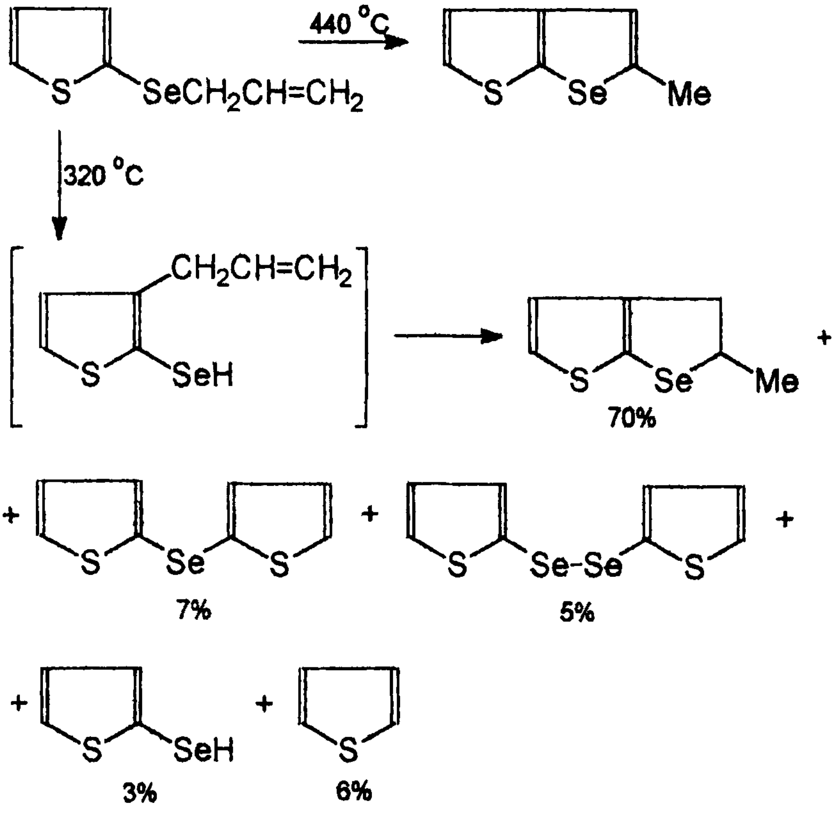
SCHEME 28

Analogously, the strained benzocyclobutane is generated from 1,2-bis(phenylselenomethyl) benzene:[53,57]



SCHEME 29

Allyl 2-thienyl selenide is subject to ready cyclization at 320 °C, preceded by a seleno-Claisen rearrangement:[58]

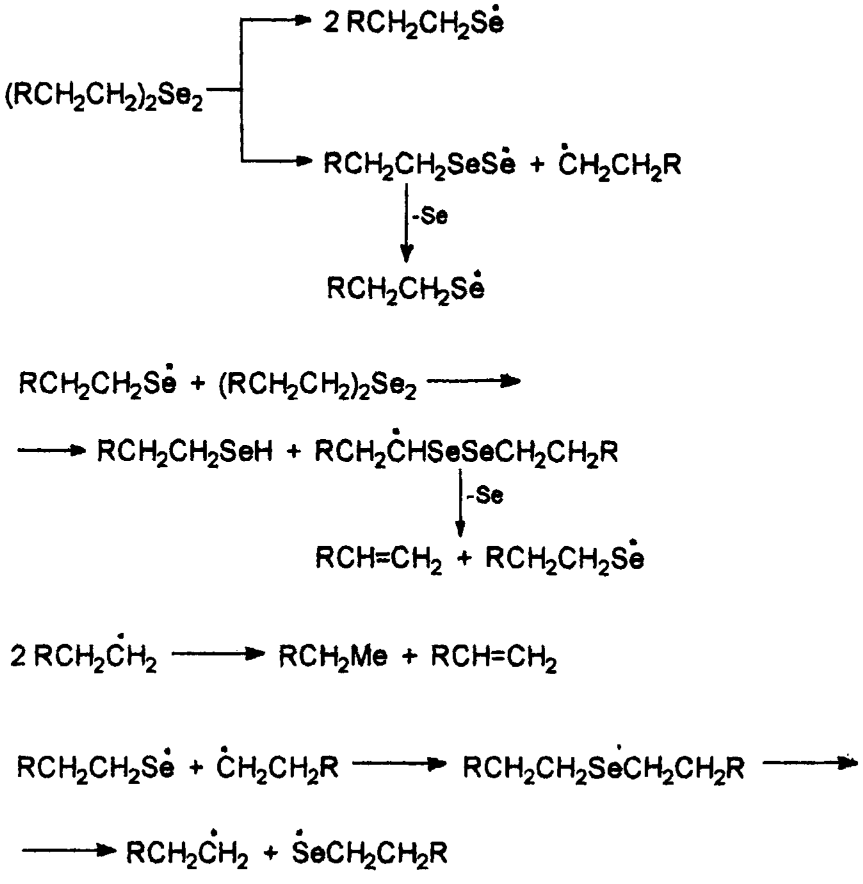


SCHEME 30

The side products of this reaction are indicative of the generation of thienyl radicals. Upon distillation *in vacuo* allyl thienyl selenide undergoes a quantitative cyclization and at 440 °C it is converted to 2-methylselenopheno[2,3-*b*]thiophene with elimination of selenium.

The direction of the thermal destruction of diorganyl selenides and diselenides is caused by generation of selenyl, perselenyl and carbon-centered radicals the conversion of which depends on their relative stability.

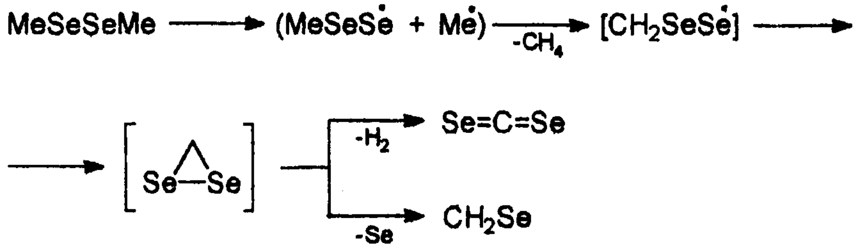
The chain free-radical mechanistic schemes of the thermal destruction of diorganyl selenides and diselenides can be explained as follows:[52,59]



R = H, Me, Et, Ph.

