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Selenonium Compounds and Their Applications in Synthesis

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The review gives a systematic account and surveys the results of studies in the chemistry of selenonium compounds (salts, ylides, ylide-salts, diylides, and imides). The methods of synthesis of selenonium compounds, their structure, their behaviour in reactions with electrophiles and nucleophiles, and also their reactions under conditions of thermolysis and rearrangements are considered.
The bibliography includes 95 references.

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I. INTRODUCTION

Selenonium compounds contain a fragment with a tricoordinate positively charged selenium atom; they include selenoxides, selenimides, selenonium salts, selenium ylides, and also bis-onium compounds (ylide-salts and di-ylides) containing, together with the selenonium fragments, also fragments based on other heteroatoms (nitrogen, phosphorus, arsenic, and sulphur). The present review does not include data from the chemistry of selenoxides, because the reactivity of the latter has been described in detail in a series of reviews published in recent years.[1-3]

The sharp growth of interest in the chemistry of selenonium compounds (salts, ylides, and ylide-salts) in recent years is due to their ready availability and high reactivity, which as a rule greatly exceeds the reactivity of the corresponding sulphonium compounds and in many cases has no analogy in the chemistry of the onium compounds of Group V and VI elements. The interest of chemists in these compounds is associated not only with their importance for theoretical organic chemistry but also with the real possibility of their practical use as convenient active synthons for fine organic synthesis, the majority of the reactions with the participation of which proceed stereospecifically and regioselectively.

This review gives a systematic account and surveys the results of studies on the development of the methods of synthesis, the structures, physicochemical properties, and reactivities of selenonium compounds (salts, ylides, ylide-salts, diylides, and also selenimides) during the last 15 years. Until 1972, the chemistry of these compounds was hardly investigated and there have been only individual studies on the synthesis of selenonium salts, which have been surveyed in a monograph.[4]

Wherever possible, the reactivities of selenonium systems have been compared with sulphur compounds of analogous structure.

II. SELENONIUM SALTS

The first and most general method of synthesis of selenonium salts involves the alkylation of selenides with alkyl halides, α-bromoacids and their esters, and α-bromoketones.

Alkyl diphenylselenonium tetrafluoroborates have been obtained by alkylating diphenyl selenide with alkyl halides in the presence of a stoichiometric amount of silver tetrafluoroborate:[5]

$$Ph_2Se + \begin{matrix} R^1 \\ R^2 \end{matrix}\!\!>\!CHX \xrightarrow{AgBF_4} Ph_2\overset{\oplus}{S}e\text{-}CH\!<\!\begin{matrix} R^1 \\ R^2 \end{matrix}\ \overset{\ominus}{B}F_4$$

$R^1 = R^2 = H$, X = I; $R^1 = H$, $R^2 = Me$, X = Br; $R^1 = R^2 = Me$, X = I

The alkylation of a selenide containing the trifluoromethyl group has been described:[6]

$$PhSeCF_3 \xrightarrow{MeI,\ AgBF_4} Ph\text{—}\overset{\oplus}{\underset{\displaystyle Me}{Se}}\text{—}CF_3\ \overset{\ominus}{B}F_4$$

A convenient method of synthesis of selenonium salts containing the benzyl group involves the methylation of selenides with trimethyloxonium tetrafluoroborate and also with methyl fluorosulphonate,[7] for example:

$$RCH_2SePh \xrightarrow{Me_3\overset{\oplus}{O}\ \overset{\ominus}{B}F_4} RCH_2\overset{\oplus}{\underset{\displaystyle Me}{Se}}Ph\ \overset{\ominus}{B}F_4$$

R = Ph, *p*-ClC_6H_4, *m*-ClC_6H_4, *p*-MeC_6H_4.

Unsaturated selenides are smoothly alkylated with methyl fluorosulphonate:[8]

$$\text{—CH=C}\!<\!\begin{matrix} R \\ R^1 \end{matrix} \xrightarrow{MeSO_3F} \text{—CH=C}\!<\!\begin{matrix} R \\ R^1 \end{matrix}\ SO_3^{\ominus}F$$

(SePh; $\overset{\oplus}{S}eMe$, Ph)

R = H, Me; $R^1 = C_6H_{13}$, C_8H_{17}

Diaryl selenides are arylated with iodonium salts in the presence of copper(II) benzoate:[9]

$$Ph_2Se + Ar_2\overset{\oplus}{I}\ \overset{\ominus}{A}sF_6 \xrightarrow{Cu\,(II)} ArPh_2\overset{\oplus}{S}e\ \overset{\ominus}{A}sF_6 + ArI$$

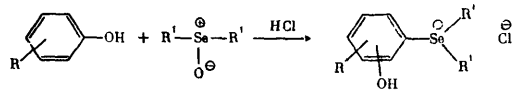
Ar = Ph, *p*-t-BuC_6H_4, *p*-MeC_6H_4, 3,4-$Me_2C_6H_3$

Diaryl selenides readily react with t-butyl hypochlorite:[10]

$$Ar_2Se + t\text{-}BuOCl \rightarrow Ar_2\overset{\oplus}{S}eOBu\text{-}t\ \overset{\ominus}{Cl}.$$

Methods of synthesis of selenonium salts on the basis of organic derivatives of selenium(IV), namely selenoxides, diorganoselenium dihalides, and selenium halides and oxides halides, are known. A method of synthesis of dialkyl- or

alkylphenylhydroxyphenylselenonium chlorides by the reaction of phenols with selenoxides and hydrogen chloride has been developed:[11]



R = Me; R' = Me, Et, Ph

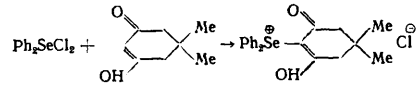
Tri-p-tolylselenonium chloride has been obtained by the reaction of toluene with selenium dioxide in the presence of sulphuric acid.[12]

Triarylselenonium salts have been synthesised from selenium oxide chloride and arylmagnesium bromides:[13]

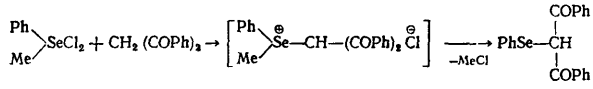
$$RC_6H_4MgCl + SeOCl_2 \xrightarrow{HX} (RC_6H_4)_3\overset{\oplus}{S}e\,\overset{\ominus}{X}$$

X = Cl, Br, I; R = H, *o*-Me, *m*-Me, *p*-Me.

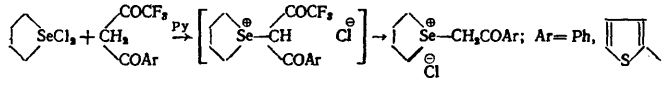
The synthesis of triarylselenonium salts by the reaction of diarylselenium dichlorides with activated arenes has been described.[20] Diphenylselenium dichloride reacts with dimedone to form a selenonium salt. The ease of this reaction is due to the fact that the enolic proton in the fixed *trans*-enol structure of dimedone can promote the polarisation of the Se–Cl bond:[14]



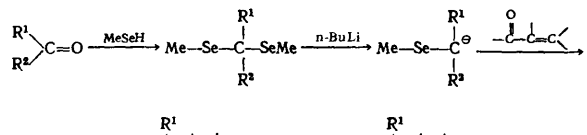
In the reaction of methylphenylselenium dichloride with dibenzoylmethane, the intermediate selenonium salt is demethylated:[15]

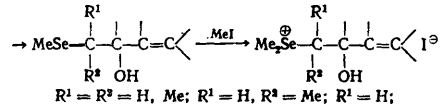


In the case of β-diketones containing the trifluoroacetyl group, the cleavage of the intermediate diketoselenonium salts by a nucleophile (Py or $Cl^{\ominus}$) proceeds differently, which can be accounted for by the large positive charge on the carbonyl carbon atom of the CF_3 group of the diketoselenonium salt:[16]



