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Selenium- and tellurium-centred radicals

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Abstract. The principal types of radicals formed in various types of initiation of the reactions of organic compounds of selenium and tellurium, the methods for their detection, and their properties and reactivities are examined. The bibliography includes 98 references.

I. Introduction

During recent years the chemistry of selenium and tellurium has begun to develop vigorously, promoted to a considerable extent by their extensive application in medicine, the electronics industry, etc. Selenium plays an important role as a trace element in living organisms.

Selenium- and tellurium-centred radicals are short lived intermediates in many photolytic thermal reactions of organoselenium and organotellurium compounds. The first information about them appeared in the literature little more than twenty years ago and their study began to develop vigorously only in recent years. This was promoted primarily by the discovery of the important role of selenium as a trace element in living organisms, in food products for animals and man, and in biochemical processes,[1] as well as its employment in microelectronics.[2,3] In the second half of the present century, eight natural selenoproteins were discovered. It was observed that the deficiency of selenium in food and in soil can induce certain diseases in animals and anomalies in the growth and development of a number of plant species.[1]

Organoselenium and organotellurium compounds are used in the electronics industry, in xerography, in photoelectronics and in the glass, ceramics, and pigments industries. Selenium-containing polymers with semiconducting properties and photosensitivity have been obtained.[2,3] Neurotropic and psychotropic medicinal preparations, with much lower toxicity than their sulfur analogues, have been developed based on selenophene.[4,5]

Homolytic processes, which include the formation of free selenium- and tellurium-centred radicals, play an important role in the reactions of organoselenium compounds and to a lesser extent of their tellurium analogues. This is due to the low energies of the C–Se, Se–Se, and Se–E (E = heteroatom) as well as C–Te and Te–Te bonds, which are responsible for their ready homolytic dissociation.[4,7]

This review deals with the main types of radical formed in various types of initiation of reactions of organic compounds of selenium and tellurium, the methods for their detection, and their properties and reactivities. A comparison is made with the analogous data for sulfur-centred radicals.

Whereas radical reactions of the organic compounds of sulfur have been investigated quite fully,[7–10] information about the fairly similar free-radical reactions of organoselenium compounds, mainly photochemical reactions, has been surveyed only in brief reviews.[11,12] Data on the radical reactions of organotellurium compounds are scattered among various communications and the aim of the present review is to survey the existing literature on this question.

The following types of selenium- and tellurium-centred radicals are known: for selenium, these are the selenyl (RSe˙), perselenyl (RSeSe˙), selenuranyl [$R_2Se^{\cdot}-SeR$ and $R_2Se^{\cdot}-X$; X = Cl, Br, $OSiMe_3$, C(Me)OMe, SC(O)R′], seleninyl (RSe˙O), and selenonyl ($RSe^{\cdot}O_2$) radicals and for tellurium only the telluryl radicals (RTe˙).

II. Selenyl and telluryl radicals

1. Detection and physical properties

The simplest selenium-centred radicals—the selenyl radicals RSe˙—were first detected in the photolysis of diorganyl diselenides.[13]

Selenyl (HSe˙) and telluryl (HTe˙) radicals are generated by passing hydrogen through a microwave absorption cell, the walls of which are coated with selenium or tellurium respectively, in a silent electric discharge (the HS˙ radicals are generated similarly). Certain physicochemical characteristics of the radicals HE˙ (E = Se, Te, S) are presented in Table 1.

Table 1. Physicochemical characteristics of the radicals.[14]

Parameter	HSe˙	HTe˙	HS˙
I	60	3	240
P/Torr	5	1	10
$10^{-8}D$/electrostatic units	0.2	0.1	0.3
A_0/cm^{-1}	1600 ± 50	2250 ± 200	–

Note. I is the intensity of the microwave radiation, P the partial pressure, D the dipole moment, and A_0 the spin–orbit coupling constant of the ground state of the radical measured by the EPR method.

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The adiabatic ionisation potential of the radical HSe̊ (9.845 ± 0.003 eV) and the bond dissociation energies D_0(HSe−H) = 78.99 and D_0(H−Se̊) = 74.27 kcal mol^{-1} were determined on photoionisation of the radical HSe̊ generated in the spectrometer cell during the interaction of atomic hydrogen with hydrogen selenide.

$$\dot{H} + H_2Se \longrightarrow H\dot{S}e + H_2$$

Organoselenyl radicals RSe̊ are formed on photolysis of diorganyl diselenides.[13] Their direct detection by the EPR method is difficult (particularly in the liquid phase) owing to the high degree of spin−orbit coupling and in certain cases the occurrence of specific interactions,[16] which lead to orbitally degenerate (or almost degenerate) ground states and to a greater anisotropy of the *g*-factor.[17] As a result of this, the radicals RSe̊ have short relaxation times and give rise to extremely broad lines in the EPR spectra.[9,16,17] Nevertheless, the selenyl radicals formed on photolysis of toluene-ω-selenol, and didodecyl, dioctadecyl, and diphenyl selenides have been detected by the EPR method. Because of anisotropy of the *g*-factor, selenyl radicals have (like thiyl radicals[11]) asymmetric spectra, the *g*-factor differing significantly from the values characteristic of the free electron and carbon-centred radicals.[18,19]

Radical	$g_\perp$	$g_\parallel$
PhSe̊	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

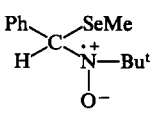
The methylselenyl radical MeSe̊ could not be detected directly by the EPR method[18] and the available information concerning the measurement of the EPR spectrum of the PhSe̊ radical is fairly contradictory.[18,20] The detection of the RTe̊ radicals by the EPR method has not been reported at all.

Arylselenyl radicals can be detected by UV spectroscopy.[21,22] The absorption band of the radical PhSe̊ is in the region of 490 nm (like that of PhS̊), while that of the radical 4-$MeOC_6H_4S\dot{e}$ is in the region of 535 nm (in methanol). The corresponding absorption bands of the radicals 4-$MeOC_6H_4S$̊ and 4-$MeOC_6H_4T\dot{e}$ are in the region of 525 and 508 nm.[22,23]

Like thiyl radicals,[9] selenyl radicals RSe̊ can be readily identified by the EPR method as adducts with nitroso-compound spin-trapping agents.[24]

Methylselenyl radicals, formed on photolysis of dimethyl diselenide, do not interact with 2-methyl-2-nitrosopropane but are effectively bound by *tert*-butyl phenyl nitrone.[17] The adduct **1** is characterised by a high value of the *g*-factor (2.0097), the hyperfine structure (hfs) constants confirming its structure: a_N = 13.5 G, a_H(1H) = 2.06 G, and a_H(3H) = 0.85 G.[17]

$$Me_2Se_2 \xrightarrow{h\nu} 2MeS\dot{e} \xrightarrow{PhCH=N(O)Bu^t}$$



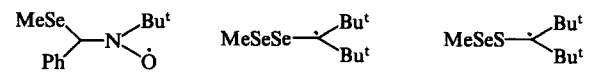
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The arylselenyl radicals PhSe̊ and 4-$O_2NC_6H_4S\dot{e}$ have been detected as adducts with nitrosodurene.[17,25]

The radical complexes RSe̊·MX_3 (X = Cl, Br), formed from selenides and diselenides on their interaction with aluminium and gallium halides, can also be detected by EPR spectroscopy. The EPR spectra of the Ar_2Se_2–$AlBr_3$–C_6H_6 system consists of three singlet signals ($g \sim 2.07$, $g \sim 2.03$, and $g \sim 2.0025$). They have been assigned to the radicals Ar̊, ArSe̊, and ArSeSe̊ bound in the complex.[26]

