SOME ASPECTS OF THE ORGANIC CHEMISTRY OF SELENIUM

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I. INTRODUCTION AND SCOPE OF THE REVIEW

The literature of the past seventy-five years is replete with references to organic compounds containing selenium. The references are, however, widely scattered, and only a few serious attempts have been made to study systematically the properties of these compounds. Furthermore, attempts to collect and evaluate the existing literature are few (55, 56, 57, 58, 59, 62, 63, 139, 281).

It is the intent of this article to collect the available information on the preparation and some of the unique properties of organoselenium compounds, in order to stimulate additional research in the field.

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To the best of our knowledge, the data cited in the tables and in the text are complete and accurate, although in a work of this type certain errors and omissions are inevitable. For the sake of a certain amount of brevity, the authors have not exhaustively considered the extensive literature on compounds in which the selenium is incorporated in a ring with nitrogen, except for a few interesting examples, nor have they considered the many complicated and highly specialized structures containing selenium which appear in the patent literature, principally as potential dyes or dye precursors.

TABLE 1

Nomenclature of organoselenium compounds

CLASS OF COMPOUND	GENERAL FORMULA	EXAMPLE	
		Formula	Name
Selenols	RSeH	C_2H_5SeH	Ethyl selenol or ethaneselenol
Selenoxides	RSeOR	$C_6H_5Se(=O)C_6H_4Cl$-4	4-Chlorophenyl phenyl selenoxide
Selenones	$RSeO_2R$	$C_6H_5SeO_2CH_3$	Methyl phenyl selenone
Selenium acids	$RSeO_3H$	$C_2H_5SeO_3H$	Ethylselenonic acid
	$RSeO_2H$	$C_2H_5SeO_2H$	Ethylseleninic acid
	RSeOH	C_2H_5SeOH	Ethylselenenic acid
Selenides	RSeR	CH_3SeCH_3	Methyl selenide or dimethyl selenide
Diselenides	RSeSeR	$CH_3SeSeC_2H_5$	Ethyl methyl diselenide
Derivatives of selenides	R_2SeX_2	$(C_6H_5)_2SeBr_2$	Diphenylselenium dibromide
	$RSeX_3$	CH_3SeCl_3	Methylselenium trichloride
	R_3SeX	$(C_6H_5)_3Se^+Br^-$	Triphenylselenonium bromide
Selenium analogs of ketones	RCSeR	$C_6H_5C(=Se)C_6H_5$	Selenobenzophenone
		$CH_3C(=Se)C_2H_5$	Seleno-2-butanone
Selenocyanates	RSeCN	4-$CH_3C_6H_4SeCN$	4-Selenocyanotoluene (when named as a derivative of toluene) or the 4-tolyl ester of selenocyanic acid

The body of the review contains a few leading references which apply to each type of reaction described. For complete references on a given compound or type of compounds, the reader should consult the appropriate tables.

II. NOMENCLATURE OF ORGANOSELENIUM COMPOUNDS

The nomenclature for organoselenium compounds retaining a systematic relationship to the nomenclature for other organic compounds of similar nature has been established for the use of *Chemical Abstracts*. Examples are given in table 1.

TABLE 2

Examples of the nomenclature used by Chemical Abstracts for organoselenium compounds

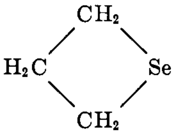
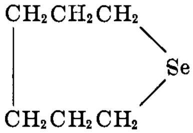
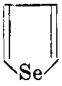
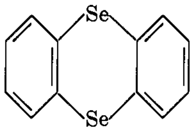
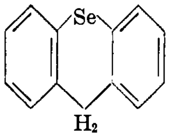
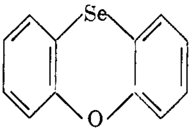
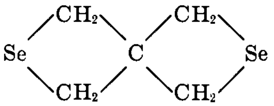
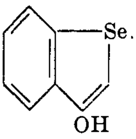
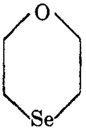
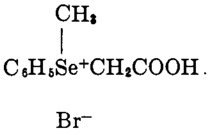
STRUCTURAL FORMULA	NAME
CH_3COSeH	Selenoacetic acid
CH_3SeCH_2COOH	(Methylselenyl)acetic acid
HO_2SeCH_2COOH	Seleninoacetic acid
$CH_3SeBr_2CH_2COOH$	(Methylselenyl)acetic acid, *Se*-dibromide
	Selenetane
	Selenepane
	Selenophene
	Dihydroselenophene dioxide
	Selenanthrene
	Selenoxanthene
	Phenoxaselenin
	2,6-Diselenaspiro[3.3]heptane