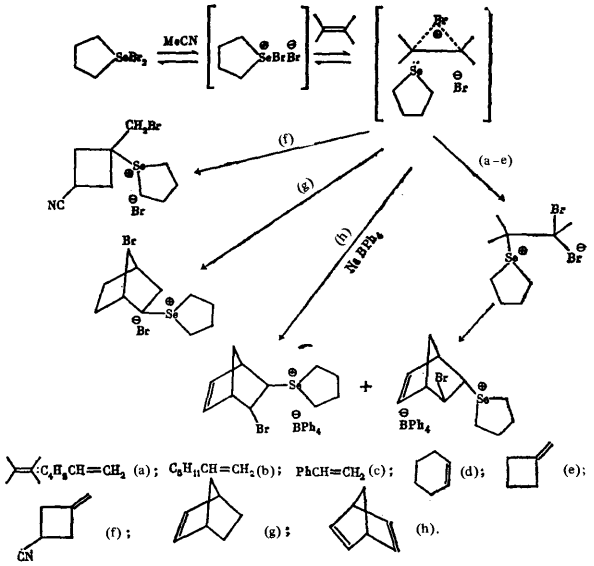
The synthesis of γδ-unsaturated β-hydroxyselenonium salts from carbonyl compounds and a selenol in accordance with the following scheme has been described:[17]





$R^1 = R^3 = H$, Me; $R^1 = H$, $R^2 = Me$; $R^1 = H$; $R^2 = Me(CH_2)_5$—

A method of synthesis of a new type of selenonium compounds, namely β-bromoselenonium salts, based on the interaction of tetramethylselenium dibromide with olefins having different structures (acyclic, cyclic, and skeletal), has been developed recently.[18] The electrophilic addition of tetramethyleneselenium dibromide to acyclic and cyclic olefins proceeds *trans*-stereospecifically with formation of 2-bromoalkyltetramethyleneselenonium bromides together with dibromoalkanes. The addition of tetramethyleneselenium dibromide to norbornene is accompanied by a rearrangement as a result of a 7,2-hydride shift and the addition to norbornadiene takes place with formation of a 3 : 1 salt mixture comprising 2-*endo*-bromo-3-*exo*-(tetramethyleneselenonium)- and 2-*exo*-bromo-3-*endo*-(tetramethyleneselenonium)-norbornene bromides:

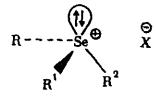


Dinitro-substituted selenonium salts have been obtained by protonating diphenylselenonium dinitromethylide with inorganic acids having a weakly nucleophilic anion:[19]

$$Ph_2\overset{\oplus}{S}e\overset{\ominus}{C}(NO_2)_2 + HX \rightleftharpoons Ph_2\overset{\oplus}{S}eCH(NO_2)_2\,\overset{\ominus}{X}$$

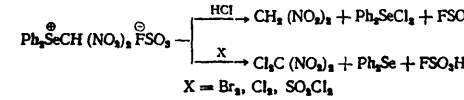
X = SO_3F; BF_4; F

The selenium atom in selenonium compounds is in the sp^3-hybrid state and the selenonium group therefore has a pyramidal structure:



A series of optically active selenonium salts have been obtained, whose stability indicates a high barrier to inversion at the selenonium chiral centre.[21] X-Ray diffraction,[22] UV spectroscopic,[23] IR spectroscopic,[24] and ^{77}Se NMR [25] data as well as the electrical conductivities of aqueous solutions of selenonium salts and the ability of the salts to exchange readily their anions[26] have confirmed their ionic structure. Selenonium tetraphenylborates are soluble in organic solvents, which makes it possible to use them in homogeneous reactions.[27] Selenonium salts with two electron-accepting groups are unstable and readily decompose.[28]

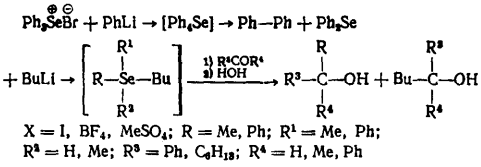
On treatment with electrophiles, diphenyl(dinitromethyl)-selenonium salts are cleaved at the Se–CNO_2 bond:[19]



X = Br_2, Cl_2, SO_2Cl_2

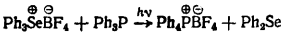
Reactions with nucleophiles are most characteristic of selenonium salts. On treatment with organolithium compounds, the intermediate σ-selenuranes undergo further

reactions: [29]



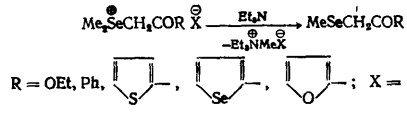
The last reaction can be used to synthesise tertiary alcohols.[29]

The photochemical reaction of triphenylselenonium tetrafluoroborate with triphenylphosphine via a radical mechanism has been described: [30]

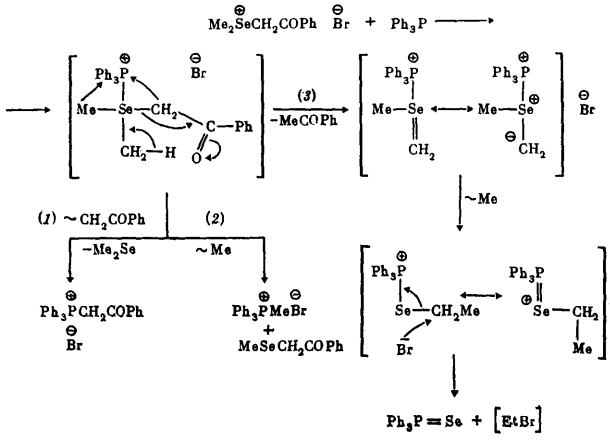


The homolytic character of the dissociation of the bond in the initial selenonium salt is confirmed by the fact that the reaction does not proceed in the dark and that benzene is formed as a side product. [30]

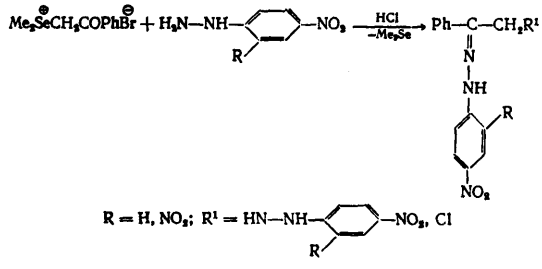
The interaction of arylacyl- and alkoxycarbonyl-methyl-(dimethyl)selenonium salts with nucleophiles (tertiary amines, substituted hydrazines, and triphenylphosphine) has been investigated. The demethylation of selenonium salts with triethylamine, which takes place with formation of α-methylselenocarbonyl compounds, is a convenient method of their synthesis: [27]



The reaction of dimethylphenylacylselenonium bromide with triphenylphosphine apparently proceeds via the primary attack by the nucleophile on the selenium atom with the subsequent migration of the phenylacyl or methyl group from selenium to phosphorus (pathways 1 and 2) and the elimination of acetophenone from the σ-selenurane intermediate (pathway 3): [27]

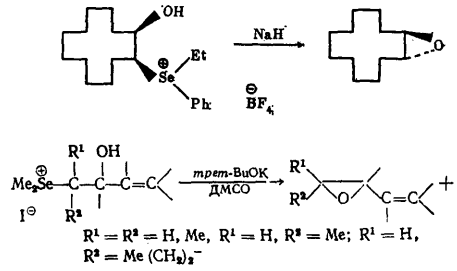


The interaction of dimethylphenylacylselenonium bromide with substituted hydrazines is accompanied by the elimination of dimethyl selenide: [27]



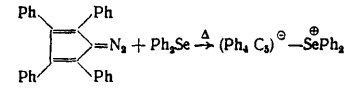
The reactions of selenonium salts with bases are very important. They are the basis of a general preparative method of synthesis of unstabilised selenium ylides and also of monostabilised ylides containing one electron-accepting group at the ylide carbon atom.