2. The formation reactions of organic compounds of selenium and tellurium on photolysis and radiolysis

The selenyl radicals generated by the photolysis of diorganyl selenides readily add to the C=C, C=S, C=Se, etc. multiple bonds. The methylselenyl radicals formed on photolysis of dimethyl diselenide add to the multiple bonds of the corresponding spin-trapping agents, affording adducts of the following type:[17]



The photolysis of dibenzyl diselenide takes place differently, beginning with the dissociation of the Se−C bond and the formation of dibenzyl selenide and selenium. The benzylselenyl radical is then generated in the stage involving the decomposition of the benzylperselenyl radical formed initially and then interacts rapidly with the benzyl radical.[27]

$$PhCH_2SeSeCH_2Ph \xrightarrow{h\nu} \begin{cases} 2\,PhCH_2S\dot{e} \\ PhCH_2SeS\dot{e} + \dot{C}H_2Ph \end{cases}$$

$$PhCH_2SeS\dot{e} \longrightarrow PhCH_2S\dot{e} + Se$$

$$Ph\dot{C}H_2 + PhCH_2SeSeCH_2Ph \longrightarrow PhCH_2S\dot{e} + PhCH_2SeCH_2Ph$$

$$PhCH_2S\dot{e} + \dot{C}H_2Ph \longrightarrow PhCH_2SeCH_2Ph$$

$$2\,PhCH_2S\dot{e} \longrightarrow PhCH_2SeSeCH_2Ph$$

When dibenzyl diselenide in solution in benzene is irradiated in air or in acetonitrile, benzaldehyde, benzyl alcohol, and elemental selenium are formed,[28] whereas in carbon tetrachloride the product is benzyl chloride.[29] This confirms the preferential dissociation of the C−Se bond on photolysis of dibenzyl diselenide. Photolysis of diphenyl diselenide leads to the formation of phenylselenyl radicals PhSe̊, which are distinguished by a low reactivity in their reactions with hydrogen, oxygen, or halogen donors but add readily to activated olefins.[23,30,31]

$$PhSeSePh \overset{h\nu}{\rightleftharpoons} 2\,PhS\dot{e}$$

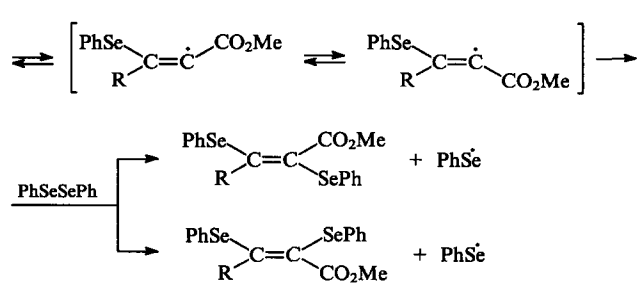
$$PhS\dot{e} + CH_2{=}CHR \rightleftharpoons PhSeCH_2{-}\dot{C}HR$$

The rate constant for the addition reaction ranges from 2.0×10^6 mol^{-1} s^{-1} for α-methylstyrene to $\sim 10^3$ mol^{-1} s^{-1} for vinyl acetate. These values are lower by a factor of 10−50 than in the case of the radical PhS̊, which indicates a greater stability of the phenylselenyl radical.

The phenylselenyl radicals generated on UV irradiation add effectively to activated acetylenes, but their addition to non-activated acetylenes, for example to dec-1-yne, is very slow.[32]

$$PhSeSePh \overset{h\nu}{\rightleftharpoons} 2\,PhS\dot{e}$$

$$PhS\dot{e} + RC{\equiv}CCOOMe \rightleftharpoons$$



The (*E*)-isomers predominate in the mixture of the di(phenylseleno)ethylenes formed. Owing to steric hindrance, dimesityl diselenide reacts with activated acetylenes only slowly.

Phenylselenyl radicals are also generated on photolysis of phenylareneselenosulfonates, inducing the chain decomposition of the latter with formation of diphenyl diselenide and arenesulfonic anhydride.[33]

$$PhSeSO_2Ar \xrightarrow{h\nu} PhSe^{\bullet} + {}^{\bullet}SO_2Ar$$

$$PhSe^{\bullet} + PhSeSO_2Ar \longrightarrow PhSeSePh + {}^{\bullet}SO_2Ar$$

$$2\,ArSO_2^{\bullet} \longrightarrow \left[ArS(=O)(=O)-O-S(=O)(=O)Ar \right] \longrightarrow \longrightarrow$$

$$\longrightarrow ArS(=O)(=O)-O-S(=O)(=O)Ar + \text{other products}$$

$$2\,PhSe^{\bullet} \longrightarrow PhSeSePh$$

The photolysis of phenylareneselenosulfonates in the presence of alkenes leads to aryl β-phenylselenoalkyl sulfones. The reaction is strictly stereoselective and involves the formation of *trans*-adducts.[34]

$$PhSeSO_2Ar + \longrightarrow \text{(1-SO}_2\text{Ar, 2-SePh)}$$

The photolytic addition of selenosulfonates to alkenes is faster than the thermal addition (in boiling chloroform or benzene). In both cases, the reaction proceeds via a free-radical chain mechanism. It is accelerated on initiation with azobisisobutyronitrile (AIBN) and is inhibited by 2,6-di-*tert*-butyl-*p*-cresol.[35]

$$ArSO_2SePh \xrightarrow{h\nu \text{ or } \Delta} ArSO_2^{\bullet} + Se^{\bullet}Ph$$

$$ArSO_2^{\bullet} + \text{(R}^1\text{,R}^2\text{-C=C-R}^3\text{,R}^4\text{)} \longrightarrow \text{(R}^1\text{,ArSO}_2\text{-C-C}^{\bullet}\text{(R}^2\text{)-R}^3\text{,R}^4\text{)} \xrightarrow{ArSO_2SePh}$$

$$\longrightarrow \text{(R}^1\text{,ArSO}_2\text{-C(R}^2\text{)-C(SePh)-R}^3\text{,R}^4\text{)} + ArSO_2^{\bullet}$$

The aryl β-phenylselenoalkyl sulfones formed eliminate spontaneously benzeneselenol in the presence of *m*-chloroperbenzoic acid or hydrogen peroxide and are converted into the corresponding vinyl sulfones.

The photolysis of diorganyl diselenides is accelerated by tertiary phosphines, whereupon the Se–Se bond dissociates preferentially both in diphenyl diselenide and in dibenzyl diselenide.[36–38]

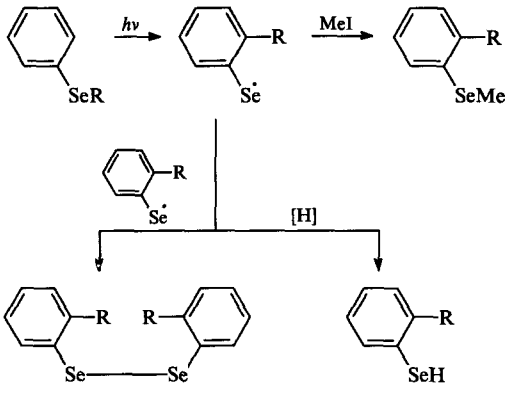
$$RSeSeR \overset{h\nu}{\rightleftharpoons} 2\,RSe^{\bullet}$$

$$RSe^{\bullet} + R'_3P \longrightarrow RSe-\dot{P}R'_3$$

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

$$R^{\bullet} + RSeSeR \longrightarrow RSeR + Se^{\bullet}R$$

Arylselenyl radicals are generated[39] also in the photorearrangements of aryl benzyl selenides containing a weakened Se–C bond.