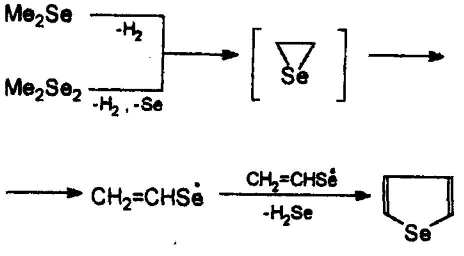
SCHEME 31

The thermolysis of dimethyl diselenide follows another scheme:[52]



SCHEME 32

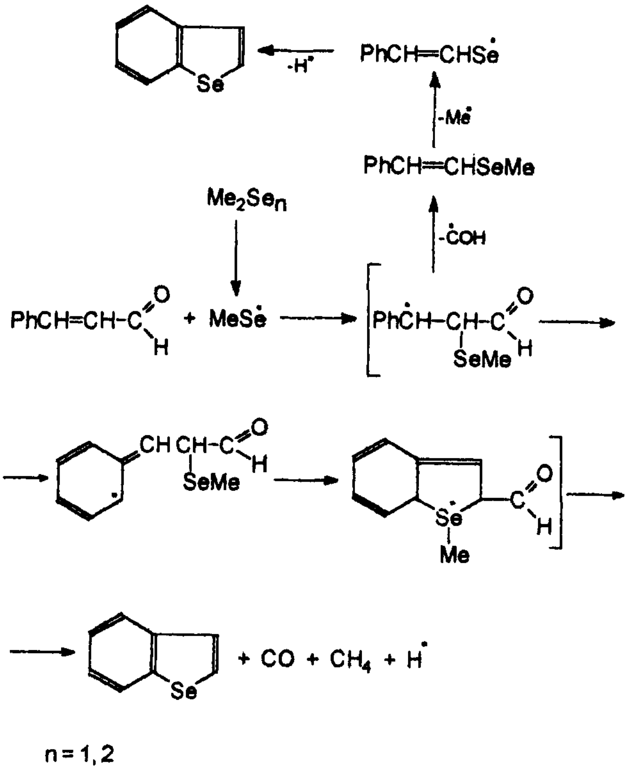
The formation of selenophene in the thermolysis of dimethyl selenide and diselenide is due to the generation of vinylselenyl radicals according to the scheme:



SCHEME 33

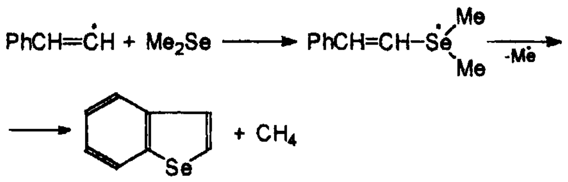
The thermolysis of benzyl organyl selenides always leads to the generation of stable benzyl radicals which are subject to recombination to dibenzyl. Phenylselenyl radicals, also prone to recombination, are eliminated from phenyl organyl selenides.

A series of chemical traps for thermally generated alkylselenyl radicals has been proposed. Thus, the reaction of cinnamic aldehyde with dimethyl selenide or diselenide at 600–650 °C affords benzoselenophene in 53% yield. The reaction mechanism involves the addition of the methylselenyl radical to a C=C double bond:



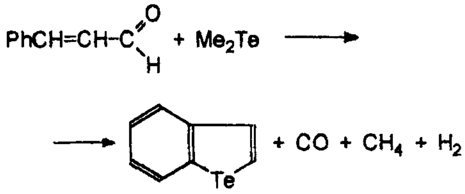
SCHEME 34

An alternative reaction is also possible:



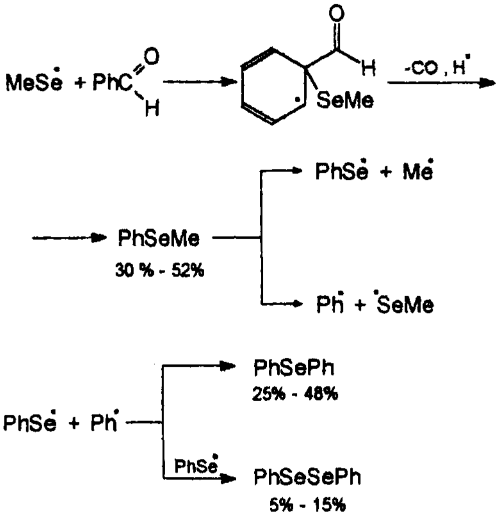
SCHEME 35

Dimethyl telluride reacts with cinnamic aldehyde at a lower temperature (500–550 °C) to form benzotellurophene; however, the yield does not exceed 12–17%:



SCHEME 36

The reaction of Me_2Se and Me_2Se_2 with benzaldehyde occurs already at 400–500 °C to give mainly methyl phenyl selenide and diphenyl selenide.[60] Here an attack of methylselenyl radicals at the benzene C-1 position followed by substitution of the formyl group is suggested:

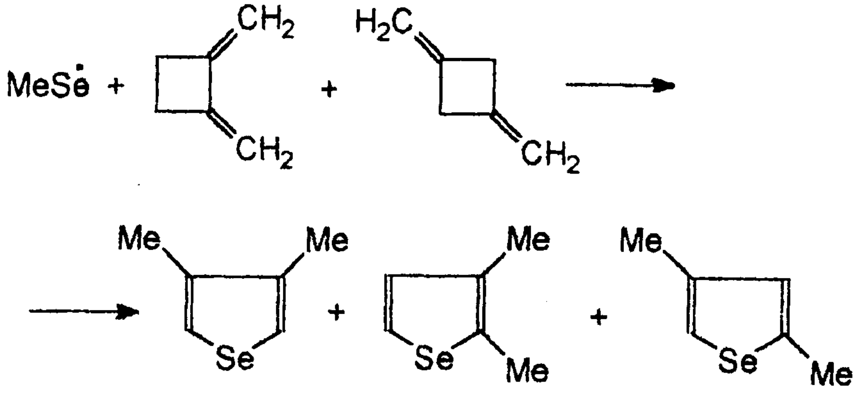


SCHEME 37

Ethylselenyl radicals react with benzaldehyde with much more difficulty (PhSeEt yield 6–9%).

Dimethyl telluride reacts with benzaldehyde analogously to dimethyl selenide to form, at 350–400 °C, PhTeMe and PhTePh in 40 and 3–6% yield, respectively.

The thermal reaction of dimethyl selenide with 1,2- and 1,3-dimethylenecyclobutane (a 3:1 mixture of isomers)[16] leads to a mixture of 3,4-, 2,3- and 2,4-dimethylselenophene in a ratio of 3:1:1. The total yield is 58%:



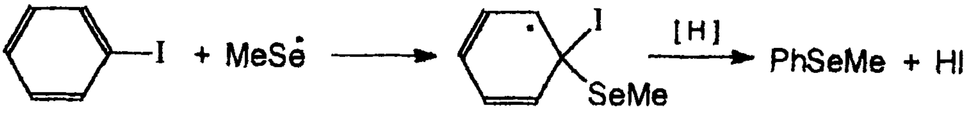
SCHEME 38

The predominance of the 1,2-isomer in the mixture of isomeric dimethylenecyclobutanes as well as the electronically and the sterically advantageous attack of the MeSe radical on the ring bond remote from the methylene groups facilitate the formation of 3,4-dimethylselenophene as the main reaction product.

Alkylthiyl radicals react with dimethylenecyclobutanes in a similar manner, only the yields of dimethylthiophenes do not exceed 42%.

Alkylselenyl radicals in the gas phase readily react with iodobenzene and 2-iodothiophene.