Treatment of β-hydroxyselenonium salts with bases results in a stereospecific reaction involving the intramolecular nucleophilic substitution of the selenonium group with formation of epoxides, [33] including αβ-unsaturated epoxides: [17]

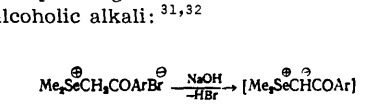


III. UNSTABILISED AND MONOSTABILISED SELENIUM YLIDES

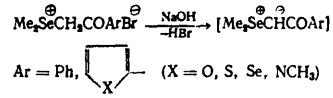
A general preparative method of synthesis of monostabilised selenium ylides involves the interaction of their conjugate acids with bases [31,32] or the decomposition of diazocompounds in the presence of selenides, [33,34] which takes place via the formation of a carbene: [35]



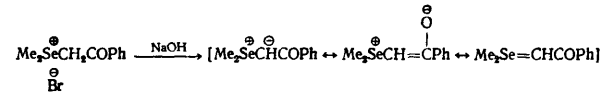
Potassium t-butoxide is normally used to generate unstabilised selenium methylides *in situ*: [6]



Monocarbonyl-stabilised selenium ylides are obtained *in situ* when the corresponding selenonium salts are treated with aqueous or alcoholic alkali: [31,32]

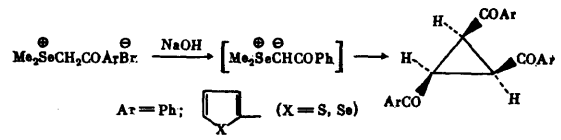


Only one selenium monoketoylide, namely dimethylselenobenzoylmethylide, has been isolated. It is an extremely labile crystalline compound, whose IR spectrum indicates the involvement of the carbonyl group in the declocalisation of the charge on the ylide carbanion: [31]



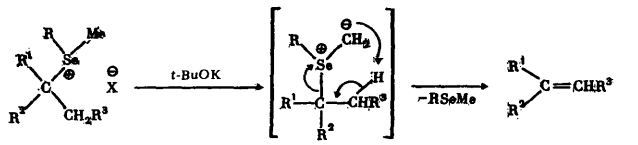
In the light or on slight heating, dimethylselenonium benzoylmethylide decomposes via a carbenoid mechanism with formation of *trans*-tribenzoylcyclopropane. [31] This reaction

is a convenient method of synthesis of heteroaroylcyclopropanes:[36]



Unstabilised selenium ylides usually do not form carbenoid decomposition products. However, when benzylselenonium salts were treated with sodium amide, small amounts of *trans*-stilbene, which is formally a product of the dimerisation of phenylcarbene, were isolated.[37]

The reaction involving the intramolecular cleavage of unstabilised selenonium ylides is used to synthesise various olefins including sterically hindered olefins:[8]



X = I, SO_3F; R = Me, Ph; R^1 = H, Me; R^2 = H, Me; R^1R^2 = $-(CH_2)_2-$;

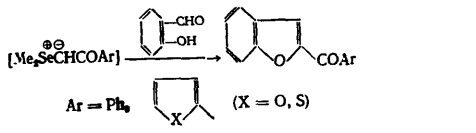
R^3 = H, C_8H_{17}, $C_{10}H_{21}$

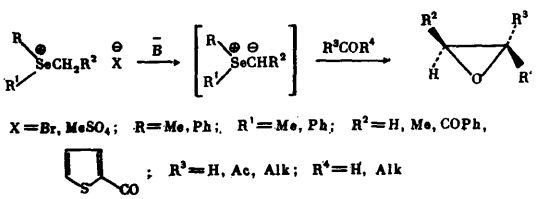
As a rule, unstabilised and monostabilised selenium ylides are not isolated but are used *in situ*, being generated from salts in the presence of the substrates with which the reaction is carried out.

As carbenoid species, monostabilised selenium ylides are more nucleophilic than their sulphur analogues and they readily interact with electrophiles. The most convenient and productive method of carrying out the reactions of ketoselenonium ylides with electrophilic substrates involves the use of a two-phase system: chloroform–water with sodium hydroxide as the base. The ylide generated in the aqueous phase on treatment of the selenonium salt with alkali is immediately extracted chloroform. The salt which failed to react remains in the aqueous phase, which suppresses the secondary reaction of the ylide with the salt leading to a triarylcyclopropane.

The reactions of carbanions with electrophiles in a two-phase system are carried out[38] in the presence of a phase transfer catalyst. The reactions of selenium ylides do not as a rule require special catalysis.

The selenonium ylides stabilised with a phenylacyl[39] or cyclopentadienyl group[34] react with nitrosobenzene to form the corresponding nitrones. The reactions of selenium ylides with various carbonyl compounds lead to oxirans having the *trans*-confirguration[40–42] and the reactions with salicylaldehyde lead to 2-aroylbenzofurans:[41]



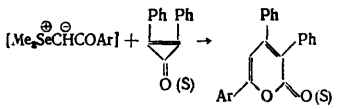


X = Br, $MeSO_4$; R = Me, Ph; R^1 = Me, Ph; R^2 = H, Me, COPh,

; R^3 = H, Ac, Alk; R^4 = H, Alk

The interaction of selenonium ylides with activated multiple bonds usually begins as the Michael addition, the subsequent reactions of the betaines formed as a rule involving the elimination of the readily removed selenonium group as a result of intramolecular nucleophilic substitution.

A convenient preparative method of synthesis of trisubstituted α-pyrones and α-pyranthiones by the [3 + 3]dipolar cycloaddition of selenium monoketoylides to diphenylcyclopropenone or its thio-analogue has been developed:[32]

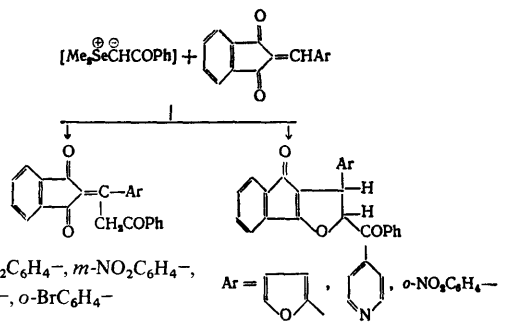


Ar = Ph,  (X = O, S, Se, N–CH_3)

The reactions of cyclic selenium diketoylides, namely dimethylselenonium diketoylides formed from dimedone and indan-1,3-dione, with diphenylcyclopropenone can be used to synthesise condensed α- and γ-pyrones.[43]

The interaction of selenium monoketoylides with activated acetylenes (dialkyl acetylenedicarboxylate or dibenzoylacetylene) leads to the formation of the corresponding trisubstituted furans.[44,45]

In contrast to sulphur ylides, the reactions of selenium monoketoylides with *para*-substituted 2-benzylideneindan-1,3-diones, having a conjugated bond system, begin with nucleophilic attack by the ylide carbon atom on the activated double bond. The betaine formed in this reaction splits off dimethyl selenide and, depending on the character of the substituent in the benzylidene group, either a 1,2-hydride shift takes place with formation of the Michael addition product or the dihydrofuran ring is formed. The reaction takes place stereoselectively and only the *cis*-isomers of dihydrofurans are formed:[46]

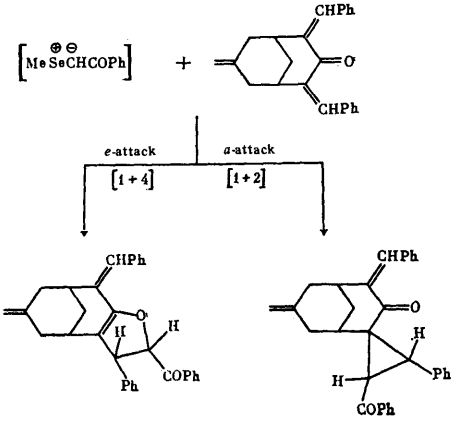


Ar = *p*-$NO_2C_6H_4$–, *m*-$NO_2C_6H_4$–, *p*-Cl-C_6H_4–, *o*-BrC_6H_4–

Ar = , , *o*-$NO_2C_6H_4$–

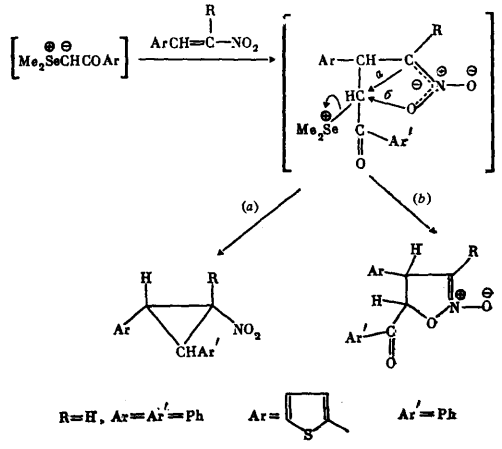
The reaction of selenium monoketoylide with dibenzylidene derivatives of a series of ketones (acyclic, cyclic, and bicyclic) in which both [1 + 2]- and [1 + 4]-cycloaddition is possible, have been investigated. It has been established that the interaction of selenium ylide with dibenzylidene derivatives of acetone, cyclopentanone, and cyclohexanone takes place as [1 + 2]cycloaddition to one of the double bonds of the dieonone with formation of two isomeric cyclopropyl ketones. In the case of the dibenzylidene derivative of bicyclo[3.3.1]ionan-3-one, the type of reaction, i.e. [1 + 2]- or [1 + 4]-cycloaddition, is determined by the direction of attack by the selenonium ylide (axial or equatorial). The attack by the ylide from the equatorial side relative to the given cyclohexane ring leads to the formation of the dihydrofuran ring as a consequence of the mutual approach of the carbonyl oxygen atom and the ylide carbon atom in the transition state. On the other hand, the attack from the axial side leads to the oxygen and ylide carbon atoms moving apart in the transition state and the formation of a three-membered ring becomes preferable. The reaction

takes place stereospecifically with formation of cyclopropane having the *cis*-configuration and of the *cis*-isomer of dihydrofuran:[47]

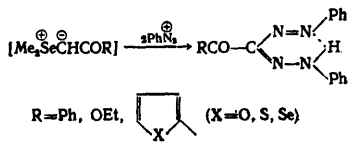


In all the cases investigated, the reaction involves only one benzylidene group.