TABLE 2—*Concluded*

STRUCTURAL FORMULA	NAME
	2-Selenonaphthenal or 3-hydroxyselenonaphthene (in references prior to 1937)
	1,4-Selenoxane
$4\text{-}CNSeC_6H_4SeSeC_6H_4SeCN\text{-}4$	Bis(4-selenocyanophenyl) diselenide
$C_6H_5SeCH_2CH_2OH$	2-(Phenylselenyl)ethanol
 $C_6H_5\overset{CH_3}{\underset{Br^-}{Se^+}}CH_2COOH$	(Carboxymethyl)methylphenylselenonium bromide
$(C_6H_5)_3Se^+Br^-$	Triphenylselenonium bromide

The nomenclature for more complex compounds is in most cases not as obvious. As a general rule the compound is identified by its functional group corresponding to a carbon-containing functional group with the added suffix "seleno" or variation of "seleno" which best describes its function in the compound. A number of examples of the nomenclature employed by *Chemical Abstracts* for the more complex selenium compounds are given in table 2.

In many cases, the names used by *Chemical Abstracts* for indexing compounds are somewhat awkward and unnecessarily involved. Consequently, certain liberties have been taken with the *Chemical Abstracts* system in the body of this manuscript, where such liberties do not lead to any ambiguity and are, indeed, used consistently in the prior literature.

III. ANALYSIS OF ORGANOSELENIUM COMPOUNDS

Routine combustion analyses of organoselenium compounds cannot be carried out, since the selenium soon fouls the train; special methods are therefore required.

There are many procedures in the literature whereby an organoselenium compound can be degraded either to elementary selenium, which is determined gravimetrically, or to selenious acid, which is determined volumetrically (1, 62, 234, 277). A particularly suitable scheme of the latter type has been developed (234) which can be used routinely, once the apparatus has been set up.

Certain classes of organoselenium compounds can be analyzed directly, by volumetric methods, whereby an equivalent weight can be determined. Thus, selenide halides, selenoxides, and selenious acids react with acidified potassium iodide to liberate iodine, which can be determined in the usual way (234), while diselenides may be determined by titration to the iodine chloride end point (234):

$$R_2Se_2 + 6ICl \rightarrow 2RSeCl_3 + 3I_2$$
$$2I_2 + IO_3^- + 6H^+ + 5Cl^- = 3H_2O + 5ICl$$

IV. EVALUATION OF THE METHODS OF SYNTHESIS GIVEN IN THE LITERATURE FOR VARIOUS CLASSES OF ORGANOSELENIUM COMPOUNDS

A. Selenocyanates (see table 3)

The two most important methods for the introduction of the —SeCN group into an organic molecule are represented by equations 1 and 2:

$$RN_2^+ + SeCN^- \rightarrow RSeCN + N_2 \qquad (1)$$

$$RX + SeCN^- \rightarrow RSeCN + N_2 \qquad (2)$$

Reaction 1 is almost universally applicable for the preparation of compounds in which R is aromatic; the only limitation is that the corresponding diazonium compound be available. The reaction is very similar to the Gatterman modification of the Sandmeyer synthesis of aromatic iodides, and the yields and techniques are quite comparable (16, 26, 36, 37, 73, 81, 185, 189).

Method 2 is more generally applicable and may be used in any situation where the halogen in the halide is readily displaced by nucleophilic reagents (71, 72, 88, 106, 120, 124, 129, 142, 175, 346, 348).