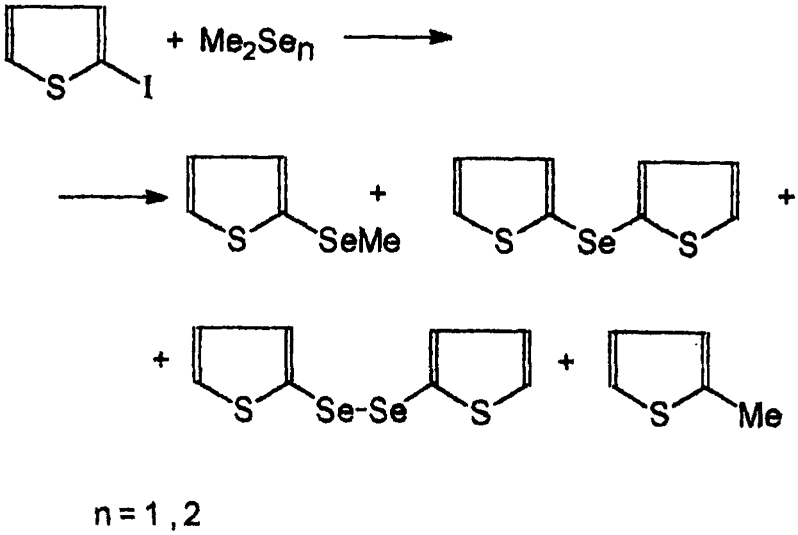
The co-thermolysis of Me_2Se or Me_2Se_2 with iodobenzene at 430 °C leads to selenoanisole in 33% yield:[62]



SCHEME 39

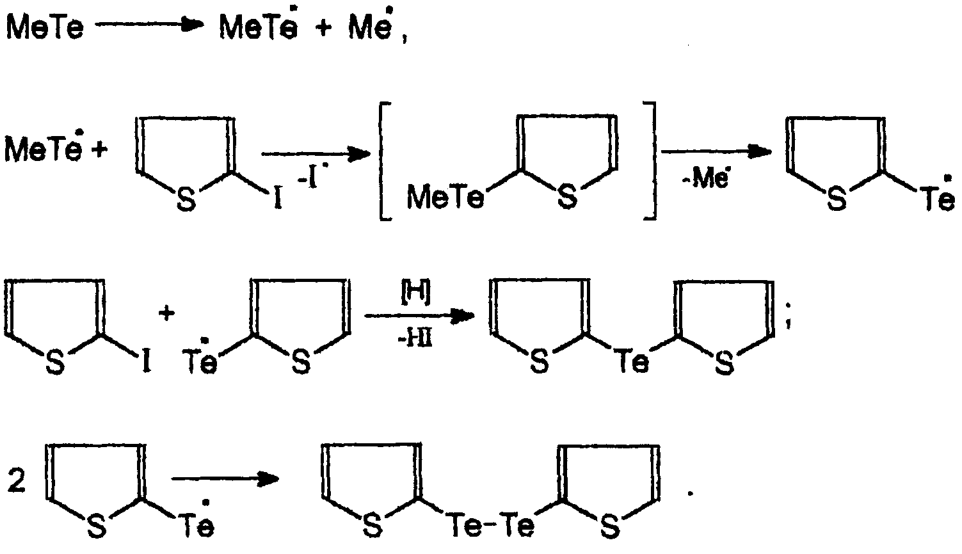
The simultaneous formation of selenophene, diphenyl selenide and diphenyl diselenide provides evidence for further thermal destruction of selenoanisole involving the generation of PhSe˙ radicals.

The reaction of 2-iodothiophene with Me_2Se_2 at 400 °C gives methyl 2-thienyl selenide in 69% yield. The products of the decomposition of the latter are di(2-thienyl) selenide, di(2-thienyl) diselenide, and 2-methylthiophene in 16–28, 7–8 and 2–4% yield, respectively:[63]



SCHEME 40

The chloro and bromo derivatives of benzene and thiophene do not react with selenyl radicals (unlike thiyl radicals).[7] The reaction of 2-iodothiophene with Me_2Te is accompanied by decomposition of the latter to tellurium metal and hydrocarbons. Nevertheless, the simultaneous formation of thiophene (30%), di(2-thienyl) telluride (8%) and di(2-thienyl) ditelluride (15%) indicates initial trapping of the methyltelluryl radical by 2-iodothiophene. Further the unstable methyl thienyl telluride generates the radical $2\text{-}C_4H_3S\text{-}Te^{\cdot}$:



SCHEME 41

The labile halogen atom in allyl bromide and benzyl chloride is substituted by alkylselenyl radicals under comparatively mild conditions at as low as 90–180 °C in solution.[64] Here the alkylselenyl radicals are generated from dialkyl diselenide:

$$2\,PhCH_2Cl + R_2Se_2 \longrightarrow 2\,PhCH_2SeR + Cl_2$$

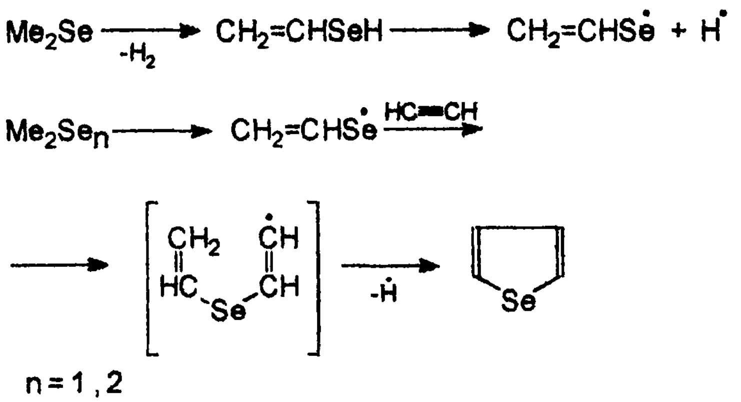
$$2\,CH_2{=}CHCH_2Br + R_2Se_2 \longrightarrow 2\,CH_2{=}CHCH_2SeR + Br_2$$

R = Me, Et.

SCHEME 42

Gas phase reactions of alkylselenyl radicals with acetylene do not form any addition products, i.e. vinyl alkyl selenides. This may be due to either low stability of the adduct of acetylene with the alkylselenyl radical or to the low reactivity of the latter in this reaction.

