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Aza analogues of organic and inorganic oxygen compounds of selenium

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ABSTRACT. In this review information is presented on the methods of synthesis and physical and chemical properties of the aza analogues of selenoxides, selenones, derivatives of seleninic and selenous acids, and selenium dioxide—compounds which formally contain selenium–nitrogen double bonds.

The bibliography includes 56 references.

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I. Introduction

For organic and organoelemental chemistry the last 20–30 years have been characterised by a rapid growth of studies into the chemistry of aza analogues of organic and inorganic oxygen compounds of elements in Groups V and VI of the Periodic Table, formed by the formal replacement of oxygen atoms in the E = O or $E(=O)_2$ group (E = P, As, Sb, Bi, S, Se, Te by an imino group (=NR). Compounds that contain E = NR, E(O) = NR, or $E(=NR)_2$ groups are of interest because they often have properties which are not typical of their oxygen analogues. Moreover, the variation in character of the radical on the imide nitrogen atom within each separate class of compounds leads not only to a wide structural diversity but also to a considerable variation in properties. Especially marked progress has been made in the chemistry of imido compounds of phosphorus and sulphur. At the present time there exist the extensive separate branches of organophosphorus and organosulphur chemistry, which have undoubtedly stimulated research into the chemistry of imido compounds of other elements, in particular, selenium.

The first examples of imido compounds of selenium—*N*-arylsulphonylselenimides—were obtained in 1962, but more intensive and systematic studies in this field were started in the 1970's.

Aza analogues of selenoxides, selenones, seleninic and selenous acid derivatives, and selenium dioxide are known at the present time. There is still no standard nomenclature for these classes of selenium compounds. In the present review we shall follow the nomenclature accepted for the analogous sulphur compounds which appear to us to correspond most closely to the IUPAC rules:

$R^1R^2Se = NR$—selenimides,
$R^1R^2Se(O) = NR$—selenoximides,
$R^1Se(=NR)Hal$—arene-*N*-R-imidoseleninyl halides,
$Hal_2Se = NR$—*N*-R-imidoselenous dihalides
N-R-imidoselenyl halides,
$RN = Se = NR^1$—selenium diimide derivatives,
RN = Se = O—selenylamines.

II. Selenimides

Among the aza analogues of selenoxides—*N*-R-selenimides—*N*-arylsulphonyl- and *N*-carbacyl-selenimides $R^1R^2Se = NR$ [R = SO_2R^3 (I), COR^3 (II)] are known at the present time. The methods of synthesis of *N*-R-selenimides and thier sulphur analogues, the corresponding *N*-R-sulphimides,[1] as a rule are similar, but there are also considerable differences between them.

A general and most simple method for the synthesis of *N*-arylsulphonylselenimides (I) is the oxidative imination of selenides with *N*-sodium-*N*-chloramides of arenesulphonic acids:[2–6]

$$R^1R^2Se + ArSO_2NNaCl \rightarrow R^1R^2Se{=}NSO_2Ar + NaCl, \quad (I)$$

$R^1, R^2 = Alk, Ar, ArCH_2$.

The reaction occurs in acetonitrile,[6] dimethylformamide,[3,5] a mixture of acetonitrile and methanol,[3] and methanol,[4] generally at 20 °C and using anhydrous arenesulphonic acid *N*-sodium-*N*-chloramides.

Selenimides (I) are also obtained by the successive treatment of selenides with t-butyl hypochlorite and *N*-sodium arenesulphonamides at –25 to –40 °C in acetonitrile or chloroform[7,8] or at 20 °C in carbon tetrachloride:[9]

$$R^1R^2Se \xrightarrow[2)\ ArSO_2NHNa]{1)\ t\text{-}BuOCl} (I) + NaCl + t\text{-}BuOH.$$

An analogous reaction is used to obtain *N*-R-sulphimides.[10] It has been proposed that a t-butoxychlorosulphurane is formed as an intermediate in this process. Treatment of diaryl or aryl alkyl selenides with t-butyl hypochlorite gives t-butoxychloroselenanes, which have been isolated and characterised:[9,11]

$$R^1R^2Se + t\text{-}BuOCl \underset{150°C}{\overset{20°C}{\rightleftarrows}} R^1R^2Se(OBu\text{-}t)Cl. \quad (III)$$

Compounds (III) are colourless crystalline products, soluble in organic solvents (benzene, chloroform, methylene chloride, 1,2-dichloroethane), and on heating to 130–140 °C in a vacuum they sublime but at atmospheric pressure at 150 °C decompose to the initial selenides and t-butyl hypochlorite. The Se – Cl bond in compounds (III) is covalent; their specific electrical conductivity in dichloroethane is virtually the same as the electrical conductivity of the solvent.[9] Compound (III), $R^1 = R^2 = Ph$, is hardly hydrolysed at all after the prolonged action of water at 20 °C, but on boiling for 2–3 h it decomposes to form a mixture of diphenyl selenoxide and

diphenylselenium dichloride (the latter is formed by the reaction of diphenyl selenoxide and hydrogen chloride):

$$Ph_2Se(OBu\text{-}t)Cl \xrightarrow[-t\text{-}BuOH]{H_2O} [Ph_2SeO + HCl] \rightarrow$$
$$\rightarrow {}^1/_2\, Ph_2SeCl_2 + {}^1/_2\, Ph_2SeO + {}^1/_2\, H_2O.$$

If hydrogen chloride is removed from the reaction mixture (by prolonged standing in a vacuum desiccator above caustic potash), only diphenyl selenoxide is obtained.[9]

Compound (III), $R^1 = R^2 = Ph$, is also formed by reaction of diphenylselenium dichloride with t-butyl hypochlorite, but this reaction is reversible and is displaced towards formation of the selenane only by removal of chlorine from the reaction mixture:[9]

$$Ph_2SeCl_2 + t\text{-}BuOCl \underset{0^\circ C}{\overset{60^\circ C}{\rightleftharpoons}} (III) + Cl_2.$$

Alkoxychloroselenanes (III) are also formed by the reaction of R^1R^2-selenium dichlorides with alkoxides in a molar ratio of 1 : 1.[12] When compounds (III) are treated with the sodium derivative of benzenesulphonamide or benzamide, the corresponding *N*-R-selenimides (I) and (II) are obtained:[9]

$$(III) + RNHNa \xrightarrow{20\ ^\circ C,\ CCl_4} \underset{(I),\ (II)}{Ph_2Se = NR} + t\text{-}BuOH,$$
$$R = PhSO_2\ (I),\ PhC(O)\ (II).$$

However, in order to prepare compounds (I) or (II) it is not necessary to isolate compounds (III) since the reaction can be carried out in one stage as shown below.