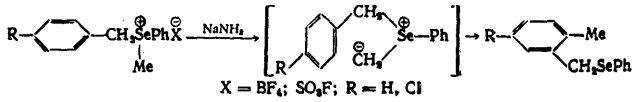
The conjugated nitro-olefins, in which there is a possibility of both [1 + 2]- and [1 + 4]-cycloaddition with formation of substituted cyclopropanes or isoxazoline *N*-oxides, constitute a convenient model for the study of reactions involving the cycloaddition of selenium ylides to an activated multiple bond. A necessary and sufficient condition for the occurrence of a reaction of the [1 + 4]-cycloaddition type is the presence of a substituent in the α-position relative to the nitro-group in the initial nitro-olefin. The nature of the substituent (alkyl, aryl, heteroaryl, or halogeno-) does not then influence the mode of reaction. The reaction takes place stereoselectively and is a convenient preparative method of synthesis of trisubstituted isoxazoline *N*-oxides in the *trans*-configuration:[48]



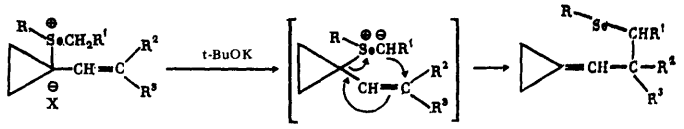
Among the electrophiles having the electrophilic centre at a heteroatom, detailed studies have been made of the interaction of selenonium acylmethylides with benzenediazonium chloride.[49] In contrast to phosphorus, nitrogen, and sulphur ylides, this reaction takes place with formation of 3-keto-1,5-diphenylformazans and constitutes a preparative method of their synthesis:



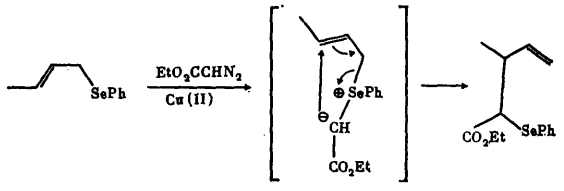
The [2,3]sigmatropic rearrangement of benzylselenonium ylides on treatment of the corresponding salts with sodium amide in liquid ammonia has been described:[37]



The [2,3]sigmatropic rearrangement of allylselenonium ylides is used to synthesise olefins:[9]



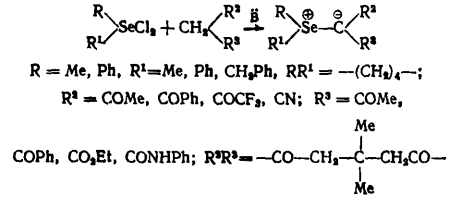
An analogous rearrangement has been observed on treating allyl selenide with diazoacetic ester in the presence of copper(II) sulphate:[33]



Thus unstabilised and monostabilised selenium ylides are convenient and very active reagents for the synthesis of various classes of organic compounds. Their ylide bond $\geq\bar{C}-\overset{+}{Se}<$ is weaker than the $\geq\bar{C}-\overset{+}{S}<$ bond in sulphonium ylides. R_2Se is a group which is more readily eliminated than R_2S. All the reactions with participation of selenonium ylides takes place under mild conditions. In terms of their behaviour, selenium ylides resemble nitrogen ylides more than sulphur ylides.

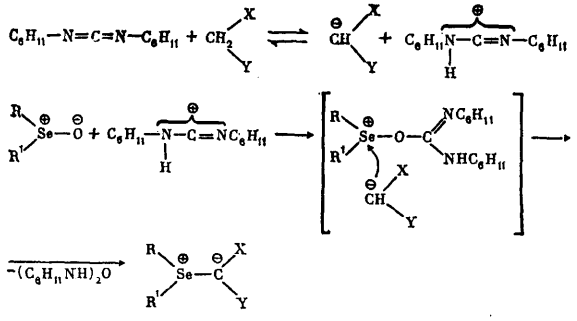
IV. DISTABILISED SELENIUM YLIDES

Distabilised selenium ylides have been obtained in satisfactory yields by condensing diorganoselenium dichlorides with compounds containing an active methylene group in the presence of a base (sodium ethoxide, potassium hydroxide, pyridine, alumina):[14,50–53]



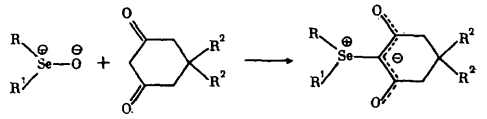
A general convenient preparative method of synthesis of distabilised selenium ylides involves the condensation of selenoxides with compounds containing an active methylene

group in the presence of dicyclohexylcarbodiimide: [16,51,52,54]



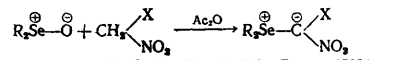
R=R¹=Ph; R=Ph, R¹=PhCH₂; R=R¹=—(CH₂)₄—, X=Y=—CO—CH₂—C(Me)₂—CH₂—CO—; X=Y=COPh; X=COPh, Y=COCF₃; X=COCF₃, Y=CO—(thienyl)

The asymmetric synthesis of a number of optically active selenonium diketoylides by the reaction of cyclic β-diketones with selenoxides in the presence of camphor-10α-sulphonic acid and anhydrous sodium sulphate has been achieved: [55]



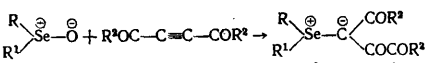
R = Ph, α-naphthyl, *o*-MeC₆H₄; 1,2,3-Me₃C₆H₂; R¹=Me, Ph; R²=H, Me

Selenonium nitroylides have been obtained by this method: [19,56]



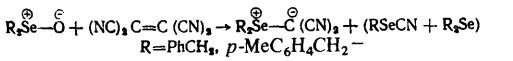
X = NO₂, CO₂Me, COPh; R=Ph, PhCH₂; R₂= —(CH₂)₄—

It is also known that selenoxides form selenium ylides by reaction with dimethylacetylenedicarboxylate [57,58] and dibenzoylacetylene: [59]



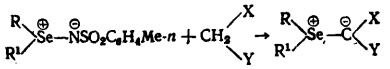
R=Me, R¹=Ph; R=R¹=PhCH₂, Ph; R²=OMe, Ph

Selenium dicyanomethylides have been obtained by the reaction of selenoxides with tetracyanoethylene: [57]



R=PhCH₂, *p*-MeC₆H₄CH₂—

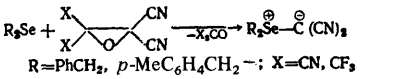
A method of synthesis of distabilised selenonium ylides from readily available selenimides and compounds with active methylene groups has been developed: [54]



R = R¹ = PhCH₂, Ph; RR¹ = —(CH₂)₄—, X, Y=CN, COOMe, COMe, SO₂Ph

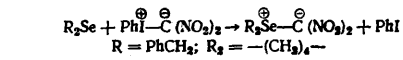
The rate of this reaction depends on the stability of the ylides formed.

Selenonium dicyanomethylides have been obtained by the reaction of selenides with activated oxirans: [57]



R=PhCH₂, *p*-MeC₆H₄CH₂—; X=CN, CF₃

Only one example of the synthesis of selenonium ylides from the ylides of other elements is known: [56]



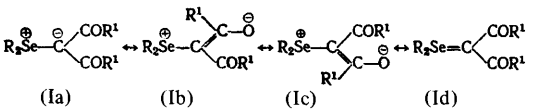
R = PhCH₂; R₂ = —(CH₂)₄—

The yield of the ylides in this reaction depends on the nucleophilicity of the selenide used.