The selenocyanate ion (most readily obtained from potassium selenocyanate, which may be prepared from potassium cyanide and selenium (38, 72)) is a good displacing agent. It has been clearly demonstrated that a Walden inversion occurs when the alkyl group of an alkyl *p*-toluenesulfonate is displaced by —SeCN (197). The similarity of selenocyanogen and the selenocyanate ion to the halogens and halide ions is noteworthy. Selenocyanogen has been classified as a "pseudohalogen" (82, 247, 344) with an activity which falls in the series F > ONC > OCN > Cl > N_3 > Br > CN > SCN > I > SeCN > TeCN.

Other methods which have been used for the preparation of selenocyanates, but which have no particular advantages for preparative purposes, are represented by equations 3, 4, and 5:

$$RSeX + KCN \rightarrow KX + RSeCN \qquad (3)$$

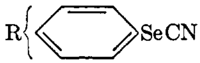
$$R_2Se_2 \xrightarrow[HgCl_2]{Hg(CN)_2} RSeCN \qquad (4)$$

$$R_3Bi + Se_3(CN)_2 \rightarrow R_2BiSeCN + RSeCN + Se \qquad (5)$$

Method 3 appears to give good yields, but has few advantages over method 1 or 2, since the prior synthesis of RSeX is required. This method has been employed for the preparation of selenothiocyanates (ArSeSCN) and selenylseleno-

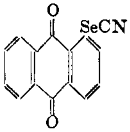
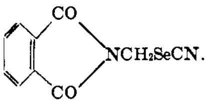
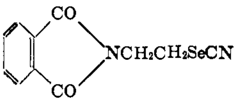
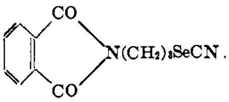
TABLE 3

Selenocyanates:



R	REFERENCES	R	REFERENCES
H	(37, 81)	4-OCH$_3$	(36, 172)
4-CH$_3$	(36, 82, 189, 303)	2-OCH$_3$	(36)
		4-COOH	(143)
3-CH$_3$	(36, 189)	4-COOCH$_3$	(196)
2-CH$_3$	(36, 189)	3-COOCH$_3$	(196)
2-C$_2$H$_5$	(29)	2-COOCH$_3$	(194)
2-C$_6$H$_5$	(29)	2-COCl	(218)
4-C$_6$H$_5$	(29)	4-CH$_3$COO$^-$	(191)
4-Cl	(81, 303)	4-CH$_3$CONH	(19, 81, 289)
3-Cl	(36, 38)	4-SCN	(73, 81)
2-Cl	(36)	4-CH$_3$-3-NO$_2$	(185)
2,4,6-Br$_3$	(32)	4-CH$_3$-2-NO$_2$	(187)
4-NO$_2$	(16, 19, 26, 36, 73, 81, 82)	3-CH$_3$-4-NO$_2$	(185)
		2-CH$_3$-5-NO$_2$	(185)
3-NO$_2$	(36, 81, 186)	2-CH$_3$-4-NO$_2$	(185)
2-NO$_2$	(16, 26, 36, 38, 81)	4,5-(CH$_3$)$_2$-2-NO$_2$	(185)
		3,4-(CH$_3$)$_2$-2-NO$_2$	(185)
2,4-(NO$_2$)$_2$	(30)	2,5-(CH$_3$)$_2$-4-NO$_2$	(185)
4-NH$_2$	(19, 36, 73, 82, 83)	2,3-(CH$_3$)$_2$-6-NO$_2$	(185)
		2-NO$_2$-4-Br	(30)
4-NHCH$_3$	(244)	3-NO$_2$-4-NH$_2$	(81)
4-N(CH$_3$)$_2$	(73, 82, 244)	3-NO$_2$-4-CH$_3$CONH	(81)
4-NHC$_2$H$_5$	(244)	3-COOH-4-CH$_3$COO$^-$	(195)
4-N(C$_2$H$_5$)$_2$	(244)		