The following relatively simple and general method for the synthesis of *N*-R-selenimides (I) and (II) is the reaction of selenoxides with sulphonamides and carboxamides:[5,7,13-15]

$$R^1R^2SeO + RNH_2 \rightarrow \underset{(I),\ (II)}{R^1R^2Se{=}NR} + H_2O.$$

The reaction conditions are dependent on the nature of the amides and the substituents on the selenium atom. Dibenzyl selenoxide and methyl aryl selenoxides react with arenesulphonamides and trifluoroacetamide in chloroform, acetonitrile, or benzene on heating[5,7,13,15] or even at 20 °C when water is removed.[7,14] Acetamide or chloroacetamide do not react under these conditions. When diphenyl selenoxide is refluxed with *p*-nitrobenzamide, the corresponding *N*-*p*-nitrobenzoylselenimide is formed in low yield.[13] The reaction of diaryl selenoxide with benzamide or trichloroacetamide was carried out in the presence of acetic anhydride.[15]

When diphenyl selenoxide is heated with aromatic amines in the presence of dehydrating media, and also when diphenylselenium dichloride is reacted with aromatic amines in the presence of triethylamine, diphenyl selenide and the corresponding azobenzenes are formed.[16]

N-Arylsulphonylselenimides (I) are readily obtained by the reaction of diaryl selenoxides with bis(arylsulphonyl)diimides of sulphur or selenium[17] and also with aldimines:[18]

$$Ar_2SeO \xrightarrow[-Ar^2CHO]{\overset{(ArSO_2N{=})_2E,\ (E=S,\ Se)}{-EO_2}\quad \overset{Ar^1SO_2N{=}CHAr^2}{}} Ar_2Se{=}NSO_2Ar.$$

Arene-*N*-arylsulphonylimidoseleninyl chlorides react with styrene to form *Se*-aryl-*Se*-styryl-*N*-arylsulphonylselenimides:[19]

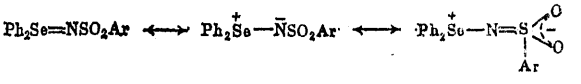
$$ArSe(=NSO_2Ar^1)Cl + CH_2{=}CHPh \rightarrow Ar(PhCH{=}CH)Se(=NSO_2Ar^1).$$

Se-Methyl-*Se*-aryl-*N*-phenylsulphonylselenimides are obtained by reaction of methylarylselenium dichloride with *Te*,*Te*-diaryl-*N*-phenylsulphonyltellurimides:[20]

$$Ar_2Te{=}NSO_2Ph + CH_3(Ar^1)SeCl_2 \xrightarrow{benzene}$$
$$\rightarrow CH_3(Ar^1)Se{=}NSO_2Ph + Ar_2TeCl_2.$$

Selenimides (I) and (II) are relatively stable, colourless crystalline compounds. According to the data of X-ray diffraction analysis of compounds $PH_2Se = NSO_2Ph$[21] and $Ph_2Se = NSO_2C_6H_4CH_3$-*p*,[22] the length of the selenium–nitrogen bond (1.82 and 1.787 Å) is greater than the calculated length of a selenium–nitrogen double bond (1.628 Å) and also a single selenium–nitrogen with a high degree of double bond character, for example, in $Ph_3P = NSeCl_3$ (1.680 Å) and $(Ph_3P = N)_2SeCl_2$ (1.725 Å[22]), whereas the sulphur (VI)–nitrogen bond (1.60 Å[21] and 1.598 Å[22]) is shorter than a single bond (1.69 Å[22]).

From the results of X-ray diffraction analysis and the IR spectra of compounds (I) and (II) (using ^{15}N isotope exchange) the following bands were attributed to ν(Se = N): 550–590 cm^{-1},[5] 572 cm^{-1},[22] 675 cm^{-1};[23] and for ν(S(VI)–N): 930–950 cm^{-1},[5,22,23] [in two studies[14,24] ν(Se = N) in compounds (I) was assigned to the regions at 890 cm^{-1} [14] and 930–950 cm^{-1},[24] while ν(S(VI–N) was assigned to 672–677 cm^{-1}.[24] The results of these studies provide the basis for the proposal that the loss of double bond character of the Se = N bond and the considerable double bond characer of S(VI)–N in compounds (I) are due to the high contribution of resonance structures with a positive charge on the selenium atom:[5,21-24]



The marked shift to longer wavelength of ν(SE = N) (470 cm^{-1})[5] and ν(C = O) (1580, 1535 cm^{-1},[5,9] and 1600–1585 cm^{-1} [15]) indicates that there is a significant contribution from an "ylide" structure in selenimides (II).

$$\underset{(II)}{R^1R^2Se{=}NCOR^3} \leftrightarrow R^1R^2Se^+{-}N{=}\underset{\displaystyle R^3}{\overset{\displaystyle |}{C}}{-}O^-.$$

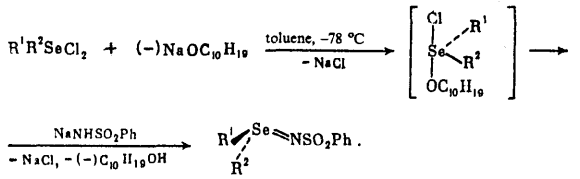
As a result of this, representation of the selenium–nitrogen bond in compounds (I) and (II) as a semipolar Se → N or SE^+–N form is evidently more rational (see the study of Oae et al.[5]).

In the UV spectra of *N*-tosylselenimides (I) there is an absorption maximum at 223–226 nm ($\lg \varepsilon_{max}$ 4.04–4.49); *N*-acylselenimides (II) absorb at 226 nm ($\lg \varepsilon$ 4.41) and 259 nm ($\lg \varepsilon$ 3.98).[5] From studies of the UV spectra of compounds (I) and (II) containing different types of substituents in the aryl groups on the selenium atom, it was proposed that the *K*-bands were due to the interaction of the π-electrons of the ring with the electrons of the *para* substituents.[5,8,15] The pK_a values of selenimides (I) (acetonitrile, 25 °C) correlate with the σ constants of the *para* substituents in the aryl ring. The best correlation is achieved when the normal averaged values of the σ constants are used, indicating that there is a relatively small effect from direct polar conjugation of the substituents on the basicity of the selenimides.[8]

In the PMR spectra of *Se*-aryl-*Se*-benzyl-*N*-arylsulphonylselenimides in $CHCl_3$, CH_2Cl_2, or CCl_2CCl_2 the diastereotopic protons of the CH_2 group appear as an AB system. The line shape of the signals does not change on heating to 140 °C. which indicates that there is a high inversion barrier for the selenium pyramid.[8]

The successive treatment of selenium dichlorides with sodium *L*-(–)-menthylate and the Na derivative of benzenesulphonamide gave optically active selenimides (I). It has been suggested that

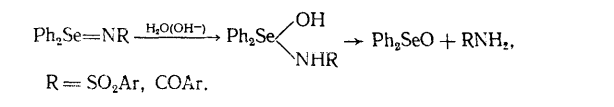
enrichment of one of the stereoisomers occurs at the stage where a compound of tetracoordinate selenium is formed:[12]



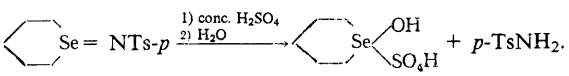
Asymmetric induction also occurs on reaction of asymmetric selenoxides with (+)- or (−)-10-camphorsulphonamides[14,18] and also with (+)- or (−)-camphorsulphonylbenzaldimine.[18]

The covalent radius of selenium (1.16 Å) is higher than the covalent radius of sulphur (1.02 Å), and the length of the Se = N bond (1.787–1.82 Å)[21,22] is greater than the length of the S = N bond (1.628–1.638 Å),[1] which is due to the greater degree of polarisation of the selenium-nitrogen bond. This is also confirmed by comparing the PMR spectra of selenimides and sulphimides with coresponding structures. The signal from the α-protons in the PMR spectra of selenimides occurs at higher field than in the corresponding sulphimides.[5]