R = CH_2Ph.

The photoinduced reaction of organocobaloximes with diphenyl diselenides involves the intermediate formation of phenylselenyl radicals.[40]

$$RCo(dmgH)_2Py \longrightarrow R^{\bullet} + Co(dmgH)_2Py$$

$$R^{\bullet} + PhSeSePh \longrightarrow RSePh + Se^{\bullet}Ph$$

$$Co^{\bullet}(dmgH)_2Py + PhSeSePh \longrightarrow PhSeCo(dmgH)_2Py + Se^{\bullet}Ph$$

$$R^{\bullet} + Se^{\bullet}Ph \longrightarrow RSePh$$

$$Co^{\bullet}(dmgH)_2Py + Se^{\bullet}Ph \longrightarrow PhSeCo(dmgH)_2Py$$

$dmgH_2$ = dimethylglyoxime

Diphenyl diselenide reacts via a similar mechanism with organic complexes of zirconium,[11] metal carbonyls,[42,43] and the adamantyl radical.[44,45]

The photolytic reaction of diphenyl diselenide with diazomethane proceeds via a free-radical chain mechanism.[45]

$$PhSeSePh \xrightarrow{h\nu} 2\,PhSe^{\bullet}$$

$$PhSe^{\bullet} + CH_2N_2 \longrightarrow PhSeCH_2N{=}\dot{N}$$

$$PhSeCH_2N{=}\dot{N} \longrightarrow PhSe\dot{C}H_2 + N_2$$

$$PhSe\dot{C}H_2 + PhSeSePh \longrightarrow PhSeCH_2SePh + Se^{\bullet}Ph$$

The photochemical reaction of diphenyl diselenide or benzeneselenosulfonate with alkylmercury halides is also initiated by the generation of selenyl radicals.[46]

$$PhSeY \xrightarrow{h\nu} PhSe^{\bullet} + Y^{\bullet}$$

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

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

$$PhSe^{\bullet} + R^{\bullet} \longrightarrow PhSeR$$

Y = SePh or SO_2Ar.

Vinyl selenides are formed similarly from vinylmercury halides.[47] The reaction mechanism includes a stage where the phenylselenyl radical adds to the double bond.

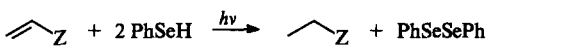
$$PhSe^{\bullet} + \text{(R, HgCl-C=C-H)} \xrightarrow{h\nu}$$

$$\longrightarrow \text{(R, SePh-C(HgCl)-C}^{\bullet}\text{-H)} \longrightarrow \text{(R, SePh-C=C-H)} + HgCl^{\bullet}$$

$$HgCl^{\bullet} + PhSeSePh \longrightarrow PhSeHgCl + Se^{\bullet}Ph$$

Pulse radiolysis of bis(4-methoxyphenyl) diselenide in methanol generates[48] two types of radicals, $ArS\dot{e}$ and $ArSeS\dot{e}$, whereas only the radicals $ArT\dot{e}$ are formed from the ditellurides under similar conditions.

On irradiation, benzeneselenol reduces via a radical mechanism α,β-unsaturated carbonyl compounds, activated olefins, and β-phenylseleno-substituted ketones to the corresponding saturated ketones and alkanes, while hydrazones, oximes, and anilides are reduced to hydrazines, hydroxylamines, and anilines.[49]



Benzyl phenyl selenide generates a benzyl radical under analogous conditions, the radical reacting with benzeneselenol to form toluene.[50]

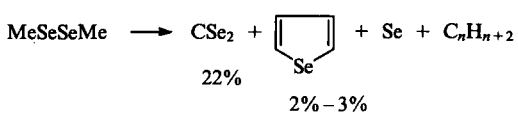
$$PhCH_2SePh + PhSeH \xrightarrow{h\nu} PhMe + PhSeSePh$$

3. The generation in thermal reactions of organic compounds of selenium and tellurium and their reactions

Diorganyl selenides and diorganyl diselenides decompose at 450–600 °C with formation of elemental selenium, hydrogen selenide, and a mixture of hydrocarbons. Pulse thermolysis of dimethyl diselenide *in vacuo* (0.1 Torr) at 550 °C leads to dimethyl selenide, methaneselenol, methane, and selenium as well as selenoformaldehyde.[51]

$$MeSeSeMe \longrightarrow MeSeMe + MeSeH + CH_4 + Se$$

On the other hand, the main product of the thermolysis of Me_2Se_2 at 430–500 °C under atmospheric pressure is carbon diselenide.[52] Selenophene and a mixture of gaseous hydrocarbons and selenium are formed together with carbon diselenide.



The corresponding alkaneselenol and dialkyl selenide predominate among the liquid products of the thermolysis of dialkyl diselenides $(C_nH_{2n+1})_2Se_2$ ($n = 2-4$) at 300–500 °C. Their formation is accompanied by the liberation of solid selenium and gaseous hydrogen selenide and alkenes as well as traces of selenophene.[51]

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

Pulse thermolysis *in vacuo* (20 Torr) at 600 °C of dihexyl, didodecyl, and bis(2-phenylethyl) diselenides leads merely to the corresponding alkenes and selenium.[53]

$$RCH_2CH_2SeSeCH_2CH_2R \longrightarrow RCH{=}CH_2 + Se$$

90%–95%

R = Ph, Bu, C_6H_{13}.

Dibenzyl selenide and dibenzyl diselenide are converted on pulse pyrolysis *in vacuo* primarily into bibenzyl and selenium.[54,55] Their substituted derivatives react similarly.

$$ArCH_2SeCH_2Ar \xrightarrow{600\,^\circ C} ArCH_2CH_2Ar + Se$$

63%–89%

$$PhCH_2SeCH_2Ar \xrightarrow{600\,^\circ C} PhCH_2CH_2Ph + PhCH_2CH_2Ar + ArCH_2CH_2Ar + Se$$

13% 24% 8%

$$PhCH_2SeSeCH_2Ph \xrightarrow{210\,^\circ C} PhCH_2CH_2Ph + Se$$

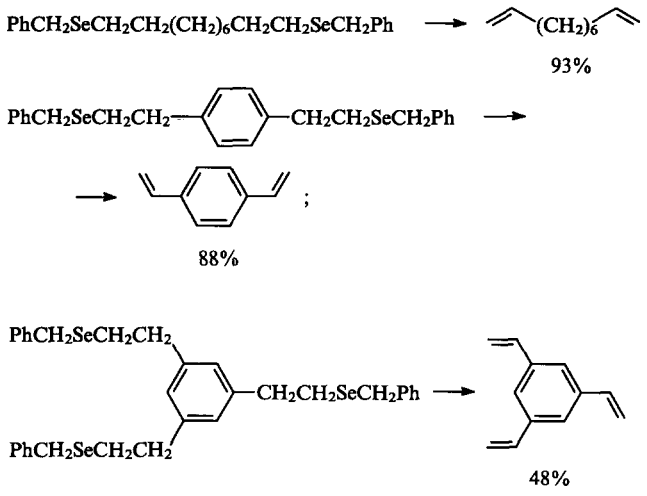
99.4%

Pulse pyrolysis *in vacuo* of alkyl benzyl selenides is accompanied by the formation of the corresponding alkenes and methane together with bibenzyl and selenium.[53]

$$PhCH_2SeCH_2CH_2Ph \xrightarrow{600\,^\circ C} (Ph\dot{C}H_2 + S\dot{e}CH_2CH_2Ph) \longrightarrow PhMe + PhCH_2CH_2Ph + PhCH{=}CH_2 + Se$$

49% 37% 96%

The following alkenes have been similarly obtained from bis- and tris-(benzyl selenides) respectively:[53]



At comparatively low temperatures (150–170 °C), the thermolysis of dibenzyl diselenide leads to a mixture of dibenzyl polyselenides and the liberation of selenium.[56]

$$PhCH_2SeSeCH_2Ph \longrightarrow PhCH_2Se_nCH_2Ph + Se$$

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

$n = 1-3$.