However, co-thermolysis of dimethyl selenide or diselenide with acetylene at 420–470 °C leads to the formation of selenophene in 80–94% yield.[65] The reaction mechanism involves generation of vinylselenyl radicals from Me_2Se and Me_2Se_2. The former further add to acetylene and the adduct radical formed undergoes cyclization:

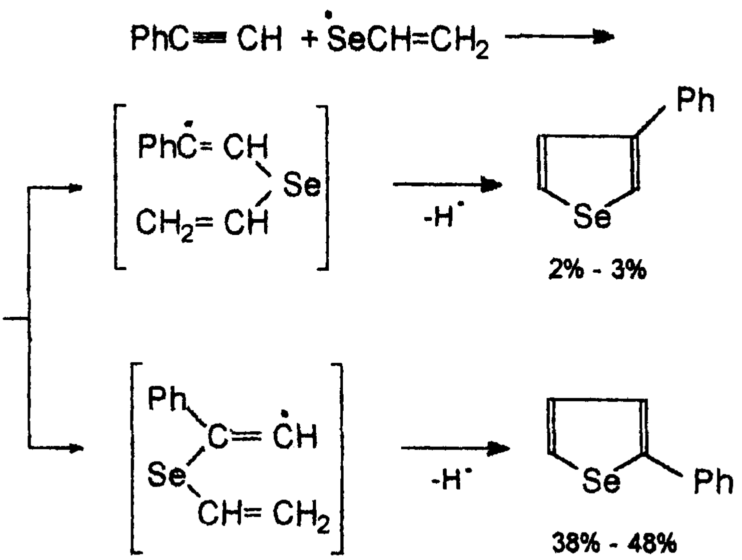


SCHEME 43

The use of other dialkyl selenides R_2Se (R = Et, Pr, Bu) in the reaction also leads to selenophene in a yield decreasing in the following order of R:

$$\text{Me} > \text{Et} >> \text{Pr} > \text{Bu}$$

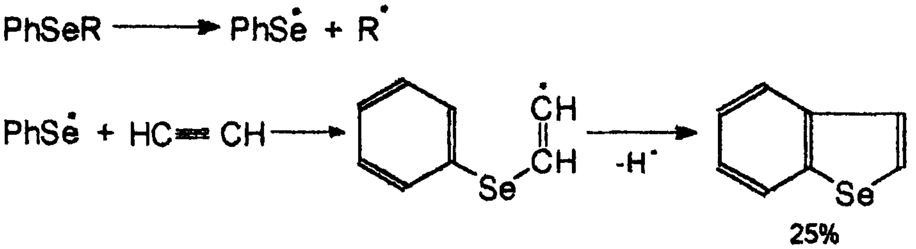
The mechanism of thermal destruction of dialkyl diselenides involving generation of vinylselenyl radicals is confirmed by the reaction of dimethyl selenide or diselenide with phenylacetylene. The major product of this reaction (carried out at 490–500 °C) is 2-phenylselenophene in a yield of 38% in both cases. The formation of 2-phenylselenophene is envisaged to follow a scheme involving the addition of vinylselenyl radicals to the C≡C triple bond, presumably in the α-position:



SCHEME 44

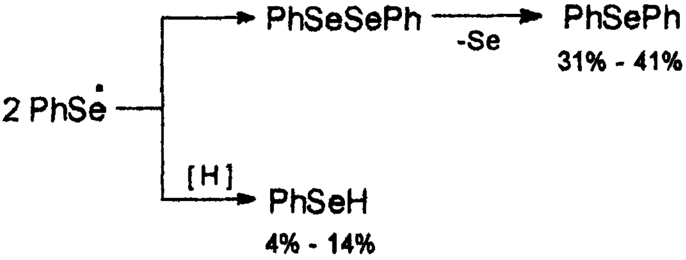
Selenophene, 3-phenylselenophene and aromatic hydrocarbons are side-products.

The co-thermolysis of methyl or allyl phenyl selenide with acetylene at 480–500°C leads to benzoselenophene which is the product of addition of the phenylselenyl radicals to the triple bond:[66]



SCHEME 45

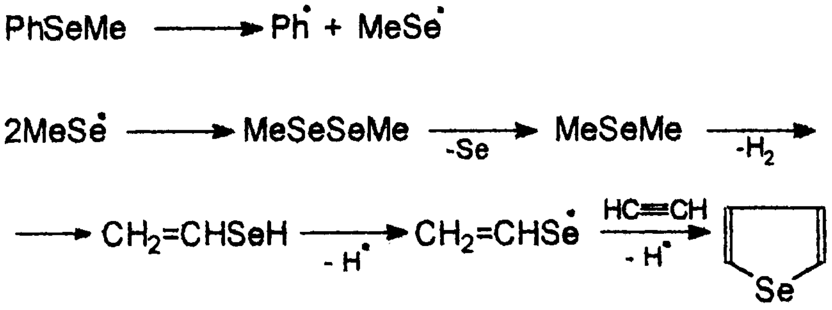
Simultaneously the PhSe• radical undergoes recombination to diphenyl diselenide. The latter readily eliminates selenium to form diphenyl selenide:



SCHEME 46

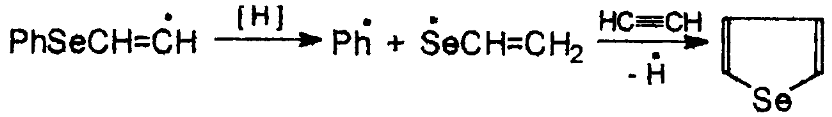
The PhSe˙ radical is partly stabilized due to abstraction of a hydrogen atom from the substrate to form selenophenol.

The co-thermolysis of PhSeR (R = CH_3, CH=$CHCH_2$) with acetylene results in the formation of selenophenol in 32% yield when R = CH_3. The thermolysis of selenoanisole seems also to be accompanied by the generation of methylselenyl radicals further conversion of which leads to vinylselenyl radicals:



SCHEME 47

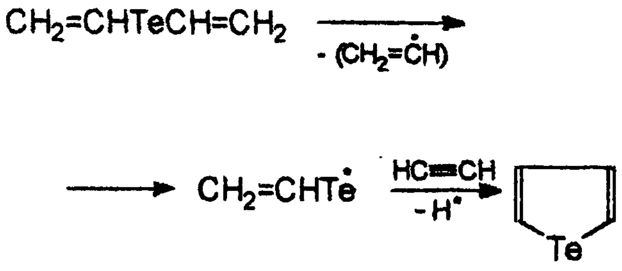
With allyl phenyl selenide no selenophene can be prepared in this way, therefore it is quite possible that the vinylselenyl radicals which give rise to the formation of the selenophene molecules are generated during the destruction of the radical adduct:



SCHEME 48

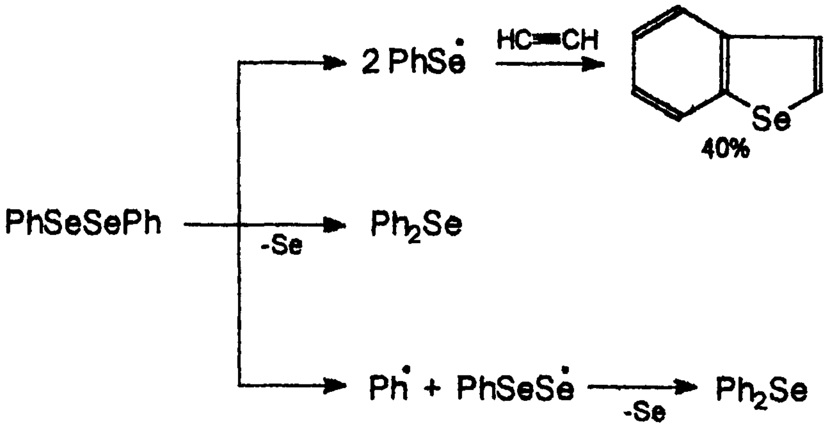
The co-thermolysis of alkyl phenyl selenides with acetylene reveals a difference in the reactivity of PhSe˙ and CH_2=CHSe˙ radicals. The latter react much more readily with acetylene. With the isostructural PhS˙ and CH_2=CHS˙ radicals quite an opposite relationship is observed.