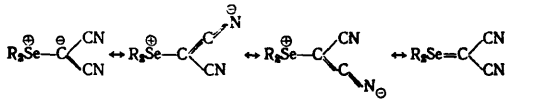
X-Ray diffraction data are available for only two distabilised selenium ylides: diphenylselenonium diacetylmethylide [56] and tetramethylselenonium dimedonylide. [60,61] These ylides have a trigonal pyramidal structure, at the apex of which the selenium atom is located.

Analysis of the bond lengths between the selenium atom and the ylide carbon atom and also of the bond lengths in the electronegative substituents indicates the involvement of electron-accepting groups in the declocalisation of the negative charge on the carbanion. [53,61] The IR. spectra of the distabilised selenonium ylides convincingly confirm this. [16,52]

The contribution of the dipolar resonance structures (Ib, c) and (IIb, c) to the ground state is extremely significant for selenonium diketo- and dicyanomethylides:



(Ia) (Ib) (Ic) (Id)

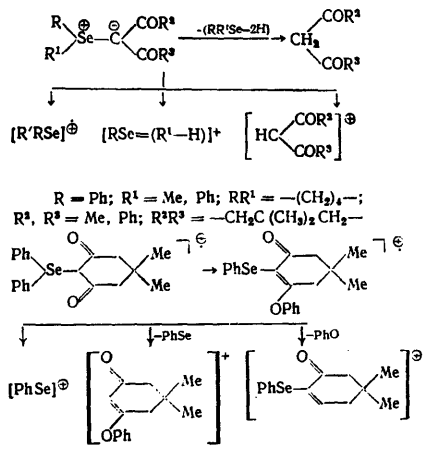


(IIa) (IIb) (IIc) (IId)

The selenium–ylide carbon bond lengths found in the distabilised selenium ylides [53,61] and also the ^{77}Se NMR data for these compounds [25] suggest a difinite contribution by the double bond character and the possibility of the formation of a p_π–d_π-bond using the selenium *d* orbital. [62] The contribution of the structures (Id) and (IId) in the selenium ylides is smaller than that of the analogous structures in sulphur ylides.

In aprotic solvents, the carbanionic fragment of selenonium ylides has the *W*-conformation, which has been confirmed by ^{1}H NMR and dipole moment data. [15]

On electron impact, selenium diketoylides decompose at the $\overset{+}{\text{Se}}-\bar{\text{C}}<$ bond together with the migration to the anionic residue of the ylide of hydrogen or the group (in the case of diphenylselenonium dimedonylide) linked to the selenium atom: [63]

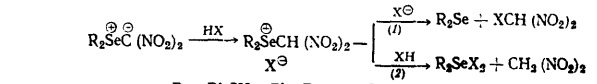


R = Ph; R¹ = Me, Ph; RR¹ = —(CH₂)₄—; R², R³ = Me, Ph; R²R³ = —CH₂C(CH₃)₂CH₂—

With the exception of nitroylides, [19] the distabilised selenium ylides are extremely stable compounds resistant to the action of various nucleophiles: aqueous and alcoholic alkali, [51,52] amines, [50] and alkali metal alkoxides. [51] As a consequence of the delocalisation of the charge on the ylide carbon atom over two electron-accepting groups, their nucleophilicity is significantly lower than that of unstabilised and monostabilised selenium ylides. However, reactions with fairly powerful electrophiles and compounds containing activated multiple

bonds are characteristic of the distabilised selenium ylides; thus, they afford the corresponding hydrochlorides, which lose HCl near their melting points.

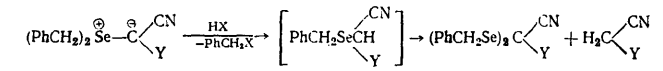
Selenonium dinitromethylides are protonated reversibly by inorganic acids containing weakly nucleophilic anions.[9] On treatment with acids having nucleophilic anions, the $\gtrless\overset{+}{S}e-\bar{C}\lessgtr$ bond dissociates. The intermediate salt is then capable of being cleaved at the $\gtrless\overset{+}{S}e-CH\lessgtr$ bond not only by the nucleophile counterion (pathway *1*) but also by the electrophilic molecule of the acid (pathway *2*):[19,56]



$R = RhCH_2$, Ph; $R_2 = -(CH_2)_4-$; X = Cl, Br

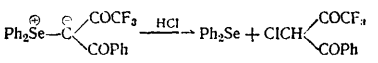
The preferred reaction pathway depends on the nucleophilic properties of the counterion; on passing from HCl to HBr, the contribution of pathway *1* increases.

Dibenzylselenonium dicyano- and cyanomethoxycarbonylmethylides are cleaved by acids only at the $\gtrless\overset{+}{S}e-CH_2Ph$ bond:[28]

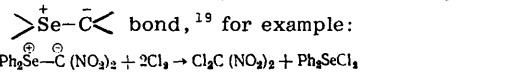


X = Cl, Br, NO_3, HSO_4, CF_3COO, $ClCH_2COO$; Y = COOMe, CN

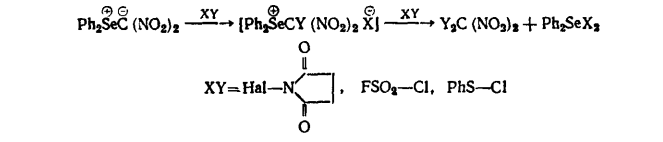
On the other hand, diphenylselenonium trifluoroacetylbenzoylmethylide is cleaved at the $\gtrless\overset{+}{S}e-\bar{C}\lessgtr$ bond on treatment with hydrogen chloride:[16]



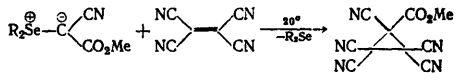
On interaction with powerful electrophiles (Cl_2, Br_2, SO_2Cl_2), diphenylselenonium nitroylides are also readily cleaved at the $\gtrless\overset{+}{S}e-\bar{C}\lessgtr$ bond,[19] for example:



Compounds with a "positive" halogen and benzeneulphenyl chloride also react with selenonium nitroylides under mild conditions, two "electrophilic" components of the reagent being joined to the carbanionic fragment, as in the interaction of distabilised ylides with acids:[19]

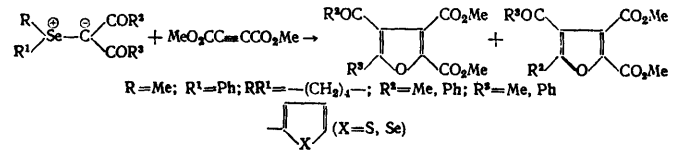


Distabilised selenonium ylides do not as a rule react with αβ-unsaturated ketones. However, substituted cyclopropanes have been obtained by the reaction of selenium cyanomethoxycarbonylmethylides with the highly electrophilic tetracyanoethylene:[57]

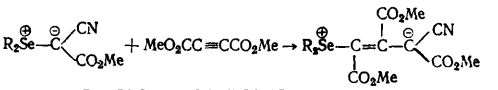


$R = PhCH_2$, p-$MeC_6H_4CH_2$.

The interaction of selenonium diketoylides with dimethyl acetylenedicarboxylate leads to tetrasubstituted furans:[50]

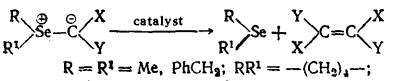


The reaction of selenium cyanomethoxycarbonylmethylides with dimethyl acetylenedicarboxylate results in the formation of only betaines, probably as a consequence of the reduced electrophilicity of the methoxycarbonyl group:[50,57]



$R = PhCH_2$, p-$MeC_6H_4CH_2$; $R_2 = -(CH_2)_4-$

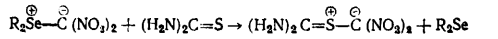
Distabilised selenium ylides readily decompose into the corresponding selenides and the products of the dimerisation of the carbanionic fragment on treatment with catalysts: tetramethylthioureas,[64] thioamides,[65] and episulphides:[66]



$R = R^1 = Me$, $PhCH_2$; $RR^1 = -(CH_2)_4-$;
X = CN, Y = CN, COOMe, COOEt

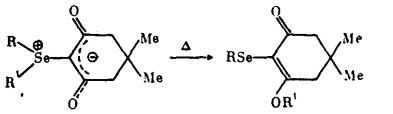
The mechanisms of all these reactions involve the initial attack on the thioderivatives by the ylides carbon atoms and the elimination of the selenide.[64-66]

Selenonium dinitromethylides are known to react with thiourea as follows:[56]



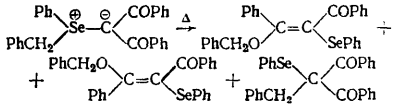
The course of the reaction depends greatly on the structure of the groups attached to the selenium atom. Thus, whereas in the case where $R_2 = -(CH_2)_4-$ a thiuronium ylide is formed in a high yield, when $R = PhCH_2$ the product is a 1:1 complex with thiourea, and in the case where R = Ph the reaction does not occur at all.