Bis(diphenylmethyl) selenide reacts similarly.[55]

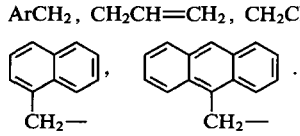
$$Ph_2CHSeCHPh_2 \xrightarrow{140\,^\circ C} Ph_2CHSe_nCHPh_2 + Se$$

Organyl phenyl selenides RSePh, where R represents a relatively stable radical, dissociate on thermolysis with rupture of the R–Se bond. The phenylselenyl radical is then generated.[53,57] Both radicals then dimerise.

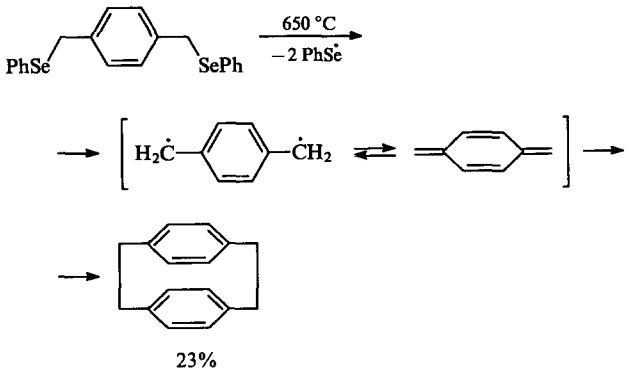
$$RSePh \xrightarrow{600\,^\circ C} \dot{R} + S\dot{e}Ph \longrightarrow R{-}R + PhSeSePh$$

50%–90% 80%–90%

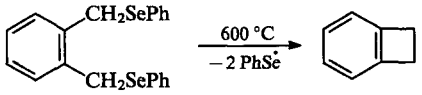
R = $ArCH_2$, $CH_2CH{=}CH_2$, CH_2CN, CH_2COMe,



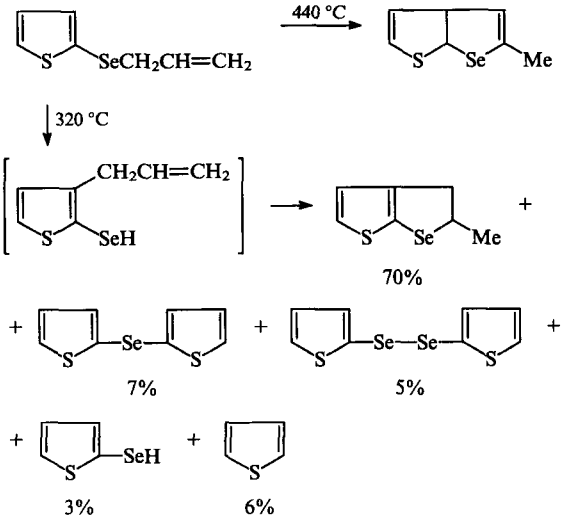
This mode of thermal decomposition of phenyl selenides makes it possible to employ the thermolysis of 1,4-bis(phenylselenomethyl)benzene in order to obtain [2,2]paracyclophane.[53,57]



The strained benzocyclobutene is formed similarly from 1,2-bis(phenylselenomethyl)benzene.[53,57]



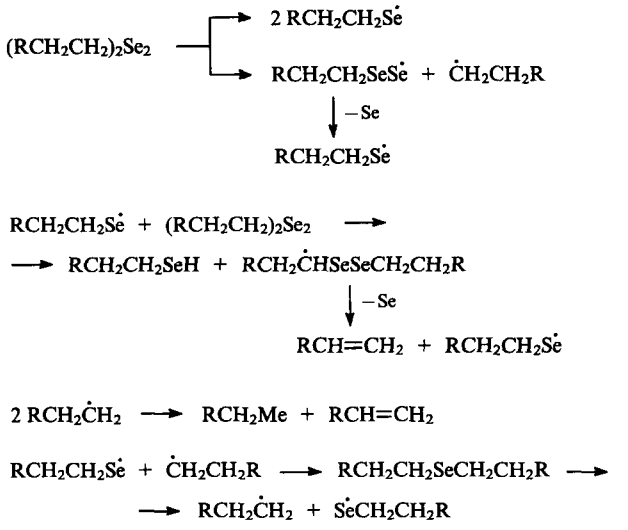
Allyl 2-thienyl selenide readily cyclises at 320 °C, this being preceded by the seleno-Claisen rearrangement.[58]



The reaction side products indicate the generation of thienylselenyl radicals. On vacuum distillation, allyl thienyl selenide cyclises quantitatively and at 440 °C is converted into 2-methylselenopheno[2,3-*b*]thiophene.

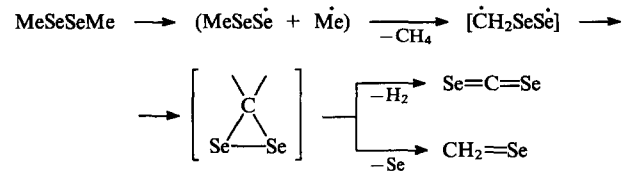
The mode of the thermal decomposition of diorganyl selenides and diorganyl diselenides is determined by the generation of selenyl, perselenyl, and carbon-centred radicals, the reactions of which are determined by their relative stabilities.

Free-radical chain mechanisms have been proposed for the thermal decomposition of diorganyl selenides and diorganyl diselenides.[52]

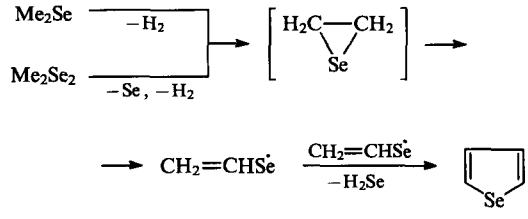


R = H, Me, Et, Ph.

The thermolysis of dimethyl diselenide proceeds via a different mechanism.[52]



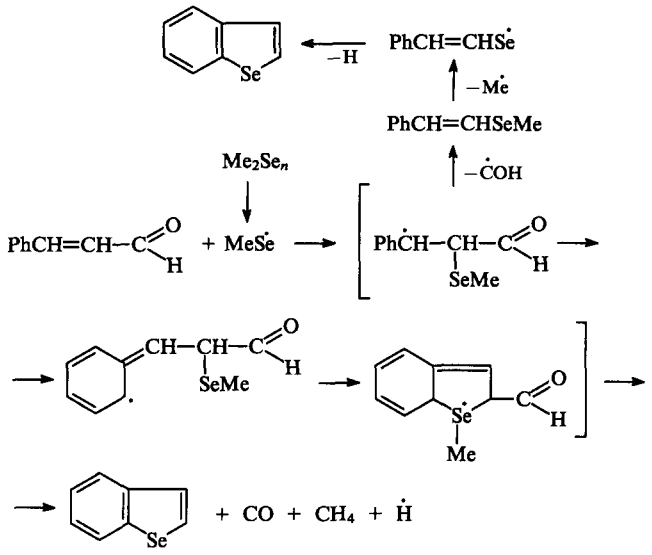
The formation of selenophene as a side product in the thermolysis of dimethyl selenide and dimethyl diselenide is due to the generation of vinylselenyl radicals.