At 440 °C allyl phenyl telluride does not react with acetylene and completely decomposes to give diphenyl telluride and ditelluride. At 500 °C, however, the reaction proceeds with formation of benzotellurophene and tellurophene in a total yield not exceeding 3–4%, which indicates low reactivity of the PhTe˙ radicals in their reaction with acetylene. At the same time, the CH_2=CHTe˙ radicals generated by thermolysis of divinyl telluride add to the acetylene multiple bond already at 420–450 °C to form tellurophene (yield 40 %):[67]



SCHEME 49

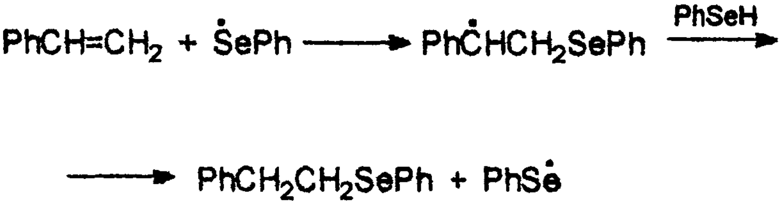
The reaction of diphenyl diselenide with acetylene at 500–580 °C leads to benzoselenophene, selenophene and diphenyl selenide due to generation of PhSe˙ radicals and elimination of selenium atom:[68]



SCHEME 50

In the reaction of diphenyl ditelluride with acetylene only traces of benzotellurophene were found.

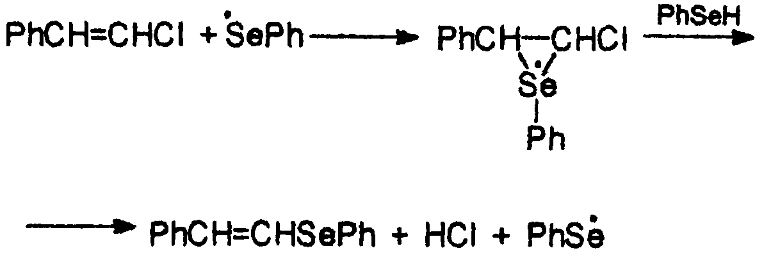
Benzeneselenol adds to styrene at 80–140 °C to form 1-phenyl-2-(phenylseleno)ethane (*i.e.* the *anti*-Markovnikov adduct). This is indicative of a radical mechanism:[69]



$$PhCH{=}CH_2 + \dot{S}ePh \longrightarrow Ph\dot{C}HCH_2SePh \xrightarrow{PhSeH} PhCH_2CH_2SePh + PhS\dot{e}$$

SCHEME 51

In the reaction of β-chlorostyrene with benzeneselenol in solution (80–140 °C) the chlorine atom is substituted by the PhSe˙ radical the reaction being strictly stereospecific:[69]



$$\mathrm{PhCH{=}CHCl} + \dot{\mathrm{S}}\mathrm{ePh} \longrightarrow \underset{\substack{\backslash\cdot/ \\ \mathrm{Se} \\ | \\ \mathrm{Ph}}}{\mathrm{PhCH{-}CHCl}} \xrightarrow{\mathrm{PhSeH}} \mathrm{PhCH{=}CHSePh} + \mathrm{HCl} + \mathrm{PhS}\dot{\mathrm{e}}$$

SCHEME 52

Simultaneously β-chlorostyrene is in part reduced to styrene which further reacts with PhSe$^{\cdot}$ according to the above scheme, while the phenylselenyl radicals undergo recombination.

3.1.4. *Chemically initiated generation and reactions* A number of reductions by selenols follow a radical mechanism involving chemical initiation. Thus, in their reactions with PhSeH arenediazofluoroborates are converted to a mixture of phenyl aryl selenides and arenes according to the following scheme:[70]

$$\mathrm{ArN_2^+BF_4^-} + \mathrm{HSePh} \longrightarrow \mathrm{ArSePh} + \mathrm{N_2} + \mathrm{HBF_4}$$

$$\mathrm{ArN_2^+} + \mathrm{PhSeH} \longrightarrow \mathrm{A}\dot{\mathrm{r}} + \mathrm{PhS}\dot{\mathrm{e}} + \mathrm{N_2} + \mathrm{H^+}$$

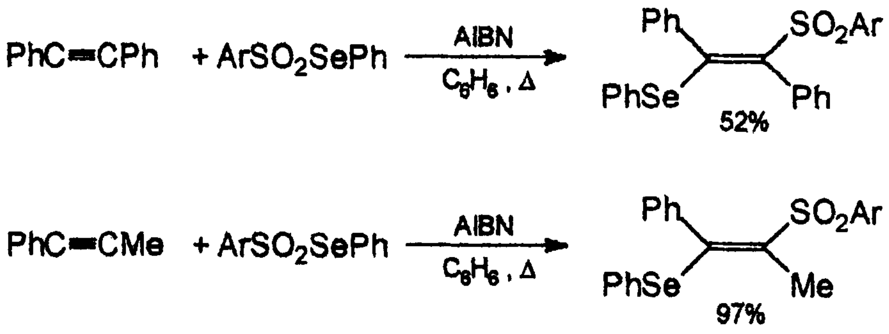
$$\mathrm{A}\dot{\mathrm{r}} + \mathrm{PhSeH} \longrightarrow \mathrm{ArH} + \mathrm{PhS}\dot{\mathrm{e}}$$

$$2\,\mathrm{PhS}\dot{\mathrm{e}} \longrightarrow \mathrm{PhSeSePh}$$

$$\mathrm{A}\dot{\mathrm{r}} + \mathrm{PhSeSePh}\ (\text{or } \mathrm{PhS}\dot{\mathrm{e}}) \longrightarrow \mathrm{ArSePh}$$

SCHEME 53

Se-Phenyl areneselenosulfonates react with activated alkynes already upon slight heating and under chemical initiation to form *anti*-Markovnikov adducts. The latter are readily peroxidized to selenoxides which spontaneously eliminate selenophenol and form acetylenic sulfones:[71–73]



SCHEME 54

The mechanism of the reaction of *Se*-phenyl areneselenosulfonates with monosubstituted alkynes is described by a standard scheme accepted for chain free-radical reactions (see above).