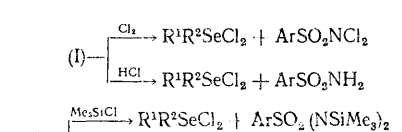
The difference in the length of E = N bonds (E = S, Se) and their degree of polarity also affect the relative reactivity of selenimides and sulphimides. In contrast to *N*-arylsulphonylsulphimides,[1] selenimides (I) are much less stable towards hydrolysis. Compounds (I) and (II) are unchanged on treatment with dilute acids and bases at 20 °C, but on heating or on treatment with concentrated alkali in alcohol they are rapidly hydrolysed to the corresponding selenoxide and arenesulphonamide.[3,4] The formation of an intermediate hydrated structure has been proposed when hydrolysis occurs or in the preparation of selenimides from selenoxides and amides.[5,6]

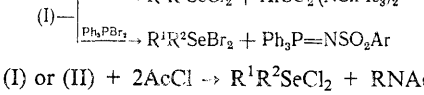


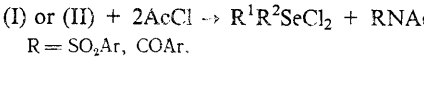
A compound with a selenurane structure was obtained by reaction of *N*-tosyl-*Se*,*Se*-pentamethyleneselenimide with sulphuric acid (−50 °C) followed by hydrolysis:[5]

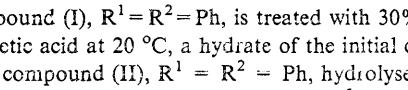


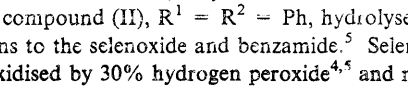
The Se = N bond in selenimides is very readily cleaved on treatment with chlorine, hydrogen chloride,[4] acetyl chloride, trimethylchlorosilane, or triphenylphosphine dibromide:[25]











When compound (I), $R^1 = R^2 = Ph$, is treated with 30% hydrogen peroxide in acetic acid at 20 °C, a hydrate of the initial compound is formed, while compound (II), $R^1 = R^2 = Ph$, hydrolyses under these conditions to the selenoxide and benzamide.[5] Selenimides (I) and (II) are oxidised by 30% hydrogen peroxide[4,5] and nitrogen dioxide[4] at 20 °C or with an aqueous solution of potassium permanganate on boiling[5] to the corresponding selenones and amides:

When selenimides (I) are reacted with triphenylphosphine, the corresponding selenide and triphenylphosphine imide are formed in quantitative yield:[5]

Selenimides (II) decompose on heating to selenides and isocyanates[5]

In a study of the kinetics of thermolysis of selenimides and sulphimides $Ph_2Se=NCOPh$ and $Ph_2S = NCOPh$ it was established that the former decomposes 300 times faster than the latter, with the entropies of activation for these reactions being similar. This is undoubtedly due to the weaker selenium–nitrogen bond.[5]

III. Selenoximides

At the present time only *Se*,*Se*-diaryl-*N*-arylsulphonylselenoximides (IV) are known among amido derivaties of hexavalent selenium. Compounds (IV) are obtained by the reaction of diaryl selenones with *N*-sulphonylarenesulphonamides,[4,26] and also with *N*,*N*′-diarylsulphonyldiimides of selenium or sulphur:[17]

It should be noted that sulphones do not react with *N*-sulphonylarenesulphonamides.

In the IR spectra of compounds (IV), ν(Se = N) occurs in the region 930–910 cm^{-1}. It was concluded from the fine structure of the UV spectra that the fragment >Se(O)(=NSO_2−) has a rigid structure which interacts weakly with the π-system of the aromatic rings.[27]

Compounds (IV) remain unchanged on prolonged standing in air, they are stable to water at 100 °C, and are not affected by acids and bases at 20 °C. However, on prolonged heating with a 2 N solution of caustic soda they are hydrolysed to diaryl selenones and arenesulphonamides.

When treated with dry hydrogen chloride compounds (IV) decompose to form diarylselenium dichlorides, arenesulphonamides, chlorine, and water.

In contrast to selenimides (I), selenoximides (IV) do not react with elemental chlorine.[26]

IV. Arene-*N*-R-imidoseleninyl chlorides

The main method for the synthesis of arene-*N*-R-imidoseleninyl chlorides (V) is the oxidative imination of areneselenenyl chlorides or selenol derivatives with *N*-halo compounds. Compounds (V) are very readily formed by reaction of *Se*-trimethylsilyl- or *Se*-benzoylselenols with *N,N*-dichloramides of arenesulphonic acids, carboxylic, carbon, or phosphoric acids.[19,28-30] The reactions occur very readily, and trimethylchlorosilane or benzoyl chloride are easily extracted from the reaction mixture:

$$ArSeSiMe_3 + RNCl_2 \xrightarrow[-15\text{ to }5\ ^\circ C]{CCl_4} \underset{(V)}{ArSe(=NR)Cl} + Me_3SiCl,$$

$$R = SO_2Ar,\ COAr\ \ COOC_2H_5,\ (AlkO)_2P(O).$$

$$p\text{-}BrC_6H_4SeCOPh + PhSO_2NCl_2 \rightarrow p\text{-}BrC_6H_4Se(=NSO_2Ph)Cl + PhCOCl.$$

Arene-*N*-arylsulphonylimidoseleninyl chlorides are also formed by reaction of areneselenenyl chlorides with *N*-sodium-*N*-chloramides of arenesulphonic acids:[19]

$$ArSeCl + PhSO_2NNaCl \xrightarrow[10-20^\circ C]{CCl_4} (V) + NaCl.$$

When areneselenenyl chlorides are reacted with *N,N*-dichloramides of sulphonic and carboxylic acids, arylselenium trichlorides are formed together with chlorides (V):[19,29]

$$2ArSeCl + RNCl_2 \rightarrow (V) + ArSeCl_3,$$
$$R = SO_2Ar^1,\ COAr^1.$$

Diselenides also readily react with *N,N*-dichloramides to form chlorides (V) and areneselenenyl chlorides:[19,29]

$$ArSeSeAr + RNCl_2 \rightarrow (V) + ArSeCl.$$

Most likely when ArSeX reacts with *N,N*-dichloramides compounds of tetracoordinate selenium are first formed, undergoing subsequent conversion to form chlorides (V):

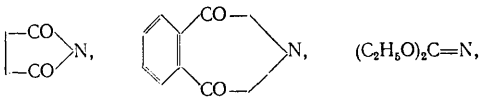
$$ArSeX + RNClZ \longrightarrow \left[\begin{array}{c} Cl \\ | \\ ArSe-X \\ | \\ R-N-Z \end{array}\right] \longrightarrow (V) + XZ,$$

$X = SiMe_3$, COR, SeR, Cl; $Z = Cl$, Na.

This is confirmed by studying the reactions of areneselenenyl chlorides with *N*-chlorimides and *N*-monochloramides of carboxylic acids, and with t-butyl hypochlorite, etc.

When areneselenenyl chlorides are reacted with *N*-chlorimides, fairly stable compounds of tetracoordinate selenium (VI) are obtained:[31]

$$ArSeCl + R_2NCl \rightarrow Ar(R_2N)SeCl_2,$$

$R_2N =$ , $(C_2H_5O)_2C{=}N$,

$PhC(OAlk){=}N$, $Ph_2C{=}N$ etc.