The thermolysis of benzyl organyl selenides always involves the generation of stable benzyl radicals, which recombine to form bibenzyl. Organyl phenyl selenides eliminate phenylselenyl radicals, which also tend to recombine.

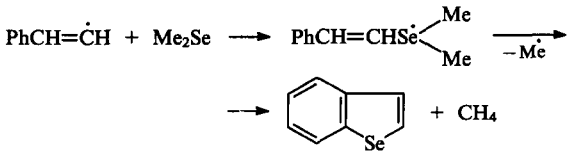
The selenyl and telluryl radicals generated on thermolysis of organic compounds of selenium and tellurium react in the gas and liquid phases with various unsaturated compounds.

A number of chemical trapping agents have been proposed for the alkylselenyl radicals formed as a result of the thermolysis. Thus the reaction of cinnamaldehyde with dimethyl selenide or dimethyl diselenide at 600–650 °C leads to benzoselenophene, the yield of which reaches 53%.[59] The reaction mechanism involves a stage where the methylselenyl radical adds to the double bond of cinnamaldehyde.

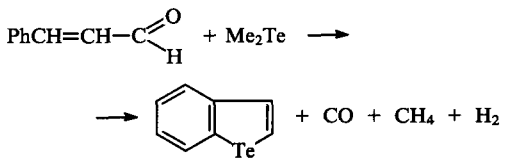


$n = 1, 2.$

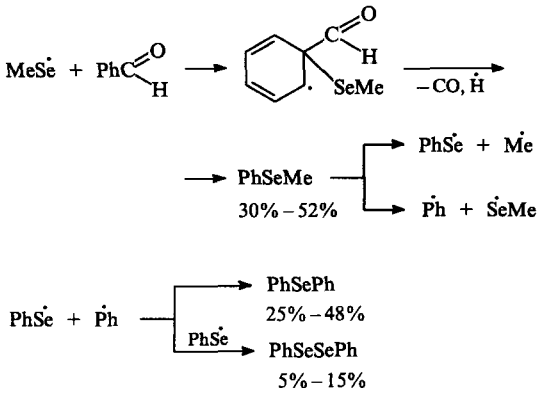
The possibility of the occurrence of the following reaction cannot be ruled out either:



Dimethyl telluride reacts with cinnamaldehyde at a lower temperature (500–550 °C) with formation of benzotellurophene, but its yield does not exceed 12%–17%.



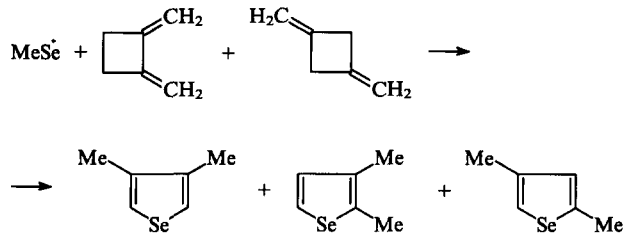
The reaction of Me_2Se or Me_2Se_2 with benzaldehyde takes place already at 400–500 °C with formation of mainly methyl phenyl selenide and diphenyl selenide.[60] Here too methylselenyl radicals attack the carbon atom of the benzene ring bound to the aldehyde group, which is followed by its substitution.



The reaction of ethylselenyl radicals with benzaldehyde is much more difficult (the yield of PhSeEt is 6%–9%).

Dimethyl telluride reacts with benzaldehyde similarly to dimethyl selenide, affording PhTeMe (40%) and PhTePh (3%–6%) at 350–400 °C.

The thermal reaction of dimethyl selenide with 1,2- and 1,3-dimethylenecyclobutanes (a mixture of isomers in proportions of 3:1)[61] leads to a mixture of 3,4-, 2,3-, and 2,4-dimethylselenophenes in proportions of 3:1:1.5. Their overall yield is 58%.

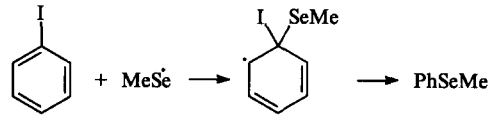


The predominance of the 1,2-isomer in the mixture of the isomeric dimethylenecyclobutanes and the easier, from the electronic and steric standpoints, attack by the radical $MeSe^{\cdot}$ on the ring bond remote from the methylene groups are responsible for the preferential formation of 3,4-dimethylseleneophene.

Alkylthiyl radicals react similarly with dimethylenecyclobutanes, but the yields of dimethylthiophenes do not then exceed 42%.

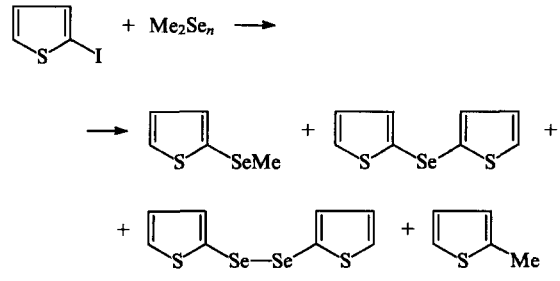
Alkylselenyl radicals react effectively with iodobenzene and iodothiophene in the gas phase.

The cothermolysis of Me_2Se or Me_2Se_2 with iodobenzene at 430 °C leads to selenoanisole (in 33% yield).[62]



The simultaneous formation of selenophenol, diphenyl selenide, and diphenyl diselenide indicates the successive thermal decompositon of selenoanisole accompanied by the formation of the $PhSe^{\cdot}$ radicals.

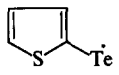
The main product of the reaction of 2-iodothiophene with Me_2Se_2 at 400 °C is methyl 2-thienyl selenide, the yield of which reaches 64%. The latter decomposes to di(2-thienyl) selenide (16%–28%), di(2-thienyl) diselenide (7%–8%), and 2-methylthiophene (2%–4%).[63]



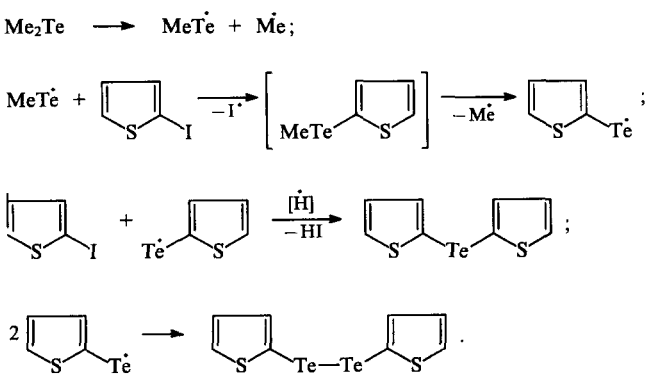
$n = 1, 2.$

Chloro- and bromo-derivatives of benzene and thiophene do not react with selenyl radicals (in contrast to thiyl radicals[7]).