Miscellaneous selenocyanates

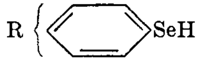
COMPOUND	REFERENCES	COMPOUND	REFERENCES
2-O$_2$NC$_6$H$_4$CH$_2$SeCN	(142, 175)	C$_6$H$_5$NHCOCH$_2$SeCN	(32)
C$_6$H$_5$CH$_2$SeCN	(175)	CH$_3$C$_6$H$_4$NHCOCH$_2$SeCN (*o*, *m*, and *p*)	(32)
(—SeC$_6$H$_4$SeCN-4)$_2$	(186)		
(—SeC$_6$H$_4$SeCN-3)$_2$	(186)	3-ClC$_6$H$_4$NHCOCH$_2$SeCN	(32)
Se(SeCN)$_3$	(344)	2-C$_2$H$_5$C$_6$H$_4$NHCOCH$_2$SeCN	(32)
2-C$_{10}$H$_7$SeCN	(225)	CH$_3$SeCN	(44)
2-O$_2$NC$_6$H$_4$SeSCN	(110)	C$_2$H$_5$SeCN	(44, 348)
(CH$_3$)$_2$C(CH$_2$SeCN)$_2$	(15)	*n*-C$_4$H$_9$SeCN	(346)
		tert-C$_4$H$_9$SeCN	(64)
	(32)	*n*-C$_6$H$_{13}$SeCN	(346)
		n-C$_{10}$H$_{21}$SeCN	(346)
		ClCH$_2$CH$_2$SeCN	(64)
		Cl$_2$CHCH$_2$SeCN	(64)
		Cl(CH$_2$)$_3$SeCN	(64)
		CH$_2$=CBrCH$_2$SeCN	(64)
		NCSe(CH$_2$)$_3$SeCN	(320)
NCSeCH$_2$C$_6$H$_4$CH$_2$SeCN-4	(64)	CH$_3$CH(SeCN)CH$_2$SeCN	(320)
		NCSe(CH$_2$)$_2$SeCN	(320)
		CH$_3$CH$_2$CH(CH$_3$)SeCN	(325)
		NCSeCH$_2$COOH	(35, 167)
	(64)	NCSeCH$_2$CH$_2$COOH	(121)
		CH$_3$CH$_2$CH(SeCN)COOH	(121)
		(CH$_3$)$_2$C(SeCN)COOH	(121)
		(CH$_3$)$_2$CHCH(SeCN)COOH	(124)
		CH$_2$=C(SeCN)COOH	(123)
	(64, 88)	CH$_3$COCH$_2$SeCN	(114, 167)
		CH$_3$CH(SeCN)COOK	(120, 121)
		HOOCCH(SeCN)CH$_2$CH$_2$CH(SeCN)-COOH	(126, 129)
		HOOCCH$_2$SeCN	(35, 121)
		HOOCCH$_2$CH$_2$SeCN	(120, 121)
	(88)	HOOCCH(CH$_3$)SeCN	(121)
		HOOCCH(SeCN)CH$_3$	(121)
		KOOC(SeCN)C=CH$_2$ (also the acid)	(123)
		[HOOCCH(SeCN)CH$_2$]$_2$	(126)
2-NCC$_6$H$_4$CH$_2$SeCN	(106)	C$_6$H$_5$NHCOCH$_2$SeCN	(321)

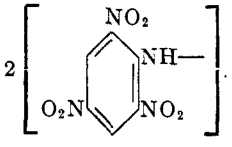
cyanates (ArSeSeCN) (110, 300a, 300b) (see table 6). Methods 4 and 5 are of no value synthetically (44, 82).

In addition, certain selenocyanates may be prepared in good yield by the direct selenocyanation of reactive intermediates, such as aniline and dimethylaniline (73, 82), with selenocyanogen (344), and in poor yield by the electrolysis of a mixture of potassium selenocyanate and an aromatic hydrocarbon (244).