Compounds of tetracoordinate selenium (VII) and (VIII) are formed by reaction of areneselenenyl chlorides with carboxylic acid *N*-monochloramides[32,33] or with 6-butyl hypochlorite:[11,34]

$$ArSeCl + RCONHCl \rightarrow \underset{(VII)}{Ar(RCONH)SeCl_2},$$

$$ArSeCl + t\text{-}BuOCl \rightarrow \underset{(VIII)}{Ar(t\text{-}BuO)SeCl_2}.$$

Arene-*N*-R-imidoseleninyl chlorides (V) are very readily obtained when arylselenium trichlorides are treated with bis(trimethylsilyl)-amides of sulphonic or carboxylic acids[29] or by heating arylselenenium trichlorides with *N,N*-dichloramides.[29] However, the latter reaction is reversible and chlorides (V) are only obtained when chlorine is removed from the reaction mixture.

$$ArSeCl_3 \left\{\begin{array}{l} \xrightarrow{RN(SiMe_3)_2} (V) + 2Me_3SiCl \\ \xrightarrow{RNCl_2,\ \Delta} (V) + Cl_2 \end{array}\right.$$

$R = SO_2Ph$, COPh.

When *N*-chlorohexamethyldisilazane is reacted with areneselenenyl chloride and arylselenium trichloride in the ratio 1 : 1 : 1, compounds which apparently have the structure of arene-*N*-[aryl(dichloro)-seleno]imidoseleninyl chlorides (IX) are formed.[35] The above-mentioned reactions of areneseleninyl chlorides with *N*-chlorimides and areneselenium trichlorides with bis(trimethylsilyl)amides provided the basis for the following proposed reaction scheme:

$$ArSeCl + ClN(SiMe_3)_2 \rightarrow [Ar(Cl_2)SeN(SiMe_3)_2] \rightarrow$$
$$\xrightarrow[-2Me_3SiCl]{ArSeCl_3} \underset{(IX)}{ArSe(Cl_2)N{=}Se(Cl)Ar}.$$

The formation of isomeric chlorides (IX) as a result of the following reaction acts as confirmation of this scheme and the structure of the compounds formed.

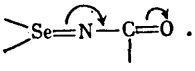
$$p\text{-}ClC_6H_4SeCl + ClN(SiMe_3)_2 \rightarrow [p\text{-}ClC_6H_4Se(Cl_2)N(SiMe_3)_2] \rightarrow$$
$$\xrightarrow{+PhSeCl_3} \underset{(IXa)}{p\text{-}ClC_6H_4Se(Cl_2)N{=}Se(Cl)Ph};$$

$$PhSeCl + ClN(SiMe_3)_2 \rightarrow [PhSe(Cl_2)N(SiMe_3)_2] \rightarrow$$
$$\xrightarrow{p\text{-}ClC_6H_4SeCl_3} \underset{(IXb)}{PhSe(Cl_2)N{=}Se(Cl)C_6H_4Cl\text{-}p}.$$

Compounds (IX) are also obtained by reaction of *N*-chlorohexamethyldisiliazane with benzeneselenenyl chloride or phenylselenium trichloride but in lower yield. The reactions are evidently more complex in these cases.[35]

N-R-Imidoseleninyl chlorides (V) and (IX) are colourless or pale yellow crystalline compounds, readily soluble in chloroform, dichloroethane, and acetonitrile; on standing in the absence of moisture they decompose after 3–5 days.[19,28,29,35]

In the IR spectra of *N*-arylsulphonylimidoseleninyl chlorides (V), $R = SO_2Ar$, $\nu(Se{=}N)$ apparently occurs in the region 910–950 cm^{-1},[24,27] while for *N*-aroylimidoseleninyl chlorides (V), R = COAr, it is in the region 845–870 cm^{-1}.[29] The shift to longer wavelength is evidently due to delocalisation of the π-electrons in the system



Chlorides (V) and (IX) are readily hydrolysed to seleninic acids and amides:[19,28,29,35]

$$(V) + 2H_2O \rightarrow ArSeOOH + RNH_2 + HCl,$$
$$(IX) + 4H_2O \rightarrow 2ArSeOOH + NH_4Cl + 2HCl.$$

When treated with dry hydrogen chloride or chlorine, compounds (V) and (IX) undergo cleavage of the Se = N bond to form arylselenium trichlorides and amides or *N,N*-dichloramides:[19,29,35]

$$(V) \left\{\begin{array}{l} \xrightarrow{2HCl} ArSeCl_3 + RNH_2 \\ \xrightarrow{2Cl_2} ArSeCl_3 + RNCl_2, \end{array}\right.$$

$$(IX)\begin{cases}\xrightarrow{4HCl} 2ArSeCl_3 + NH_4Cl\\ \xrightarrow{3Cl_2} 2ArSeCl_3 + [NCl_3]\end{cases}.$$

Chlorides (V) react with secondary amines to form the corresponding *N*-R-imidoseleninic acid amides, which are colourless crystalline or liquid, compounds that are very readily hydrolysed by atmospheric moisture and slowly decompose on standing when moisture is excluded:[19,29]

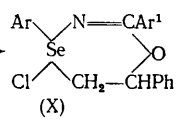
$$(V)\xrightarrow[-R_2NH.HCl\ \text{or}\ R_2NSiMe_3\ -Me_3SiCl]{2R_2NH} ArSe(=NR^1)NR_2$$

$R^1 = SO_2Ar,\ COAr;\ R_2N = (C_2H_5)_2N,$ .

Arene-*N*-arylsulphonylimidoseleninyl chlorides react with styrene to form a mixture of compounds from which *Se*-aryl-*Se*-styryl-*N*-arylsulphonylselenimides are isolated in about 50% yield:[19]

$$ArSe(=NSO_2Ar^1)Cl + PhCH{=}CH_2 \xrightarrow[-HCl]{20^\circ C} ArSe(=NSO_2Ar^1)CH{=}CHPh.$$

Arene-*N*-aroylimidoseleninyl chlorides react with styrene by a [2 + 4]-cycloaddition to form 1 : 1 adducts, which apparently have the structure of 5,6-dihydro-4-selena-1,3-oxazines (X):[29]

$$ArSe(=NCOAr^1)Cl + PhCH{=}CH_2 \rightarrow$$ 
(X)

Compounds (X) are colourless crystalline compounds, difficultly soluble in most organic solvents. In their IR spectra $\nu(C = N)$ is present at 1580 cm^{-1} and $\nu(Se-N)$ at 589 cm^{-1}, and there is no absorption in the region 840–870 cm^{-1} that is characteristic of the Se = N bond in the initial chlorides. The electrical conductivity of saturated solutions of compounds (X) in dichloroethane or methanol is higher than the electrical conductivity of the solvent by a factor of 10 or 100 respectively, which is an indication of the contribution from an ionic structure.[29]

V. *N*-R-imidoselenous dihalides

The first examples of this class of compounds—*N*-arylsulphonylimidoselenyl chlorides—were obtained in 1967 by reaction of selenium with arenesulphonic acid *N*,*N*-dichloramides.[36] It was subsequently established that oxidative imination of selenium has a wide range of application. Selenium reacts in a similar manner with the *N*,*N*-dichloramides of sulphonic and benzoic acids, and with dialkyl *N*,*N*-dichlorophosphoramidate, *N*,*N*-dichlorourethane, *N*,*N*-dichloroalkylamines, and *N*,*N*-dichloroaminopentafluorosulphur to form the corresponding *N*-R-imidoselenyl chlorides (XI):[37–41]

$$Se + RNCl_2 \xrightarrow[20^\circ C]{CH_2Cl_2\ \text{or}\ CCl_4} RN{=}SeCl_2, \quad (XI)$$

$R = SO_2Ar,\ COAr,\ C_2H_5OCO,\ (AlkO)_2PO,\ Me_2C(CN),\ (CH_2)_5(CN),\ R_F,\ F_5S.$

In inert solvents (methylene dichloride, carbon tetrachloride, dichloroethane, etc.) the reactions generally take place at 20 °C or with slight evolution of heat.