The reaction of 2-iodothiophene with Me_2Te is accompanied by appreciable decomposition of the latter to metallic tellurium and hydrocarbons. Nevertheless the formation under these conditions of thiophene (30%), di(2-thienyl) telluride (8%), and di(2-thienyl) ditelluride (15%) indicates the initial trapping of methyltelluryl radicals by iodothiophene. The unstable methyl thienyl telluride subsequently generates the radical:



in accordance with the following scheme:



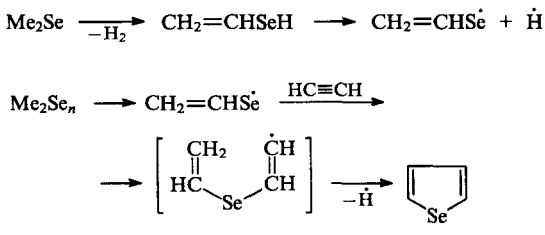
The mobile halogen atom in allyl bromide and benzyl chloride is substituted by radicals under fairly mild conditions already at 90–180 °C in the liquid phase.[64] Alkylselenyl radicals are then generated from dialkyl diselenides.

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

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

R = Me, Et.

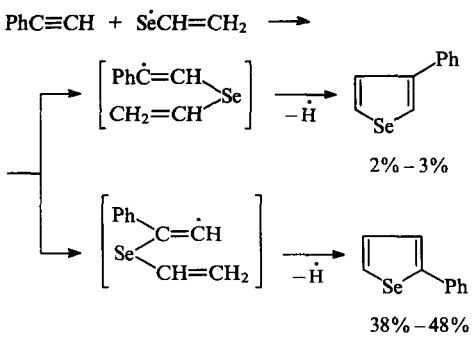
The gas-phase reactions of alkylselenyl radicals with acetylene do not lead to adducts—alkyl vinyl selenides. This may be due to either the low stability of the radical-adduct of acetylene and akylselenyl radicals or the low reactivity of the latter in the given reaction. However, the cothermolysis of dimethyl selenide and dimethyl diselenide with acetylene at 420–470 °C results in the formation of selenophene,[65] the yield of which reaches 80%–94%. The reaction mechanism involves the generation of vinylselenyl radicals from Me_2Se and Me_2Se_2. The vinylselenyl radicals subsequently add to acetylene and the resulting radical-adduct cyclises.



n = 1, 2.

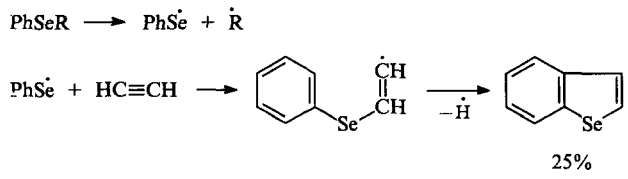
The use of other dialkyl selenides R_2Se (R = Et, Pr, Bu) in the reaction also leads to selenophene, the yield of which depends on R in the following way: Me > Et ≫ Pr > Bu.

The mechanism of the thermal decomposition of dialkyl selenide, including the stage involving the generation of vinylselenyl radicals, has been confirmed by the reaction of dimethyl selenide or dimethyl diselenide with phenylacetylene. The main product of this reaction at 490–500 °C is 2-phenylselenophene, the yield of which reaches 38% in its formation from Me_2Se and 48% in its formation from Me_2Se_2. The formation of phenylselenophene has been represented by a mechanism which involves the addition of vinylselenyl radicals to the triple bond of phenylacetylene predominantly in the α-position.

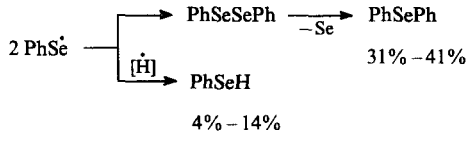


Selenophene, 3-phenylselenophene, and aromatic hydrocarbons are formed as side products.

The cothermolysis of methyl phenyl or allyl phenyl selenide with acetylene at 480–500 °C leads to benzoselenophene—the product of the addition of the phenylselenyl radical to the triple bond.[66]



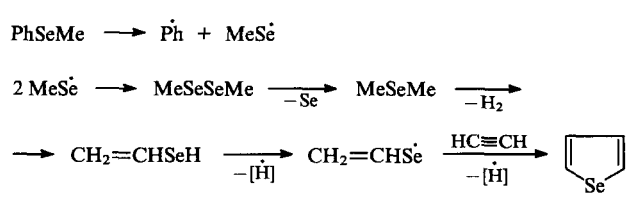
The radical PhSe̊ rccombines simultaneously to diphenyl diselenide. The latter readily eliminates a selenium atom and is converted into diphenyl selenide.



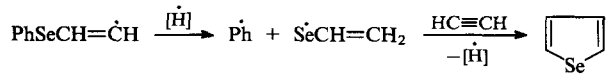
The PhSe̊ radical is partly stabilised as a result of the abstraction of a hydrogen atom from the substrate, affording selenophenol.

The cothermolysis of PhSeR (R = Me, $CH_2{=}CHCH_2$) with acetylene also results in the formation of selenophene, the yield of which reaches 32% in the case of selenoanisole (R = Me).

It has been suggested that the thermolysis of selenoanisole is accompanied by the generation of methylselenyl radicals, the subsequent reactions of which lead to the vinylselenyl radical.



For allyl phenyl selenide, this pathway to selenophene is impossible and therefore the possibility cannot be ruled out that the vinylselenyl radicals, from which the selenophene molecule is formed, are generated on degradation of the radical-adduct.



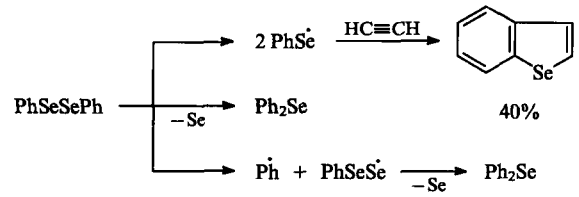
The cothermolysis of alkyl phenyl selenides with acetylene demonstrates the difference between the reactivities of radicals such as PhSe̊ and $CH_2{=}CHSe$̊. The latter reacts more readily with acetylene. On the other hand, in the case of the isostructural radicals PhS̊ and $CH_2{=}CHS$̊ the opposite relation is observed.

Allyl phenyl telluride does not react with acetylene at 440 °C but decomposes fully to diphenyl telluride and diphenyl ditelluride. However, at 500 °C the reaction takes place with formation of benzotellurophene and tellurophene in an overall yield not exceeding 3%–4%. This indicates the low reactivity of the PhTe· radicals in the interaction with acetylene. The radicals CH_2=CHTe·, generated in the thermolysis of divinyl telluride, add even at 420–450 °C to the acetylene triple bond with formation of tellurophene (yield 40%).[67]

$$CH_2{=}CHTeCH{=}CH_2 \xrightarrow[-(CH_2{=}\dot{C}H)]{} \rightarrow CH_2{=}CH\dot{T}e \xrightarrow[-\dot{H}]{HC{\equiv}CH}$$



The reaction of diphenyl diselenide with acetylene at 500–580 °C leads to benzoselenophene, selenophene, and diphenyl selenide as a result of the generation of the radical PhSe· and the elimination of a selenium atom.

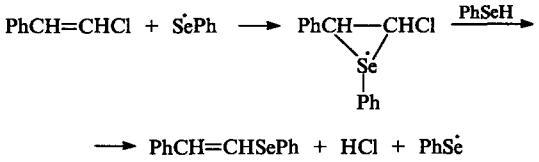


Only traces of benzotellurophene were detected in the reaction of diphenyl ditelluride with acetylene.