TABLE 4

Selenols:



R	REFERENCES	R	REFERENCES
H	(116, 191, 205, 333, 334)	4-OH	(191)
4-Cl	(112, 333)	4-OC_2H_5	(333)
4-Br	(112, 333)	4-$COOCH_3$	(196)
4-CH_3	(189, 333)	3-$COOCH_3$	(196)
3-CH_3	(189, 190)	2-$COOCH_3$	(194)
2-CH_3	(114)	4-SeH	(186)
4-*i*-C_3H_7	(7)	3-SeH	(114, 186)
4-*tert*-C_4H_9	(7)		(27)
4-NH_2	(212, 296)		
3-NH_2	(115)		
2-NH_2	(26, 91)		
4-$NHCOCH_3$	(212, 296)		
2-NO_2	(24, 26)		

Miscellaneous selenols

COMPOUND	REFERENCES	COMPOUND	REFERENCES
C_2H_5SeH	(256, 313, 339)	$HSeCH_2COOH$	(35)
n-C_3H_7SeH	(339)	$CH_3OCH_2CH_2SeH$	(345)
n-C_4H_9SeH	(339)	CH_3SeH	(107)
$HOCH_2CHOHCH_2SeH$	(21)	2-$C_{10}H_7SeH$	(225)
$HSeCH_2CHOHCH_2SeH$	(21)	1-$C_{10}H_7SeH$	(333)
$HSeCH_2CH(SeH)CH_2$-SeH	(21)	2-$O_2NC_6H_4CH_2SeH$	(142)

B. Selenols (selenomercaptans) (see table 4)

Reactions leading to the formation of this type of compound can be classified loosely as (*a*) those in which selenium is introduced into the organic molecule with the direct production of a selenomercaptan, and (*b*) those in which a selenium-containing organic compound is reduced to a selenomercaptan by one of a variety of reducing agents.

In the first classification, the reaction of elementary selenium with a Grignard reagent appears to be universally applicable where the Grignard reagent is available (71, 72, 225, 237, 238):

$$\mathrm{RMgX + Se \rightarrow RSeMgX \xrightarrow{HX} RSeH + MgX_2} \tag{6}$$

The yields are consistently good, with both aromatic and aliphatic Grignard reagents, in contrast to the similar reaction with oxygen to give alcohol or phenol. The only necessary precaution (which must be observed in all syntheses of selenols) is to avoid contact with air or other oxidizing agents, since the selenols are easily oxidized:

$$2\mathrm{RSeH} + \tfrac{1}{2}\mathrm{O_2} \rightarrow \mathrm{H_2O} + \mathrm{RSeSeR} \qquad (7)$$

Other methods in the first category involve the displacement of halogen by one of a variety of reagents. These methods may be summarized by equations 8 and 9:

$$\mathrm{RX} + \mathrm{SeH^-} \rightarrow \mathrm{RSeH} + \mathrm{X^-} \qquad (21, 339) \qquad (8)$$

$$\begin{array}{l} \mathrm{RX} + \mathrm{SeSO_3^{--}} \rightarrow \mathrm{RSeSO_3^-} + \mathrm{X^-} \qquad (32, 345) \qquad (9) \\ \qquad\qquad\qquad\quad \downarrow \mathrm{H_2O} \\ \qquad\qquad\qquad\quad \mathrm{RSeH} + \mathrm{HOSO_3^-} \end{array}$$

In all cases the yields are satisfactory provided the halide is of the type readily displaced by nucleophilic reagents. In certain instances, alkylating agents other than halides, such as alkyl sulfates (313) and esters of toluenesulfonic acid (256), have been used.

TABLE 5

Reduction of selenium compounds to selenols

COMPOUNDS WHICH CAN BE REDUCED	REDUCING AGENTS WHICH MAY BE USED
RSeCN R_2Se_2 $ArSeO_2H$	Zinc and acetic acid Zinc and sodium hydroxide Sodium amalgam Hydrogen with a catalyst Sodium Raney nickel alloy and sodium hydroxide Sodium hyposulfite Alkaline glucose

A number of selenium-containing organic compounds, available by methods discussed elsewhere, are reduced to selenols, usually in near-quantitative yield, by a variety of reducing agents (26, 71, 72, 115, 186, 190, 194, 225) (see table 5).

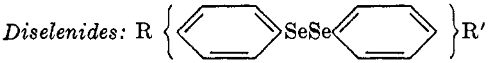
Frequently the selenols obtained by any of the above methods are not isolated, but are employed for further syntheses as the sodium or other salt. This procedure has certain advantages, since the selenols are notorious for their repulsive clinging odor and for this reason must be handled with considerable caution.