Under relatively mild conditions (refluxing in benzene or xylene), selenonium diketoylides rearrange with migration of the benzyl or phenyl group to the oxygen atom:[67]



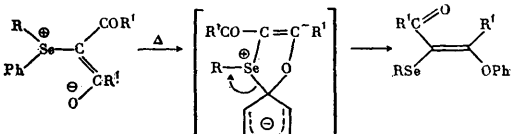
$R = PhCH_2$, Ph, Me; $R' = PhCH_2$, Ph

Only in the case of benzylphenylselenonium benzoylmethylide was the product of the Stevens rearrangement isolated together with that of the *O*-migration of the benzyl group:



The rearrangement of benzylphenylselenonium diketoylides apparently takes place stepwise via the formation of a radical pair and its subsequent recombination within a cage.

The migration of the phenyl group in methylphenyl- and diphenyl-selenonium diketoylides takes place via a mechanism involving intramolecular nucleophilic substitution in the benzene ring:[67]



$R = Me$, Ph; $R^1 = Ph$, $R'_2 = -CH_2-C(CH_3)_2-CH_2-$

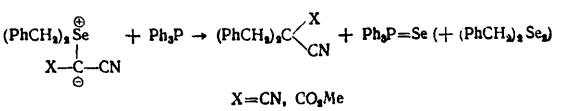
The capacity of the groups attached to the selenium atom for migration decreases in the sequence $PhCH_2$ > Ph > Me.[67]

Thermolysis of cyclic selenium diketoylides in the presence of copper(II) sulphate apparently proceeds via the formation of carbenes. As a result of the interaction with the initial ylide, the carbene is converted into the corresponding tetrasubstituted ethylene: [68]



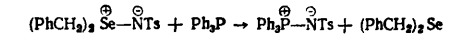
R, R^1=Me, Ph; R^2_2=—$CH_2C(CH_3)_2CH_2$—, *o*-C_6H_4—

The main pathway in the reaction of distabilised dibenzylselenonium ylides with triphenylphosphine involves the elimination of selenium with formation of triphenylphosphine selenide: [69,70]

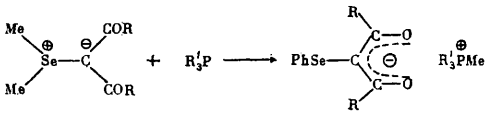


X=CN, CO_2Me

On the other hand, the reaction of dibenzylselenonium tosylimide proceeds with formation of triphenylphosphonium tosylimide: [70]

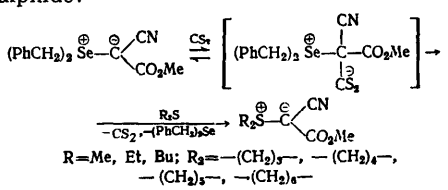


Triphenylphosphine and tris(dimethylamino)phosphine demethylate diketoylides with formation of phosphonium salts of enols: [71]



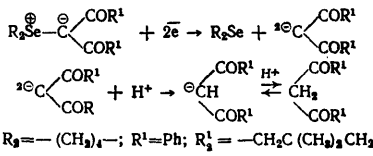
R=Ph, R_2=—$CH_2C(CH_3)_2CH_2$—, R^1=Ph, Me_2N

Dibenzylselenonium cyanomethoxycarbonylmethylide undergoes transylidation by dialkyl sulphides in the presence of carbon disulphide: [70]



R=Me, Et, Bu; R_2=—$(CH_2)_3$—, —$(CH_2)_4$—, —$(CH_2)_5$—, —$(CH_2)_6$—

In the polarographic reduction of stable selenium ylides at a dropping mercury electrode in dimethylformamide, the electrochemical cleavage of the carbon–selenium bond consists of two consecutive stages: [72]



R=Ph; R_2=—$(CH_2)_4$—; R^1=Ph; R^1_2=—$CH_2C(CH_3)_2CH_2$—

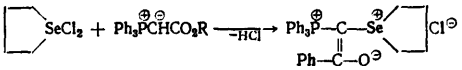
After electrolysis and treatment of the catholyte with water, dimedone and diphenyl selenide were detected in the reaction mixture. In the second stage, the dianions are apparently protonated with the initial formation of monoanions, which then combine with a proton and afford dibenzoylmthane and dimedone respectively.

V. BIS-ONIUM SELENIUM COMPOUNDS

The bis-onium compounds of selenium are ylide-salts and diylides containing, together with the selenonium fragment, onium fragments based on other heteroatoms (nitrogen, phosphorus, arsenic, selenium, and sulphur).

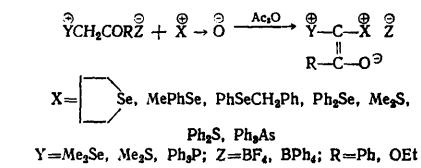
1. The Ylide-Salts of Selenium with Onium Groups at the Ylide Carbon Atom

The first attempt to synthesise ylide-salts containing the selenonium group involved the reaction of diorganoselenium dichlorides with alkoxycarbonylmethylenetriphenylphosphoranes. [73,74] Only in the case of selenolane dichloride, was the intermediate bis-salt resistant to the action of the nucleophilic chloride ion and a stable ylide-salt was obtained: [74]



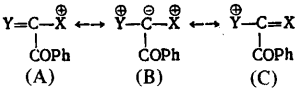
The reaction of diphenylselenium dichloride yields the corresponding α-chlorophosphorane and the reactions of the dichlorides of methylphenyl- and benzylphenylselenium involve the dealkylation of the intermediate bis-salt and the formation of α-phenylselenomethylenetriphenylphosphorane. [74]

A general preparative method of synthesis of selenium ylide-salts is the condensation of onium salts containing an active methylene group with diorganyl selenoxides, sulphoxides, and arsenoxides in the presence of acetic anhydride. The yield of the ylide-salts depends on the nucleophilicity of the initial oxide: [75–77]

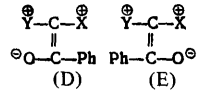


An essential condition for this reaction is the presence of sufficiently acid protons of the methylene group in the initial onium salt ($pK_a \approx 6-9$). [75] The phenyl groups attached to the onium atoms both in the initial salts and in the corresponding oxides give rise to steric hindrance to this interaction. [75,76] The high stability of the ylide-salts can be explained by the delocalisation of the negative charge on the carbanion over three centres: the two onium atoms and the carbonyl oxygen atom. This decreases the nucleophilicity of the ylide carbon atom. The ylide-salts are weaker nucleophiles than the acetate ion.

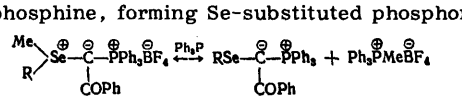
The structure of the cations of the phenylacylide-salts can be described by the set of mesomeric structures (A)–(C): [77]



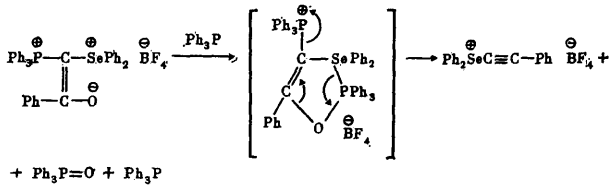
The onium groups of the phenylacylide-salts can be arranged in the following sequence in terms of their ability to stabilise the carbanion: $Ph_2S > Ph_3P > Ph_2Se > Ph_3As > Me_2S \approx$ MePhSe > Me_2Se. According to Ir and ^{1}H and ^{77}Se NMR spectra, [25,75–77] when the onium groups differ greatly (X = Me_2Se and Y = Ph_3P), the *trans*-structure (D) is formed with a considerable contribution by the structure (A), but, when the abilities of the onium groups to stabilise the carbanion are similar (X = Me_2S and Y = MePhSe), the ylide–salt consists of the *cis*- and *trans*-isomers (D) and (E).