Benzeneselenol adds to styrene at 80–140 °C with formation of 1-phenyl-2-phenylselenoethane (i.e. the anti-Markovnikov adduct), which indicates a radical reaction mechanism.

$$PhCH{=}CH_2 + \dot{S}ePh \rightarrow Ph\dot{C}HCH_2SePh \xrightarrow{PhSeH} \rightarrow PhCH_2CH_2SePh + PhSe\cdot$$

In the interaction of β-chlorostyrene with benzeneselenol in the liquid phase (80–140 °C), the chlorine atom is substituted by the PhSe· radical; the reaction takes place strictly stereospecifically.



At the same time, β-chlorostyrene is partly reduced to styrene, which subsequently reacts with PhSe· in accordance with the mechanism presented above; the phenylselenyl radicals recombine at the same time.

4. Generation of radicals and the reactions involved in chemical initiation

A series of reactions involving reduction by selenols proceed via a radical mechanism which includes a chemical initiation stage. Thus arenediazonium fluoroborates are converted into a mixture of aryl phenyl selenides and arenes in their reaction with PhSeH.[68]

$$ArN_2^+BF_4^- + HSePh \rightarrow ArSePh + N_2 + HBF_4$$

$$ArN_2^+ + PhSeH \rightarrow Ar\cdot + PhSe\cdot + N_2 + H^+$$

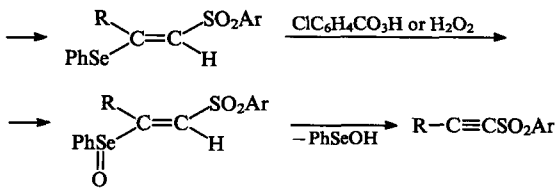
$$Ar\cdot + PhSeH \rightarrow ArH + PhSe\cdot$$

$$2\,PhSe\cdot \rightarrow PhSeSePh$$

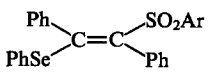
$$Ar\cdot + PhSeSePh\ (or\ PhSe)\cdot \rightarrow ArSePh$$

Selenosulfonates react with activated acetylene even on slight heating and chemical initiation with formation of anti-Markovnikov adducts. The latter are readily oxidised by H_2O_2 to selenoxides, which spontaneously eliminate selenophenol and are converted into acetylenic sulfones.[69–71]

$$R{-}CH{\equiv}CH + ArSO_2SePh \xrightarrow{\Delta\ (AIBN)}$$

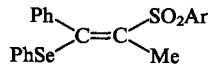


$$PhC{\equiv}CPh + ArSO_2SePh \xrightarrow[C_6H_6,\,\Delta]{AIBN}$$



52%

$$PhC{\equiv}CMe + ArSO_2SePh \xrightarrow[C_6H_6,\,\Delta]{AIBN}$$



97%

The mechanism of the reaction of selenosulfonates with monosubstituted acetylenes is the standard mechanism adopted for free-radical chain reactions (see above).

III. Perselenyl and selenuranyl radicals

The perselenyl radicals RSeSe· are formed together with selenyl radicals RSe· in the photolysis and thermolysis of diorganyl diselenides. They are less stable than the perthiyl radicals RSS·, but are more stable than the pertelluryl radicals RTeTe·.

$$RSeSeR \rightarrow RSeSe\cdot \rightarrow RSe\cdot + Se$$

The radicals RSeSe· are more readily detected by the EPR method[30] than the radicals RSe· owing to the delocalisation of the unpaired electron over the neighbouring selenium atom, which leads to the removal of the degeneracy of the levels.[16,72]

The anisotropies of the *g*-factor for the selenyl and perselenyl radicals are significantly different,[30] for example:

Radical	$g_\perp$	$g_\parallel$
PhSe·	2.003	2.016
PhSeSe·	2.026	2.043

λ_{max} = 600 nm corresponds to the radical 4-$MeOC_6H_4SeSe$· in the UV spectra.[21]

Like their sulfur and tellurium analogues, the selenuranyl radicals $R_2Se{-}X$ are intermediates in the S_N2 homolytic substitution reactions at the selenium atom occurring on treatment of organoselenium compounds with free radicals.[73,74]

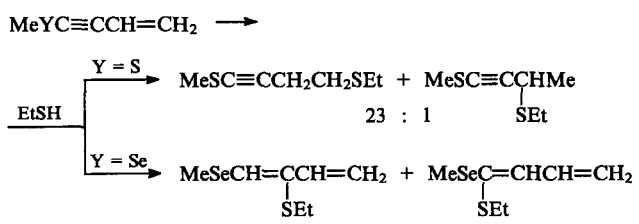
$$\dot{X} + R_2Se \rightarrow [R_2Se{-}X] \rightarrow RSeX + \dot{R}$$

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

The radicals $Ph_2Se{-}X$ are formed on X-irradiation of triphenylselenium halides Ph_3SeX and can be detected by the EPR method. Their unpaired electron is localised predominantly on the orbital connecting the selenium and halogen atoms and oriented at right angles to the CSeC plane (the σ* orbital). The spin density is ~80% localised on the selenium atom and ~20% on the halogen atom.[75]

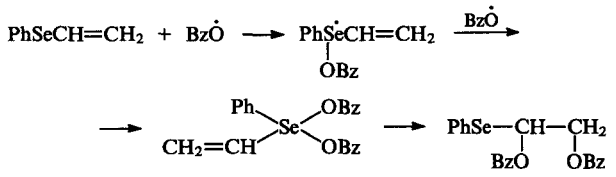
The structure of the σ*-type radical has also been confirmed by the EPR method for other selenuranyl radicals $R_2\dot{S}e-X$ [R = Me, Et, Ph, Ad (1-adamantyl)] and for their asymmetric derivatives with X = EtC(O)S, *tert*-BuC(O)S, CF_3, *tert*-BuO, and Me_3SiO.[76] For example, $a(^{77}Se)$ = 162.6 G for 1-$(Ad)_2\dot{S}e-SC(O)Bu^t$ which corresponds to 3% spin population of the 4*s* orbital of the selenium atom. The spin population of the 4*p* orbital of selenium (38%–71%), which determines the shift of the spin density in $Me_2\dot{S}e-X$, is consistent with the nature of the σ* orbital of the Se–X bond, which depends in its turn on the electronegativity of the atom X.[76]

The geometrical structure of the selenuranyl radical is identical with that of the radical-cations $(Me_2Se-SeMe_2)^{\cdot+}$, formed on γ-irradiation of dimethyl diselenide.[77] The different regiospecificities of certain reactions have been explained by the generation of selenuranyl radicals.[78]

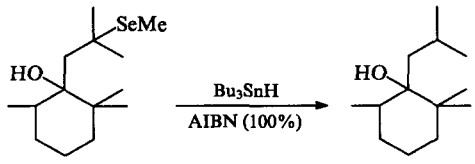


Evidently, when Y = Se, the thiyl radicals ṠEt attack the Se atom with formation of the selenuranyl radical, which subsequently rearranges with migration of the EtSe group to the neighbouring triple bond. Under these conditions, thiuranyl radicals are apparently not formed.

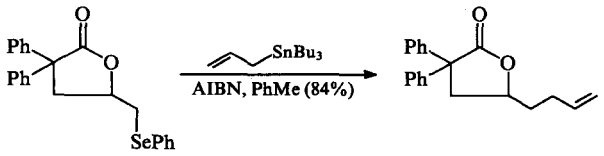
The interaction of phenyl vinyl selenide with benzoyl peroxide, which leads to the product resulting from the dibenzoyloxylation of the double bond, evidently proceeds via selenuranyl radicals.[79,80]



On initiation with AIBN, tributylstannane causes the reductive cleavage of the C–Se bond in hydroxyalkyl selenides.[81]



On chemical (AIBN) and radiation-induced initiation, allyltributylstannane reacts with phenyl selenides to form a new carbon–carbon bond (reductive allylation).[81]



The trialkylstannyl radicals, generated on photolysis of hexaalkylstannanes, cleave the alkyl–selenium bond in dialkyl selenides as well as the analogous bonds in dialkyl sulfides and dialkyl tellurides. The rate of reaction decreases in the sequence $R_2Te > R_2Se > R_2S$.[82]

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

Y = S, Se, Te.