Sulphur, as a rule, reacts with *N*,*N*-dichloramides and *N*,*N*-dichloramines in a similar manner.[42] However, it should be noted that there are some differences between the oxidative imination of sulphur and selenium. Imination of sulphur is assisted when catalysts are present (iodine, tetraalkylammonium salts, etc.).[42] In most cases selenium reacts with *N*,*N*-dichloro compounds more readily than sulphur and the reaction is unaffected by catalysts. When sulphur is reacted with sulphinic acid *N*,*N*-dichloramides, the corresponding *N*-R-imidothionyl chlorides or sulphur diimide derivatives are formed depending on the ratio of reactants and the reaction conditions.[42] When selenium reacts with these reagents only *N*-R-imidoselenyl chlorides are obtained regardless of the ratio.[37]

It was established that *N*-perfluoroalkylimidoselenyl chlorides are also formed by reaction of *N*,*N*-dichloroperfluoroalkylamines with selenium monochloride:[39,40]

$$RNCl_2 + Se_2Cl_2 \xrightarrow[-50^\circ C]{CCl_3F} (XI) + SeCl_4,$$
$$R = CF_3,\ C_2F_5.$$

It has been reported that *N*-R-imidothionyl chlorides $Cl_2 = SNCOR$, R = Ar, Alk, are obtained by reaction of sulphur with carboxylic acid *N*-monochloramides.[42] Selenium also very readily reacts with carboxylic acid *N*-monochloramides, but in this case derivatives of orthoselenous acid—bis(R-carbacylamido)selenium dichlorides (XII)—are formed:[31–33]

$$2RCONHCl + Se \rightarrow (RCONH)_2SeCl_2, \quad (XII)$$
$$R = Ar,\ Alk.$$

When selenium is reacted with *N*,*N*-dichloroperfluoroaryl- or *N*,*N*-dichlorotetrafluoropyridyl-4-amines, the corresponding azo compounds and selenium tetrachloride are formed:[39]

$$Se + 2RNCl_2 \rightarrow RN{=}NR + SeCl_4,$$
$$R = C_6F_5,\ p\text{-}CF_3C_6F_4,\ 4\text{-}C_5F_4N.$$

The reaction schemes for the oxidative imination of both selenium and sulphur have not yet been established. It has been proposed that sulphur or selenium on reacting with *N*,*N*-dichloro compounds by a radical or ionic mechanism form the intermediates RN(Cl)ECl, which, depending on the nature of R (the state of the E–Cl bond), undergo conversions by three different routes—to form *N*-R-imidothionyl chlorides (*N*-R-imidoselenyl chlorides), azo compounds, or derivatives of sulphur diimides (the latter conversion is not typical for selenium):[39]

$$RNCl_2 + E \rightarrow [RN(Cl)ECl]\begin{cases}\xrightarrow{E=S,\ Se} RN{=}ECl_2\\ \xrightarrow{-ECl_2} [RN{:}] \rightarrow {}^1/_2\,RN{=}NR\\ \xrightarrow{E=S,\ -Cl_2} [RN{=}S] \rightarrow {}^1/_2\,RN{=}S{=}NR + {}^1/_2\,S_8\end{cases}$$

N-R-Imidoselenyl chlorides and fluorides are very readily formed by the reaction of selenium tetrachloride or tetrafluoride with *N*,*N*-bis-(trimethylsilyl)amides:[43,44]

$$RN(SiMe_3)_2 + SeHal_4 \rightarrow RN{=}SeHal_2 + 2Me_3SiHal,$$
$$R = MeSO_2,\ PhSO_2,\ PhCO;\quad Hal = Cl,\ F.$$

N-Pentafluorotelluroimidoselenyl fluoride is obtained by reaction of selenium tetrafluoride with *N*-trimethylsilylpentafluorotellur-amine:[44]

$$F_5TeNHSiMe_3 + SeF_4 \rightarrow F_5TeN{=}SeF_2 + Me_3SiF + HF.$$

On heating pentafluorotelluramine with selenium tetrachloride, *N*-pentafluorotelluroimidoselenyl chloride is formed:[44]

$$F_5TeNH_2 + SeCl_4 \xrightarrow{CH_2Cl_2,\ \Delta} F_5TeN{=}SeCl_2 + 2HCl.$$

Selenium tetrachloride reacts on heating with *N,N*-dichlorobenzenesulphonamide to form *N*-phenylsulphonylimidoselenyl chloride:

$$PhSO_2NCl_2 + SeCl_4 \rightarrow PhSO_2N{=}SeCl_2 + 2Cl_2.$$
(XI)

However, this reaction is reversible and goes to the right only when chlorine is removed from the reaction mixture.[37]

N-R-Imidoselenyl chlorides and fluorides are colourless or pale yellow crystalline compounds with low stability. Their stability improves when the electronegativity of the radical R is increased. Out of the compounds of this class that are known at the present time the most stable are *N*-pentafluorotelluroimidoselenyl chlorides[44] and *N*-arylsulphonylimidoselenyl chlorides.[36,37] *N*-Perfluoroalkylimidoselenyl chlorides start to decompose immediately after preparation or distillation according to the scheme:[41]

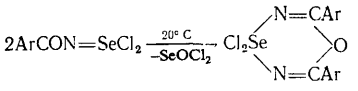
$$6R_FN{=}SeCl_2 \rightarrow 3R_FN{=}NR_F + 2SeCl_4 + 2Se_2Cl_2.$$

It is very likely that *N*-perfluoroarylimidoselenyl chlorides cannot be obtained because of their extremely low stability and not because there is a different pathway for the reaction between selenium and *N,N*-dichloroperfluoroarylamines.[39]

N-Pentafluorothioimidoselenyl chloride undergoes the following conversions even at room temperature:[40,41]

$$2F_5SN{=}SeCl_2 \xrightarrow{20^\circ C} 2F_3S{\equiv}N + SeCl_4 + SeF_4.$$

N-Aroylimidoselenyl chlorides slowly decompose at 20 °C with the elimination of selenyl chloride and giving compounds which apparently have the structure of 4-dichloro-4,1,3,5-selenaoxadiazines:



In the IR spectra of imidoselenyl chlorides (XI) the absorption due to ν(Se = N) varies over a quite broad region (Table 1). The lowest value of ν(Se = N) is that in *N*-aroylimidoselenyl chlorides; ν(C = O) (1600 cm^{-1}) is also decreased in these compounds at the same time, which is probably due to delocalisation of electron density in the group[38]

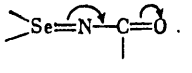


Table 1. Frequencies of the stretching vibrations of the Se = N bond in the IR spectra of *N*-R-imidoselenyl chlorides.