The phenylacylide-salts containing the selenonium and triphenylphosphonium groups are demethylated on fusion with triphenylphosphine, forming Se-substituted phosphoranes: [78]

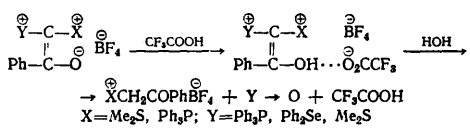


The ylide-salts without readily eliminated groups at the onium atom react differently. In this case, there is nucleophilic attack by triphenylphosphine on the selenium atom with subsequent elimination of triphenylphosphine and triphenylphosphine oxide and the formation of ethynylselenonium salts: [77]



$+ Ph_3P{=}O + Ph_3P$

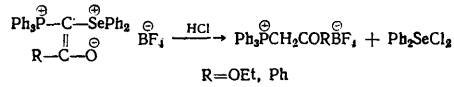
Trifluoroacetic acid protonates phenylacylide-salts at the oxygen atom and the bis-salts obtained in this process are readily hydrolysed: [79]



$\rightarrow XCH_2COPhBF_4 + Y \rightarrow O + CF_3COOH$

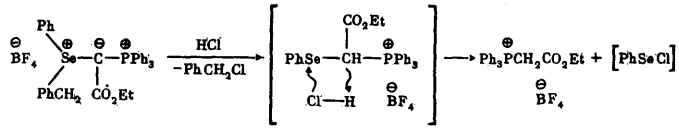
X=Me_2S, Ph_3P; Y=Ph_3P, Ph_2Se, Me_2S

The electrophilic cleavage of the phenylacylide-salts of selenium with hydrogen chloride [76,77] take place analogously to the corresponding reaction of dinitromethylselenonium salts: [56]



R=OEt, Ph

The interaction of benzylphenylselenonium ylide-salts with hydrogen chloride is accompanied by their dealkylation: [76]

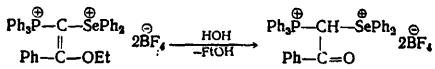


Selenonium phenylacylide-salts are alkylated at the oxygen atom [80] with formation of the (*E*)-isomer of the corresponding bis-salt with the *trans*-disposition of the triphenylphosphonium group or, in the absence of the latter, of the selenonium group, relative to the alkoxy-group:

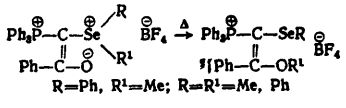


X=Me_2S, Y=Ph_2Se; X=Me_2Se, Y=Ph_3P;
X=Ph_2Se, Y=Ph_3P.

The bis-salts formed are readily hydrolysed by moist ether, for example: [80]

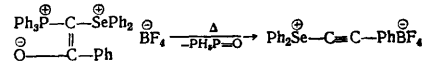


The thermolysis of selenonium phenylacylide-salts is accompanied by the migration of the methyl or phenyl group from the onium fragment to the oxygen atom as a result of the attack by the nucleophilic oxygen on the electrophilic carbon atom of the onium group. This results in the preferential formation of the (*E*)-isomer of the corresponding αβ-disubstituted triphenylstyrylphosphonium tetrafluoroborate with the *trans*-disposition of the triphenylphosphonium and alkoxy- or phenoxy-groups. The Stevens rearrangement has never been observed in such cases: [81]



R=Ph, R^1=Me; R=R^1=Me, Ph

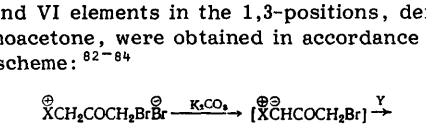
The intermolecular Wittig reaction with formation of ethynylselenonium tetrafluoroborate occurs in the rearrangement of a diphenylselenonium phenylacylide-salt: [77]



2. Selenium Ylide-Salts with Onium Groups in the 1,3-Positions

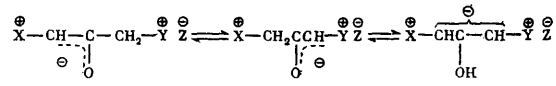
The presence in one molecule of an ylide-salt of two different onium groups in the 1,3-positions makes it possible to compare directly the degrees of their involvement in the stabilisation of the carbanion.

Ylide-salts containing two different onium centres with Group V and VI elements in the 1,3-positions, derived from 1,3-dibromoacetone, were obtained in accordance with the following scheme: [82-84]



X=Ph_3P, Py; Y=Me_2Se, MeS, Py, Ph_3As

The existence of three tautomeric forms is theoretically possible for these salts: [83]



(A) (B) (C)

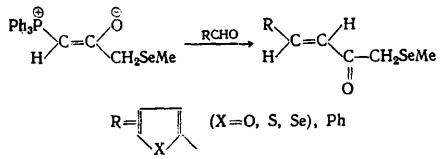
It was established from UV, IR, and ^1H, ^{31}P, ^{13}C, and ^{77}Se NMR data that the ylide-salt (I), containing together with the triphenylphosphonium group also the dimethylselenonium group (X = Ph_3P, Y = Me_2Se) exists in solution predominantly as the single tautomeric form (A) with an ylide phosphorane fragment. The ylide-salt containing the pyridinium and dimethylselenonium groups (X = Py, Y = Me_2Se) exists in solution in the form of an equilibrium between the two tautomeric forms (A) and (B) having the pyridinium ylide or salt fragment. The presence of the third form has not been detected. [25,82-84]

The ylide-salt (I) (ω-triphenylphosphoranylideneacetonyldimethylselenonium bromide) does not undergo the Wittig reaction, in contrast to the usual phosphorus ylides, as a consequence of the decrease in the nucleophilicity of the ylide carbanion under the influence of the selenonium group in close proximity. In the interaction with *p*-nitrobenzaldehyde, this ylide-salt forms a selenium-substituted αβ-unsaturated ketone. Under the influence of the nucleophilic bromide ion, the most electron-deficient $\rangle\overset{+}{S}e$–Me bond is apparently cleaved under the reaction conditions and the resulting selenium-substituted phosphorane then enters into the Wittig reaction with *p*-nitrobenzaldehyde: [85]

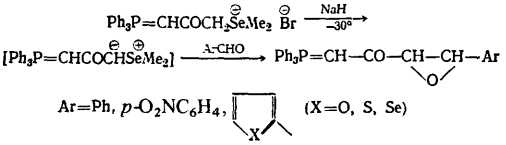
$Ph_3P{=}CHCOCH_2\overset{\oplus}{S}eMe_2\ \overset{\ominus}{Br} \xrightarrow{-MeBr} Ph_3P{=}CHCOCH_2SeMe \rightarrow$
(I)
$\xrightarrow{p\text{-}O_2NC_6H_4CHO} p\text{-}O_2NC_6H_4CH{=}CHCOCH_2SeMe$

The ylide-salt (I) with selenonium and phosphonium groups in the 1,3-positions is readily demethylated by triethylamine with formation of methylselenoacetylmethylenetriphenylphosphorane which exists as the (*Z*)-conformer in $CHCl_3$: [84]

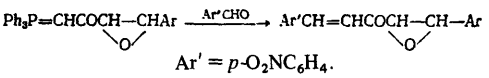
This phosphorane readily enters into the Wittig reaction not only with the reactive *p*-nitrobenzaldehyde but also with less reactive aromatic or heteroaromatic aldehydes, forming the corresponding αβ-unsaturated ketones having the *trans*-configuration and containing the Me–Se group: [84]



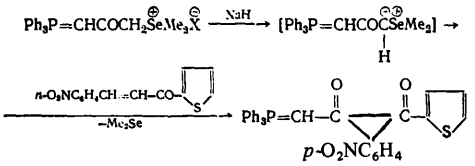
Bases such as sodium carbonate or hydroxide do not deprotonate the ylide-salt (I), although their basicity is sufficient for the formation of selenonium ketoylides from the corresponding selenonium salts. [31,32] When the ylide-salt (I) was treated with sodium hydride, a di-ylide was obtained *in situ* and its reactions with electrophiles—aromatic aldehydes and αβ-unsaturated ketones—were investigated. [82,85] Thus the reactions with aromatic aldehydes afford ketomethylenetriphenylphosphoranes containing the oxiran ring:



The selenonium ylide fragment in the di-ylide is more nucleophilic than in monoketoylides and reacts more readily with aromatic aldehydes. [82,85] The phosphorane formed under these conditions enters into the Wittig reaction under more severe conditions:



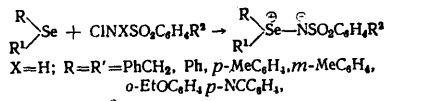
The C–P ylide bond remains unchanged in the reaction of the di-ylide with 2-(*p*-nitrophenyl)-1-(2-thenoyl)ethylene: [82,85]



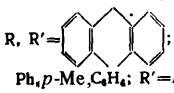
Thus, in the reactions with electrophiles, the selenurane and not the phosphorane fragment is more reactive in the di-ylide formed on deprotonation of the ylide-salt (I). The high reactivity of the di-ylides having this structure makes it possible to use them in organic synthesis, because, by selecting onium groups with different stabilising capacities and different reaction conditions, it is possible to achieve the selective interaction of a particular ylide fragment with electrophiles.