Triphenylstannane reacts in accordance with a similar scheme with alkyl phenyl selenides in boiling toluene. It has been suggested that these reactions proceed by a free-radical mechanism via the intermediate formation of selenuranyl radicals.[83–88]

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

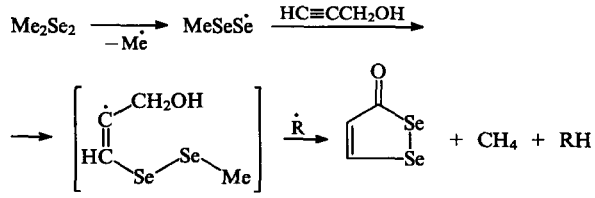
$$Ph_3\dot{S}n + RSePh \longrightarrow PhSe(SnPh_3)R \longrightarrow \dot{R} + Ph_3SnSePh$$

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

The reduction of organyl phenyl tellurides by tributylstannane apparently proceeds via similar radical states.

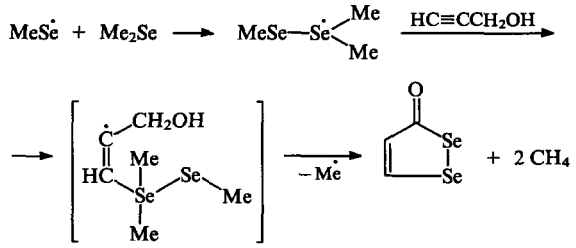
$$PhTeR + HSnBu_3 \longrightarrow PhTeSnBu_3 + RH$$

The cothermolysis 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% yields respectively.[89] The reaction mechanism includes a stage in which propargyl alcohol binds perselenyl or selenuranyl radicals generated on thermolysis of dimethyl selenide and dimethyl diselenide.



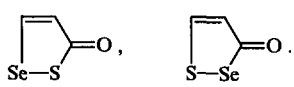
$$Me_2Se \longrightarrow MeSe\cdot + Me\cdot$$

$$2\,MeSe\cdot \longrightarrow Me_2Se_2 \xrightarrow[-Me\cdot]{} MeSeSe\cdot$$

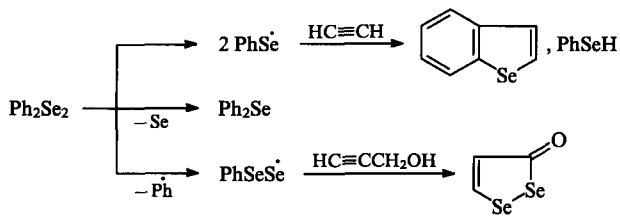


Other dialkyl diselenides, i.e. Et_2Se_2 and $Pr^i_2Se_2$, react similarly with propargyl alcohol. Propargyl alcohol traps perthiyl (sulfuranyl) radicals much less effectively and their tellurium analogues are not trapped at all

The thermolysis of a mixture of Me_2S_2 and Me_2Se_2 also results in the generation of mixed perchalcogenyl radicals, which form two mixed thiaselenolones on interaction with propargyl alcohol:



The gas-phase reaction of diphenyl diselenide with propargyl alcohol and the product of its thermolysis (acetylene) at 500–550 °C also leads to 1,2-diselenol-3-one (in 14%–16% yield). Diphenyl selenide (26%–31%), benzoselenophene (8%–12%), selenophene (2%–14%), and selenophenol (3%) are formed together with 1,2-diselenol-3-one.



Ph_2Te_2 hardly reacts with propargyl alcohol even at high temperatures.

IV. Seleninyl and selenonyl radicals

Seleninyl radicals PhSeȮ and selenonyl radicals $PhSeȮ_2$ are generated on X-radiolysis of diphenyl selenoxide[25] and on ^{60}Co γ-radiolysis of diphenyl selenone[90] respectively. They have been detected by the EPR method in the solid phase and the distribution of the spin density on the selenium, sulfur, and oxygen atoms has been determined (Table 2). In chalcogeninyl radicals, the spin density is concentrated to a greater extent on the chalcogen atoms than in chalcogenonyl radicals. In the sulfur analogues of these radicals, the spin density is localised on the sulfur atom to a greater extent than on the selenium atom in the selenium analogues.

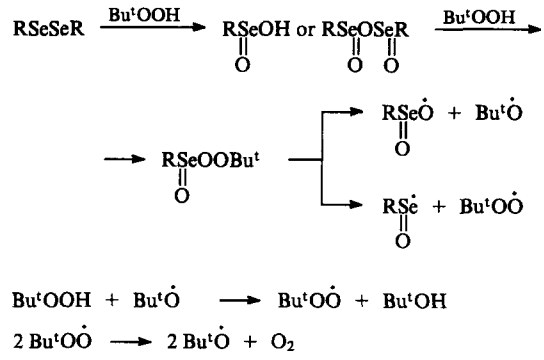
Table 2. Distribution of the spin density.

Radical	Spin density (%)		Ref.
	S, Se	O	
MeSO	87	13	92
$PhSO_2$	42 (38)	29 (31)	90 (91)
$PhSO_2$	46	27	90
PhSeO	78	22	25
$PhSeO_2$	40	30	90

The seleninyl radicals PhSeȮ, in which the selenium atom is in a positive oxidation state, are generated as a result of the radical attack on the anhydride of the corresponding seleninic acid or on *S-tert*-butyl benzenethioseleninate [PhSe(O)SBu^t].[93]

The catalytic decomposition of *tert*-butyl hydroperoxide by diselenides, seleninic acids, or their anhydrides apparently involves the formation of peroxyseleninates as intermediates. Their subsequent homolysis with dissociation of the O–O or Se–O bond leads to the radicals $RSeȮ_2$, RSeȮ, Bu^{t}Ȯ, and Bu^{t}OȮ.

Selenium-containing radicals are subsequently converted into selenium acids or their anhydrides via a hitherto unknown mechanism.[94,95]



$$Bu^tOOH + Bu^tȮ \longrightarrow Bu^tOȮ + Bu^tOH$$

$$2\,Bu^tOȮ \longrightarrow 2\,Bu^tȮ + O_2$$

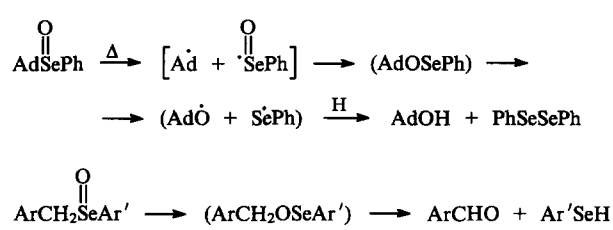
It has been suggested that thioselenates are formed as intermediates on oxidation of thiols by benzeneseleninic acid. They are subsequently destroyed via a radical mechanism.[96]

$$PhSeSR \longrightarrow PhSe· + ṠR$$

$$2\,PhSe· \longrightarrow 2\,PhSė + O_2$$

$$PhSė + ṠR \longrightarrow PhSeSePh + PhSeSR + RSSR$$

The thermolysis of aryl selenoxides includes stages involving the generation of the radicals ArSeȮ.[97,98]



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