R	ν (Se=N)·см⁻¹	Refs.	R	ν (Se=N), см⁻¹	Refs.
F_5S	1045	[40]	C_2F_5	933	[41]
F_5Te	965	[44]	$(CH_3)_3C$	960	[37]
$ArSO_2$	980—975	[24, 37]	$(CH_2)_4C(CN)$	950	[37]
CF_3	962	[41]	ArCO	765—750	[38]

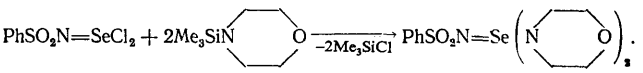
Compounds (XI) are very reactive. They are hydrolysed even by moist air to form amides and amines, selenous acid, and hydrogen chloride.[37] Acidolysis of *N*-phenylsulphonylimidoselenyl chlorides with formic acid results in the formation of benzenesulphonamide and selenyl chloride:[37]

$$PhSO_2N{=}SeCl_2 + 2HCOOH \rightarrow PhSO_2NH_2 + SeOCl_2 + 2CO.$$

Compounds (XI) very readily undergo cleavage of the Se = N bond when treated with hydrogen chloride or chlorine:[37,38]

$$(XI) \begin{cases} \xrightarrow{2HCl} RNH_2 + SeCl_4 \\ \xrightarrow{2Cl_2} RNCl_2 + SeCl_4 \end{cases}$$
R = $ArSO_2$, ArCO, Alk.

When *N*-phenylsulphonylimidoselenyl chloride is reacted with *N*-trimethylsilylmorpholine, the dimorpholide of *N*-phenylsulphonylimidoselenous acid is obtained:[37]

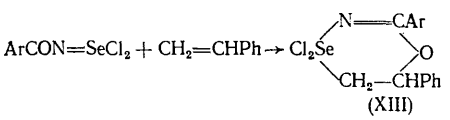


When compounds (XI) are reacted with *N,N*-bis(trimethylsilyl)-amides, selenium diimide derivatives are formed,[38,45] (see below).

N-R-Imidoselenyl chlorides react very readily with unsaturated compounds. The course of the reaction depends on the nature of the acyl residue. For example, *N*-phenylsulphonylimidoselenyl chloride reacts with styrene in the ratio 1 : 2 to form *Se,Se*-[bis(2-chloro-2-phenylethyl)]-*N*-phenylsulphonylselenimide:[37]

$$PhSO_2N{=}SeCl_2 + 2PhCH{=}CH_2 \rightarrow PhSO_2N{=}Se(CH_2CHClPh)_2.$$

N-Aroylimidoselenyl chlorides react with ethylenic hydrocarbons in the ratio 1 : 1 by a [4 + 2]-cycloaddition mechanism to form 4,4-dichloro-5,6-dihydro-4,1,3-selenaoxazines (XIII):[38,46]


(XIII)

Compounds (XIII) are colourless crystalline compounds which are difficultly soluble in most organic solvents. When compound (XIII), Ar = COPh, is treated with methanol, (2-phenyl-2-benzoyloxyethyl)-(methoxyl)selenium dichloride is obtained:[38]

$$(XIII) + MeOH \rightarrow PhC(O)OCH(Ph)CH_2Se(OMe)Cl_2.$$

For other properties of compounds (XIII), see below.

VI. Aza analogues of selenium dioxide

Out of the aza analogues of oxygen compounds of sulphur, the nitrogen analogues of sulphur dioxide—thionylamines and thionylamides RN = S = O and sulphur diimide derivatives RN = S = NR—have attracted particular attention. The high reactivity and preparative availability of these classes of compounds have offered considerable potential for their use in organic synthesis, which is suggested by the large number of publications, review articles, and monographs (see bibliograph of Bussas et al.[47]). This has undoubtedly stimulated interest in the aza analogues of selenium dioxide—derivatives of selenium diimide and selenylamines or selenylamides.

1. Selenium diimide deriatives

One of the main methods of synthesising symmetrical deriatives of selenium diimide (XIV) is the reaction of selenium tetrafluoride or tetrachloride with bis(trimethylsilyl)amides of sulphonic or carboxylic acids:[43,45,48–50]

$$SeHal_4 + 2RN(SiMe_3)_2 \xrightarrow[-4Me_3SiHal]{15-20^\circ C} RN{=}Se{=}NR, \quad (XIV)$$
$$R = ArSO_2,\ ArCO,\ AlkCO;\quad Hal = Cl,\ F.$$

Symmetric and asymmetric derivatives of selenium diimide are obtained by the reaction of hexamethyldisilylamides with *N*-acylimidoselenyl chlorides or fluorides[43,45,49]

$$RN{=}SeHal_2 + R^1N(SiMe_3)_2 \xrightarrow[-2Me_3SiHal]{\text{ether, } 0-20\ ^\circ C} RN{=}Se{=}NR^1,$$
$$R = ArSO_2,\ PhCO,\quad R^1 = ArSO_2,\ ArCO,\ AlkCO;$$
$$Hal = Cl,\ F.$$

Selenium bis(sulphonyl)diimides are unexpectedly obtained by reaction of *N*,*N*-bis(trimethylsilyl)amides with selenyl fluoride or chloride.[43,51] By analogy with the reaction of thionyl chloride[47] formation of the corresponding *N*-R-selenylamides RN = Se = O would be expected.[47] However, only selenium diimide derivatives are formed as a result of this reaction, whatever the ratio of reactants:

$$SeOHal_2 + RN(SiMe_3)_2 \xrightarrow{-Me_3SiHal} [RN{=}Se{=}O] \xrightarrow[-(Me_3Si)_2O]{RN(SiMe_3)_2} (XIV),$$
$$R = PhSO_2,\ MeSO_2,\ CF_3CO,\ CF_3SO_2;\quad Hal = Cl,\ F.$$

When *N*-phenylsulphonylimidoselenyl fluoride is reacted with hexamethyldisiloxane, selenium bis(phenylsulphonyl)diimide is obtained in place of the expected *N*-selenylbenzenesulphonamide. It has been proposed that in this reaction, as in the previous one, *N*-selenylamides are formed as intermediates:[43]

$$PhSO_2N{=}SeF_2 + (Me_3Si)_2O \xrightarrow{-2Me_3SiF} [PhSO_2N{=}Se{=}O] \rightarrow$$
$$\xrightarrow[-SeOF_2]{PhSO_2N=SeF_2} (PhSO_2N{=})_2Se.$$

Selenium *N*,*N*-bis(trimethylsilyl)diimide is obtained by reaction of Li hexamethyldisilazane with selenyl chloride:[51]

$$2(Me_3Si)_2NLi + SeOCl_2 \rightarrow (Me_3SiN{=})_2Se + Me_3SiCl + LiCl.$$

Reaction of selenium tetrachloride with t-butylamine gives selenium bis(t-butyl)diimide:[52,53]

$$SeCl_4 + 6\ t\text{-}BuNH_2 \xrightarrow[-4\ t\text{-}BuNH_2HCl]{\text{ether, } 25\ ^\circ C} (t\text{-}BuN{=})_2Se.$$

Selenium diimide derivatives (XIX) are light yellow crystalline compounds that are fairly readily soluble in methylene dichloride and dichloroethane. They have low thermal stability—at 20 °C they can be kept for 2–3 days in the absence of moisture while on heating they rapidly decompose.[18,43,45,48–52] Selenium bis(t-butyl)diimide is a liquid which decomposes at room temperature to form *N*,*N*′-di(t-butyl)-2,4,5-triselena-1,3-diazolidine, which a yellow crystalline product:[52]

$$3(t\text{-}BuN{=})_2Se \xrightarrow[-(t\text{-}BuN=)_2]{} t\text{-}Bu{-}N\begin{array}{c}Se\\|\\Se\end{array}N{-}Bu\text{-}t.$$