3.2. *Perselenyl and Selenuranyl Radicals*

Perselenyl $RSeSe^{\cdot}$ radicals are generated, together with selenyl $RSe^{\cdot}$ radicals, in the photolysis and thermolysis of diorganyl diselenides. They are less stable than perthiyl $RSS^{\cdot}$ radicals, but more stable than pertelluryl $RTeTe^{\cdot}$ radicals:

$$RSeSeR \longrightarrow RSe\dot{S}e \longrightarrow R\dot{S}e + Se$$

SCHEME 55

$RSeSe^{\cdot}$ radicals are more readily detected by EPR[30] than $RSe^{\cdot}$ radicals which is due to the delocalization of the lone electron on the neighbouring selenium atom and this cancels the degeneration of levels.[16,74]

The g-factor anisotropy is quite different in selenyl and perselenyl radicals:[30]

Radical	$g_{\perp}$	$g_{\parallel}$
$Ph\dot{S}e$	2.003	2.016
$PhSe\dot{S}e$	2.026	2.043

SCHEME 56

In the UV spectra[a] λ_{max} of 600 nm corresponds to the $4\text{-}CH_3OC_6H_4SeSe^{\cdot}$ radical.[21]

Selenouranyl $R_2Se\text{-}X^{\cdot}$ radicals, like their sulfur and tellurium analogs, are intermediates in homolytic substitutions (S_H2) at selenium atoms upon free-radical treatment of organoselenium compounds.[75,76]

$$\dot{X} + R_2Se \longrightarrow \left[R_2\dot{S}e{-}X\right] \longrightarrow RSeX + R^{\bullet}$$

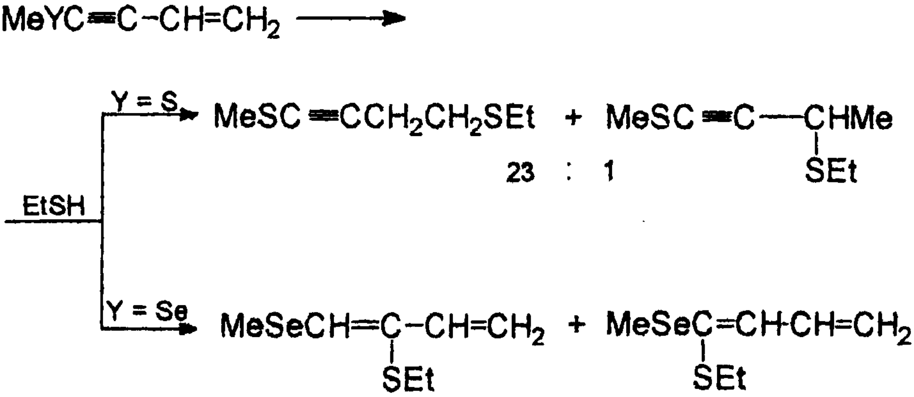
$$X = OSiMe_3,\ SCF_3,\ SCOEt,\ SCOBu^t$$

SCHEME 57

$Ph_2Se\text{-}X^{\cdot}$ radicals are formed by γ-irradiation of triphenylhaloseleniums Ph_3SeX and can be detected by EPR. In these radicals the unpaired electron is mainly localized on the orbital which links the Se and Hal atoms and is oriented perpendicularly to the CSeC plane (σ*-orbital). The proportion of spin plane localization is ~80 and ~20% for the Se and Hal atoms, respectively.[77]

A σ* type structure was proven by EPR for other types of selenuranyl radicals $R_2Se\text{-}X^{\cdot}$ as well (R = Me, Et, Ph, 1-adamantyl and their unsymmetrical derivatives; X = EtC(O)S, *t*-BuC(O)S, CF_3Me_3CO, Me_3SiO).[78] This structure is characterized by its ^{77}Se value of 162 Gs, for example, for $1\text{-}(Ad)_2Se\text{-}SC(O)CMe_3^{\cdot}$ which corresponds to 3% spin population of the Se-4s orbital. The spin population of the Se-4p orbitals (38–71%) responsible for the density shift in $Me_2Se\text{-}X^{\cdot}$ corresponds to the σ* orbital nature of the Se-X bond which, in turn, depends on the X atom electronegativity.[78]

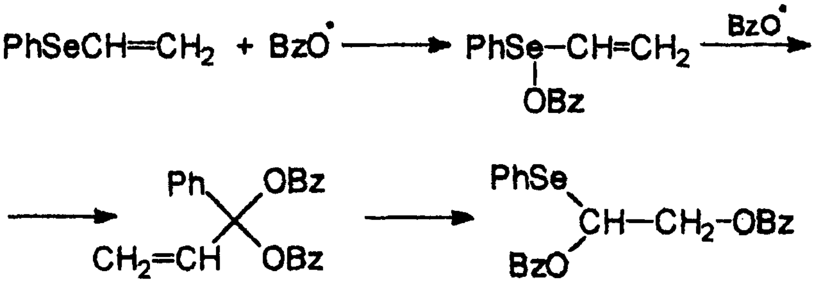
The structure of selenuranyl radicals is identical to that of the cation radicals $[Me_2Se\text{-}Se_2Me]^{+\cdot}$ formed upon exposure to γ-irradiation of dimethyl diselenide.[79] The generation of selenuranyl radicals is used to explain the differing regioselectivities of some reactions:[80]



SCHEME 58

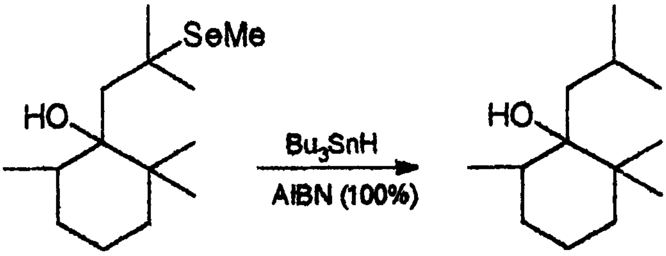
Evidently, with Y = Se the thiyl radicals attack the Se atom to form a selenuranyl radical which further rearranges with migration of the EtSe group to the neighboring triple bond. Thiouranyl radicals are not likely to be generated in this case.

Selenuranyl radicals also seem to be involved in the reaction of phenyl vinyl selenide with benzoyl peroxide which leads to dibenzoylation of the double bond:[81,82]



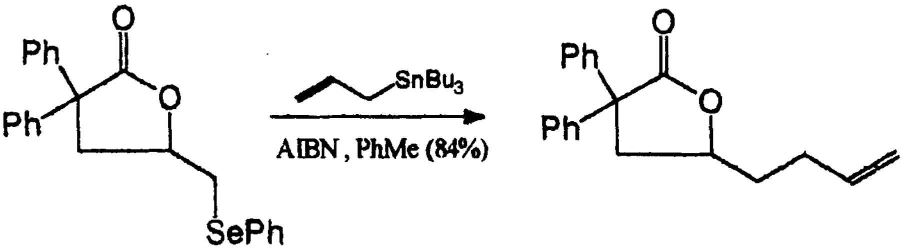
SCHEME 59

Upon AIBN initiation tributylstannane reductively cleaves a C-Se bond in hydroxyalkyl selenides:[83]



SCHEME 60

When exposed to chemical (AIBN) and radiation initiation, tributylallylstannane reacts with phenyl selenides to form new a carbon-carbon bond (reductive allylation):[83]