VI. SELENIMIDES

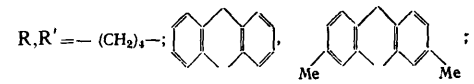
Selenimides have been synthesised by treating organic selenides with *N*-chlorosulphonamides or their sodium salts: [86–88]



X=H; R=R′=PhCH$_2$, Ph, *p*-MeC$_6$H$_4$, *m*-MeC$_6$H$_4$, *o*-EtOC$_6$H$_4$ *p*-NCC$_6$H$_4$.

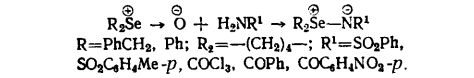


R^3=*p*-Me, X=Na; R=PhCH$_2$, Ph, *p*-Me,C$_6$H$_4$; R′=Me, PhCH$_2$, Ph, *p*-MeC$_6$H$_4$;



R^2 = H, *p*-Me, *p*-Cl, *o*-NO$_2$, *p*-NO$_2$.

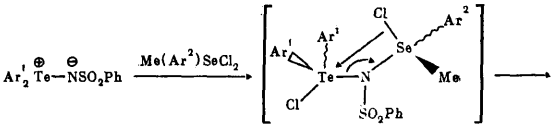
Selenimides are obtained in satisfactory yields by the condensation of selenoxides with sulphonamides and carboxylic acid amides: [51,88,90]

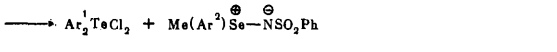


The occurrence of this reaction requires the presence of sufficiently strong electron-donating groups in the oxide and of electron-accepting groups in the amide. [90]

The reaction of *N*-(benzenesulphonyl)tellurimides with arylmethylselenium dichlorides affords *N*-benzenesulphonylselenimides and diaryltellurium dichlorides.

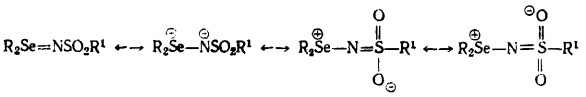
The possibility of such conversion of tellurimides into selenimides is due to the greater tendency of tellurium, compared with selenium, to form tetracoordinate compounds: [94]





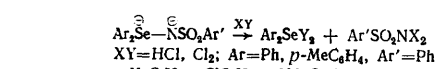
Ar′=Ph, *p*-MeOC$_6$H$_4$, *p*-MeC$_6$H$_4$; Ar^2=Ph, *p*-BrC$_6$H$_4$

IR and UV-spectroscopic and ^{1}H NMR data indicate a dipolar structure of *N*-arenesulphonylselenimides with a considerable contribution to the ground state of the molecule by resonance structures with a positive charge on the selenium atom: [91]



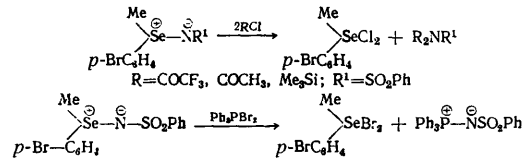
Selenimides with a chiral selenonium group have been synthesised. The pyramid of the onium selenium atom in selenimides has a high inversion barrier. [91]

Measurements of the pK_a for selenimides have shown that their basicity is close to that of the anils of aromatic aldehydes. [91] Selenimides are stable compounds resistant to the action of aqueous alkalis and water at 20 °C. However, after prolonged heating with an aqueous 2 *N* solution of sodium hydroxide, they hydrolyse to selenoxides and arenesulphonamides. [87] Diaryl selenimides are readily cleaved by hydrogen chloride or chlorine at the Se–N bond: [87]



XY=HCl, Cl$_2$; Ar=Ph, *p*-MeC$_6$H$_4$, Ar′=Ph *p*-MeC$_6$H$_4$ *p*-ClC$_6$H$_4$, *o*-NO$_2$C$_6$H$_4$, *p*-O$_2$NC$_6$H$_4$

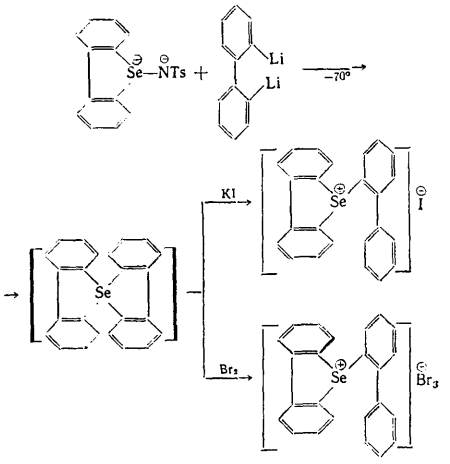
Selenimides react similarly also with acyl chlorides, triphenylphosphine dibromide, and chlorotrimethylsilane: [92]



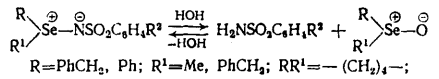
R=COCF$_3$, COCH$_3$, Me$_3$Si; R^1=SO$_2$Ph

The reaction of 2,2′-biphenyleneselenonium tosylimide with 2,2′-dilithiobiphenyl proceeds via the formation of a σ-selenurane having a spiran structure. [86] Treatment of an ethereal

solution of the latter with aqueous potassium iodide or bromine leads to its cleavage products: [86]

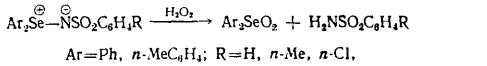


When aqueous solutions of selenides are heated, reversible hydrolysis takes place with formation of selenoxides and the corresponding amides: [87,88]



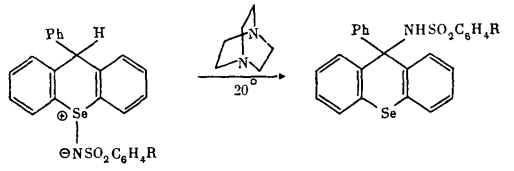
R=PhCH$_2$, Ph; R^1=Me, PhCH$_2$; RR^1=—(CH$_2$)$_4$—;
R^2=H, *n*-Cl; *o*-NO$_2$; *n*-NO$_2$

This reaction is accelerated in the presence of sodium hydroxide or silica gel. [87] Selenimides are oxidised by hydrogen peroxide or nitrogen dioxide and afford diarylselenones after subsequent treatment with water: [87]



Ar=Ph, *n*-MeC$_6$H$_4$; R=H, *n*-Me, *n*-Cl,
o-NO$_2$, *n*-NO$_2$

The reaction of *N*-arenesulphonylselenimides with 1,4-diazabicyclo[2.2.2]octane at 20 °C in benzene takes place quantitatively with formation of 9-arenesulphonamido-9-phenylselenoxanthenes, while hydrolysis on a silica gel plate (TLC) affords 9-phenylselenoxanthene 10-oxide: [93]



R=H; *n*-Me

Thus the data presented in this review show that in the last 15 years the chemistry of selenonium compounds has developed vigorously, particularly in recent years.

On the basis of selenonium compounds, in the first place the reactive and readily available selenium ylides, new preparative methods of synthesis have been developed for various classes of organic compounds: tertiary alcohols, olefins with different structures, including sterically hindered olefins, α-methylselenocarbonyl compounds, phosphoranes containing the methylseleno- or epoxy-group, heteroaroylcyclopropanes, nitrones, ketoformazans, oxirans, furans, condensed dihydrofurans, isoxazoline *N*-oxides, etc.

Various processes of the type of [1 + 2]-, [3 + 3]-, or [1 + 4]-dipolar cycloaddition with participation of selenium ylides, which in most cases proceed regioselectively and stereospecifically, are of special interest among the reactions of selenonium compounds.

All this shows that there are great prospects for the application of selenonium compounds in specific fine organic synthesis. One can undoubtedly expect the discovery of new reactions with participation of selenonium compounds, which will find practical applications. This will in its turn enhance the interest in the chemistry of selenonium compounds from the standpoint of their involvement in selective chemical processes.

The rapid development of the chemistry of organoselenium compounds is also indicated by the fact that, during the preparation of the manuscript of the review for publication, a monograph devoted to this topic appeared in the literature. [95]

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