Selenium bis(trifluoromethylseleno)diimide is stable only up to 80 °C. Above that temperature the compound decomposes:[51]

$$(F_3CSeN{=})_2Se \rightarrow CF_3SeSeCF_3 + Se + N_2.$$

Selenium bis(trimethylsilyl)diimide decomposes even at −48 °C. The structure of this compound has been demonstrated from its chemical reactions.[51]

In the IR spectra of selenium diimide derivatives, the intense absorption bands in the region 1000–900 cm^{-1} are due to the Se=N bond frequencies.[45,49] In the IR spectrum of selenium bis(t-butyl)-diimide two absorption bands at 998 cm^{-1} (*as*) and 650 cm^{-1} (*s*) have been attributed to stretching vibrations of the Se = N bond.[52] In the PMR spectrum of this compound (in $CDCl_3$ in the presence of shift reagents) at −30 °C there are two signals (δ 1.38 and 1.40) which coalesce at 5 °C. On the basis of this it was proposed that at low temperature selenium bis(t-butyl)diimide has a (*Z*/*E*)-configuration:[52]

$$\begin{array}{c}\text{Bu-t}\\ /\\ N{=}Se{=}N\\ |\\ \text{t-Bu}\end{array}.$$

Selenium diimide derivatives (XIV) are very reactive compounds. They are readily hydrolysed by atmospheric moisture to the corresponding amides or amines and selenous acid.[45,49] When treated with dry hydrogen chloride selenium diimides undergo cleavage of the Se = N bond to form the corresponding amides and selenium tetrachloride:[45]

$$(PhSO_2N{=})_2Se + 4HCl \rightarrow 2PhSO_2NH_2 + SeCl_4.$$

The reaction of selenium bis(arylsulphonyl)diimide with chlorine occurs in two stages. Firstly, when the reagents are reacted in the ratio 1 : 2, *N*,*N*-dichlorobenzenesulphonamide and *N*-phenylsulphonylimidoselenyl chloride are obtained, the latter decomposing on further treatment with chlorine to give *N*,*N*-dichlorobenzenesulphonamide and selenium tetrachloride:[45]

$$(PhSO_2N{=})_2Se \xrightarrow{2Cl_2} PhSO_2NCl_2 + PhSO_2N{=}SeCl_2 \rightarrow$$
$$\xrightarrow{2Cl_2} SeCl_4 + PhSO_2NCl_2.$$

Selenium bis(arylsulphonyl)diimides react with compounds containing an X=O group (aldehydes, dimethylformamide, diphenyl selenoxide, triphenylphosphine oxide, etc.) to form compounds with an X = NSO_2Ar group:[17]

$$(PhSO_2N{=})_2Se + 2X{=}O \rightarrow 2X{=}NSO_2Ph + SeO_2,$$
$$X = ArCH,\ Me_2NCH,\ Me_2S,\ Ph_2S,\ Ph_2Se,$$
$$Ph_3P,\ Ph_2Se(=O),\ (C_2H_5)_2NC_6H_4N.$$

Selenium bis(benzoyl)diimide (XIV), R = PhCO, reacts with dimethyl sulphoxide in a similar manner:[17]

$$(PhCON{=})_2Se + 2Me_2SO \rightarrow 2Me_2S{=}NCOPh + SeO_2.$$

Selenium bis(benzoyl)diimide does not react with aromatic aldehydes. However, in the presence of benzamide reaction occurs very readily and *N*,*N*′-dibenzoylamidals are formed.[17] Apparently in this case selenium bis(benzoyl)diimide acts as a dehydrating agent in the reaction between benzamide and aldehyde, and the rate of this reaction, which is a source of benzamide, is much higher than the rate of reaction between the selenium diimide and aldehydes. The overall equation for the reaction is as follows:

$$2ArCHO + 2PhCONH_2 + (PhCON)_2Se \rightarrow 2ArCH(NHCOPh)_2 + SeO_2.$$

Selenium bis(phenylsulphonyl)diimide initially reacts with triphenylphosphine to give a 1 : 1 adduct, which on treatment with a further mole of triphenylphosphine forms triphenylphosphine selenide and a compound which probably has the structure of *N,N'*-bis(phenylsulphonyl)-*N*-triphenylphosphoniohydrazinate:[17]

$$(PhSO_2N{=})_2Se + Ph_3P \rightarrow [PhSO_2N{-}Se{-}\overline{N}SO_2Ph] \rightarrow \underset{\overset{|}{{}^+PPh_3}}{} \xrightarrow[-Ph_3PSe]{Ph_3P} PhSO_2N{-}\overline{N}SO_2Ph.$$
$$\underset{\overset{|}{{}^+PPh_3}}{}$$

Triphenylphosphine oxide, benzonitrile, and selenium are formed from selenium bis(benzene)diimide on reacting with triphenylphosphine:[17]

$$(PhCON{=})_2Se + 2Ph_3P \rightarrow 2Ph_3PO + 2PhCN + Se.$$

Reaction of selenium bis(trimethylsilyl)diimide with benzenesulphonyl chloride gives the corresponding bis(phenylsulphonyl)diimide:[51]

$$(Me_3SiN{=})_2Se + PhSO_2Cl \rightarrow (PhSO_2N{=})_2Se + 2Me_3SiCl.$$

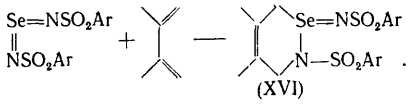
Selenium diimide derivatives react very readily with unsaturated compounds. The course of the reaction depends on the structure of the initial reagents. Disubstituted selenium diimides that contain just one acyl group on the nitrogen atom react with unsaturated compounds (styrene, cyclohexene, 1,1-diphenylethylene, etc.) by a [4 + 2]-cycloaddition mechanism to form 4-imino-5,6-dihydro-4,1,3-selenaoxazines, which are colourless crystalline compounds.[46,49] In particular, when selenium *N*-benzoyl-*N'*-phenylsulphonyldiimide is reacted with styrene, 4-phenylsulphonylimino-5,6-dihydro-2,6-diphenyl-4,1,3-selenaoxazine (XV) is formed, being identical to the compound obtained by reaction of compound (XIII), Ar = Ph, with bis(trimethylsilyl)benzenesulphonamide (see Section V):

$$\left.\begin{array}{l} PhSO_2N{=}Se{=}NCOPh + CH_2{=}CHPh \\ (XIII) + PhSO_2N(SiMe_3)_2 \end{array}\right\} \rightarrow PhSO_2N{=}Se \underset{CH_2{-}CHPh}{\overset{N{=}CPh}{\diagdown\!\!\diagup O}} \quad (XV)$$

On hydrolysis of both compound (XIII) and compound (XV) the same 2-phenyl-2-benzoyloxyethaneseleninic acid is obtained:[38,49]

$$\left.\begin{array}{l} (XIII) \xrightarrow[-HCl,\ -NH_4Cl]{3H_2O} \\ (XV) \xrightarrow[-PhSO_2NH_2,\ -NH_3]{3H_2O} \end{array}\right\} \rightarrow PhC(O)OCH(Ph)CH_2SeOOH.$$

Selenium bis(arylsulphonyl)diimide reacts with hydrocarbon dienes by a [2 + 4]-cycloaddition mechanism to form 1 : 1 adducts, which apparently have the structure of 3,6-dihydro-1-arylsulphonyl-2-arylsulphonylimino-2,1-selenazines (XVI):[50]



(XVI)

Compounds (XVI) are colourless crystalline compounds, stable on standing at 20 °C when moisture is excluded.