SCHEME 61

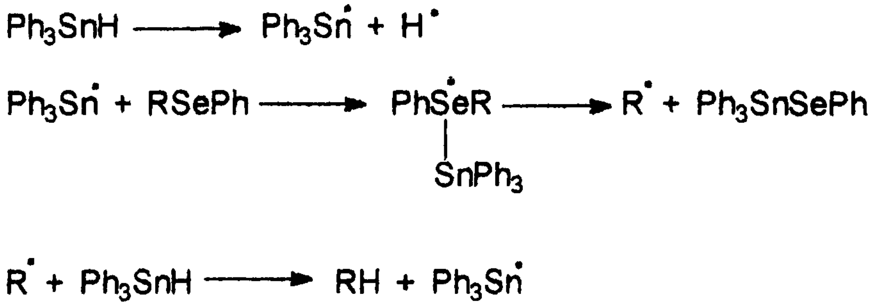
The trialkylstannyl radicals generated in the photolysis of hexaalkyldistannanes cleave the alkyl-selenium bonds of dialkyl selenides as well as analogous bonds in dialkyl sulfides and tellurides. The reaction rate diminishes in the following order $R_2Te > R_2Se > R_2S$:[84]

$$RYR + \dot{S}nBu_3 \longrightarrow RYSnBu_3$$

$$Y = S\,,\,Se\,,\,Te$$

SCHEME 62

Triphenylstannane reacts with alkyl phenyl selenides in boiling toluene in an analogous manner. These reactions are suggested to follow a free-radical mechanism *via* the intermediate formation of selenuranyl radicals:[85–90]



$$Ph_3SnH \longrightarrow Ph_3\dot{S}n + H^{\bullet}$$

$$Ph_3\dot{S}n + RSePh \longrightarrow Ph\overset{\bullet}{S}eR(SnPh_3) \longrightarrow \dot{R} + Ph_3SnSePh$$

$$\dot{R} + Ph_3SnH \longrightarrow RH + Ph_3\dot{S}n$$

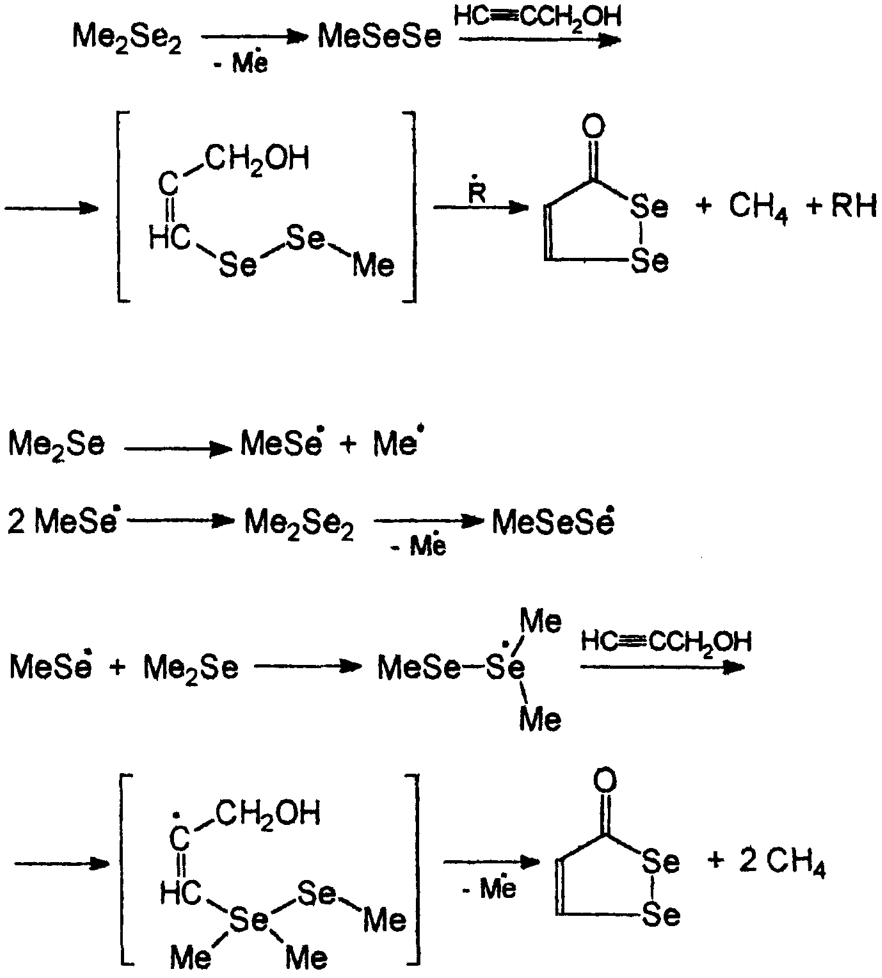
SCHEME 63

The reduction of organyl phenyl tellurides with tributylstannane likely proceeds *via* analogous radical states:

$$PhTeR + HSnBu_3 \longrightarrow PhTeSnBu_3 + RH$$

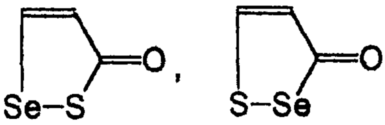
SCHEME 64

The co-thermolysis of propargyl alcohol with Me_2Se at 460 °C or with Me_2Se_2 at 400–430 °C leads to 1,2-diselenol-3-one in 16–25% and 73% yield, respectively.[91] The reaction mechanism involves interaction of the propargyl alcohol with the perselenyl or selenuranyl radicals generated in the thermolysis of dimethyl selenide and diselenide:

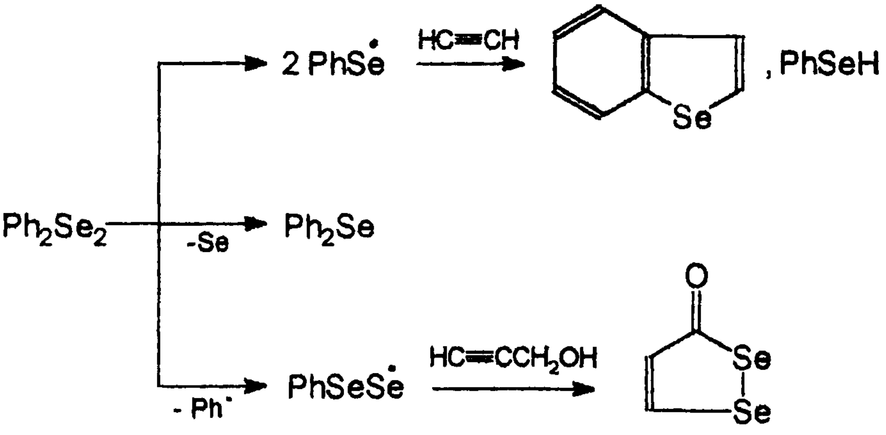


SCHEME 65

Other dialkyl diselenides such as Et_2Se_2 and i-Pr_2Se_2 react with propargyl alcohol in a similar way. It is less effectively that propargyl alcohol traps perthiyl (sulfuranyl) radicals, whereas their tellurium analogs fail to trap these radicals at all. The thermolysis of a mixture of Me_2S_2 and Me_2Se_2 generates also mixed perchalcogenyl radicals which form two isomeric thiaselenols in the reaction with propargyl alcohol:



A gas-phase reaction of diphenyl diselenide with propargyl alcohol and its thermolysis (with acetylene) at 500–550 °C also leads to 1,2-diselenol-3-one (yield 14–16%). Together with the latter, diphenyl selenide, benzoselenophene, selenophene and selenophenol are formed in a yield of 26–31, 8–12, 2–14 and 3%, respectively:[92]



SCHEME 67

Diphenyl ditelluride practically does not react with propargyl alcohol.

3.3. *Seleninyl and Selenonyl Radicals*

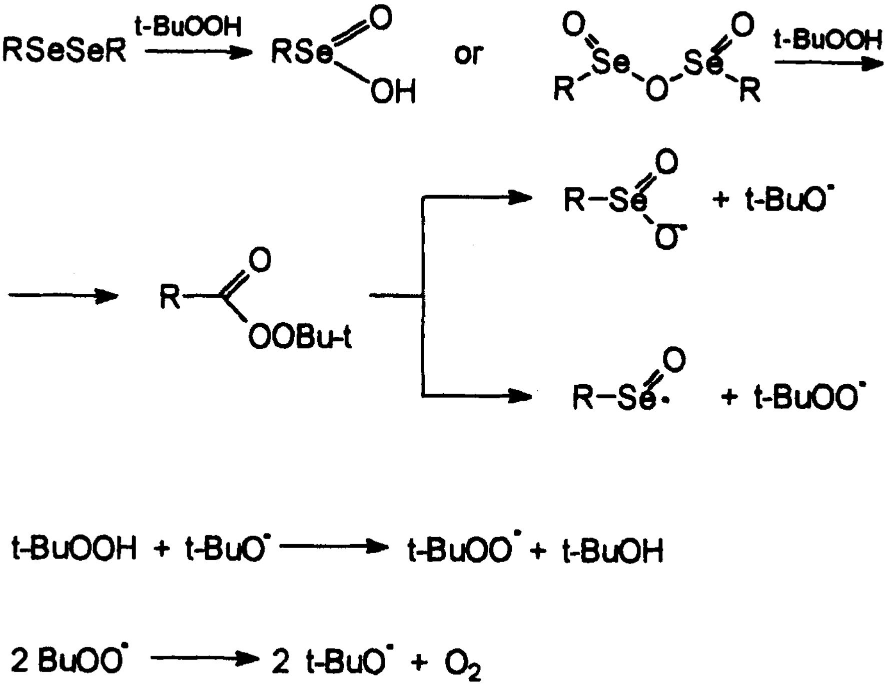
Seleninyl radicals PhSeO$^{\bullet}$ and selenonyl radicals PhSeO$_2^{\bullet}$ are generated by X-radiolysis of diphenyl selenoxide[25] and by ^{60}Co γ-radiolysis of diphenyl selenone,[93] respectively. EPR allowed this detection in the solid phase, and the spin density distribution on the oxygen and selenium atoms could be determined. In the chalcogeninyl radicals the spin density is concentrated on the chalcogen atoms to a greater degree rather than in the chalcogenonyl radicals. In the sulfur analogs of these radicals the spin density is more localized on the sulfur atom than on the selenium atom in the selenide analogs.

	Spin density, %		
R	S, Se	O	Refs.
MeSO	87	13	95
MeSO$_2$	42 (38)	29 (31)	93, 94
PhSO$_2$	46	27	93
PhSO	78	22	25
PhSeO$_2$	40	30	93

The seleninyl radicals PhSeO$^{\bullet}$ in which the selenium atom has a positive oxidation number are generated by radical attack either on the anhydride of the corresponding seleninic acid or on *S*-*t*-butyl benzenethioseleninate [PhSe(O)SCMe$_3$].[96]

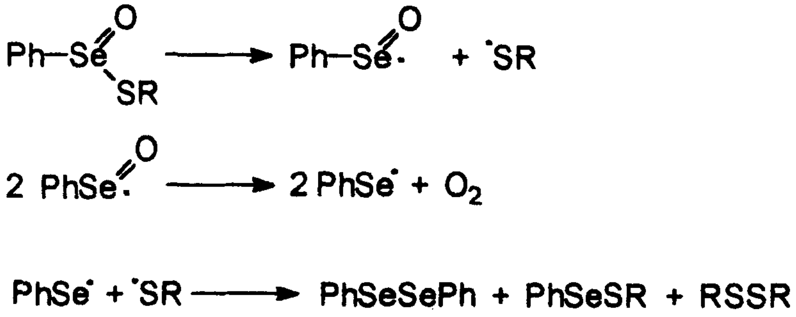
It is possible that on catalytic decomposition of *t*-butyl hydroperoxide with diselenides, seleninic acids or anhydrides peroxyseleninates are formed as intermediates. Their further thermolysis with cleavage of the O-O or Se-O bonds leads to radicals $RSeO_2^{\cdot}$, $RSeO^{\cdot}$, $Me_3CO^{\cdot}$ and $Me_3COO^{\cdot}$.

The selenium-containing radicals are further converted to seleninic acids or anhydrides by a poorly understood mechanism:[97,98]



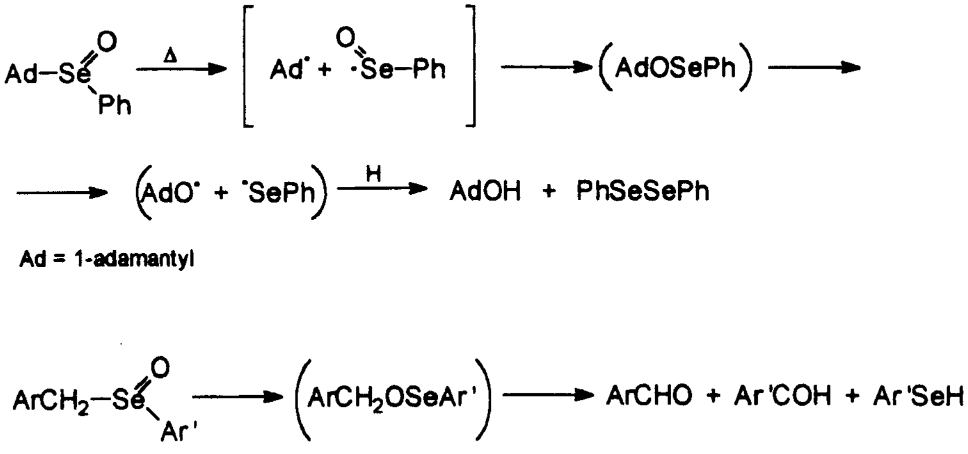
SCHEME 68

In the oxidation of thiols with benzeneseleninic acid thioseleninates are assumed to be formed as intermediates. Their further destruction follows a radical mechanism:[99]



SCHEME 69

The thermolysis of aryl selenoxides involves ArSeO radical generation:[100,101]



SCHEME 70

Ad = 1-adamantyl

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