In 1976 Sharpless et al.[53,54] reported the synthesis of selenium *N,N'*-ditosyldiimide by reaction of chloramine-T with selenium or selenium tetrachloride with *p*-toluenesulphonamide. In fact, chloramine-T and chloramine-B readily react with selenium in methylene dichloride or dichloroethane in the ratio 2 : 1. However, the compounds formed in this process differ in composition and physical and chemical properties from the coresponding selenium bis(arylsulphonyl)diimides described above.[45,49,50] The compounds obtained from chloramine-B or chloramine-T and selenium by the method of Sharpless[53,54] are colourless, finely crystalline compounds with quite a sharp melting point. In contrast to the corresponding selenium bis(arylsulphonyl)diimides, they are insoluble in methylene dichloride, dichloroethane, and other organic solvents. On the basis of this it was proposed that when chloramine-B or chloramine-T react with selenium, the *N,N'*-disodium salts of bis(arylsulphonylamido)selenium dichloride (XVII) are formed:[50]

$$Se + 2ArSO_2NNaCl \rightarrow \underset{(XVII)}{[ArSO_2N(Na)]_2SeCl_2},$$
$$Ar = Ph,\ p\text{-}MeC_6H_4.$$

Indirect evidence for the structure of the "Sharpless products" is given by the reaction of selenium with carboxylic acid monochloramides, resulting in the formation of bis(aroylamino)selenium dichlorides (XII) (see Section V).[32,33]

When selenium tetrachloride is reacted with arenesulphonamides in the presence of triethylamine in dichloroethane (see the study of Sharpless[53]) selenium bis(arylsulphonyl)diimide is also possibly obtained. In fact, on mixing the reactants an orange-yellow colour characteristic of selenium diimides immediately appears. However, after 5–10 min the reaction mixture darkens and selenium separates out almost quantitatively. It was established by independent experiments that when triethylamine hydrochloride is added to selenium bis(arylsulphonyl)diimide in dichloroethane, the reaction mixture darkens after 1–3 min, selenium separates out, and a mixture of oily products of indeterminate structure is formed. It cannot be ruled out that selenium bis(arylsulphonyl)diimide forms a bis(triethylammonium) salt, which then decomposes:[50]

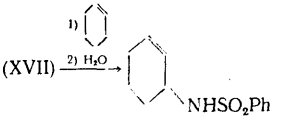
$$(ArSO_2N{=})_2Se + 2Et_3N{\cdot}HCl \rightarrow (ArSO_2NH{\cdot}Et_3N)_2SeCl_2.$$

This proposal is indirectly supported by the reaction of triethylamine hydrochloride with selenium bis(benzoyl)diimide, which results in the formation of bis(benzoylamino)selenium dichloride (XII) (see Section V):

$$(PhCON{=})_2Se + 2Et_3N{\cdot}HCl \rightarrow \underset{(XII)}{(PhCONH)_2SeCl_2} + 2Et_3N.$$

Compound (XII) has been isolated and identified; but if it is not immediately isolated from the reaction mixture, the latter gradually darkens (after 10–15 min) and selenium separates out.[50]

A difference between the properties of selenium diimide derivatives and "Sharpless products" is also revealed in reactions with unsaturated compounds. When (XVII) is reacted with olefins, products derived from allylic amidation[50] are obtained (cf. the studies of Sharpless[53,54]), for example:

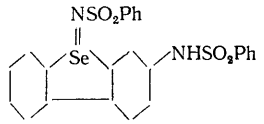


Selenium bis(arylsulphonyl)diimide also react with olefins, but the course of the reaction depends on the nature of the olefin. When α-methylstyrene is reacted with selenium bis(phenylsulphonyl)-

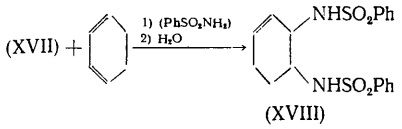
diimide, as also with compound (XVII), 2-phenyl-3-phenylsulphonylaminopropene is obtained[50] (cf. Sharpless[53,55]):

$$(PhSO_2N{=})_2Se \text{ or } (XVII) \xrightarrow[2)\ H_2O]{1)\ PhC(Me){=}CH_2} PhC(CH_2NHSO_2Ph){=}CH_2.$$

However, these compounds react in different ways with cyclohexene. Compound (XVII) gives *N*-benzenesulphonamido-2-cyclohexene, while from the products of the reaction between selenium bis(phenylsulphonyl)diimide and cyclohexene a product is isolated, which apparently has the structure of 1-phenylsulphonylamino-9-phenylsulphonylimino-9-selenaperhydrofluorene:[50]



When compounds (XVII) are reacted with cyclohexadiene in the presence of sulphonamide followed by hydrolysis, 1,2-bis(phenylsulphonylamino)-3-cyclohexene (XVIII) (cf. Sharpless[54]):



(XVIII)

When the products (XVI) of the reaction between disubstituted selenium diimides and hydrocarbon dienes were hydrolysed (Sharpless et al. suggested that these compounds were intermediates), it was not possible to obtain arylsulphonamidation compounds of the type (XVIII).[50]

2. Selenylamines

There is very little information about N = R-selenylamines and N = R-selenylamides. It was reported in 1932 that when aromatic amines are reacted with selenyl chloride, *N*-selenylarylamines (XIX) are formed:[56]

$$3ArNH_2 + SeOCl_2 \xrightarrow[-2ArNH_2\cdot HCl]{} ArN{=}Se{=}O, \quad (XIX)$$

Ar = Ph, *o*-MeC_6H_4.

Compounds (XIX) are orange-yellow oils which can be distilled under vacuum and decompose when heated at atmospheric pressure. On heating with aniline in the presence of zinc chloride, compounds (XIX) give difficultly soluble, dark green pigments containing selenium.

Reaction of t-butylamine with selenyl chloride gives *N*-t-butylselenylamine, which is a brown liquid that is extremely susceptible to hydrolysis:

$$3\ t\text{-}BuNH_2 + SeOCl_2 \xrightarrow[-2\ t\text{-}BuNH_2HCl]{\text{ether, } -10\ ^\circ C} t\text{-}BuNSeO.$$

When traces of moisture are present the product is converted to a colourless crystalline compound with mp 145 °C, which apparently has the structure of a selenous acid amide $t\text{-}BuNH_2.SeO_2$.[52] The NMR spectrum of t-butylselenylamine confirms the presence of t-butyl groups. In the IR spectrum of this compound the intense absorption and at 1110 cm^{-1} has been attributed to ν_{as}(NSeO) and the band at 625 cm^{-1} to ν_s(NSeO).[52]

As was indicated above, attempts to obtain *N*-selenylamide derivatives RNSeO, where R = $ArSO_2$, $AlkSO_2$, PhCO, AlkCO, Me_3Si, were not successful.[43,49] Evidently these compounds are extremely unstable and undergo further conversions.

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