C. Diselenides (see table 6)

Diselenides are usually prepared by either of two types of reaction: one in which the diselenide group is directly introduced into the molecule, or one in which a selenium-containing compound is oxidized or reduced to diselenide.

TABLE 6

Diselenides:



R and R'	References
H	(20, 37, 60, 80, 98, 191, 205, 226, 227, 303, 310, 330, 332)
4,4'-$(CH_3)_2$	(36, 82, 189, 303, 333)
3,3'-$(CH_3)_2$	(189)
2,2'-$(CH_3)_2$	(36, 189, 190)
4,4'-$[C(CH_3)_3]_2$	(7)
4,4'-$[CH(CH_3)_2]_2$	(7)
4,4'-Cl_2	(82, 112, 333)
2,2'-Cl_2	(32)
4,4'-Br_2	(112, 303, 333)
2,4,6,2',4',6'-Br_6	(32)
3,3'-$(NO_2)_2$	(115, 295)
2,2'-$(NO_2)_2$	(26, 38)
2,4,2',4'-$(NO_2)_4$	(32, 340)
2,2'-$(NO_2)_2$-4,4'-$(CH_3)_2$	(81)
2,2'-$(NO_2)_2$-4,4'-Br_2	(30)
4,4'-$(NH_2)_2$	(19, 188, 242, 296)

R and R'	References
3,3'-$(NH_2)_2$	(186)
2,2'-$(NH_2)_2$	(26, 32, 38, 188)
4,4'-$(NHCOCH_3)_2$	(19, 296)
3,3'-$(NHCOCH_3)_2$	(242, 295)
2,2'-$(NH_2)_2$-6,6'-$(CH_3)_2$	(187, 188)
2,2'-$(NH_2)_2$-4,4'-$(CH_3)_2$	(187, 188)
4,4'-$(OH)_2$	(191, 242)
4,4'-$(CH_3COO)_2$	(191)
4,4'-$(OCH_3)_2$	(36)
4,4'-$(OC_2H_5)_2$	(333)
2,2'-$(OCH_3)_2$	(36)
4,4'-$(OH)_2$-3,3'-$(NH_2)_2$	(192, 196)
4,4'-$(CH_3CO)_2$	(191)
4,4'-$(COOH)_2$	(143)
2,2'-$(COOH)_2$	(219, 304)
2,2'-$(CONH_2)_2$	(219)
2,2'-$(COCOOR)_2$	(217)
4,4'-$(SeCN)_2$	(186)
3,3'-$(SeCN)_2$	(186)
4,4'-$(C_6H_5)_2$	(29)
2,2'-$(C_6H_5)_2$	(29)

Miscellaneous diselenides

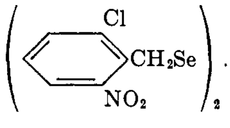
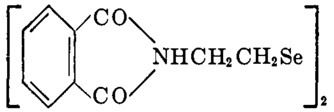
Compound	References
$(CH_3)_2Se_2$	(14, 44)
n-$(C_3H_7)_2Se_2$	(14, 44, 339)
n-$(C_4H_9)_2Se_2$	(14, 44)
$(CH_3OCH_2CH_2Se)_2$	(345)
$(C_2H_5OCH_2CH_2Se)_2$	(345)
$(C_4H_9OCH_2CH_2Se)_2$	(345)
$(H_2NCH_2CH_2Se)_2$	(72, 88)
$(H_2N(CH_2)_3Se)_2$	(72, 88)
$(2\text{-}ClC_6H_4CH_2Se)_2$	(321)
$(4\text{-}ClC_6H_4CH_2Se)_2$	(321)
$(4\text{-}BrC_6H_4CH_2Se)_2$	(321)
$(2\text{-}NCC_6H_4CH_2Se)_2$	(106)
$(C_6H_5CH_2Se)_2$	(71, 142, 173, 303, 330)
	(321)
	(72, 88)

TABLE 6—*Continued*

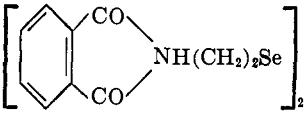
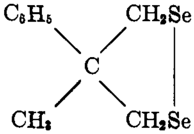
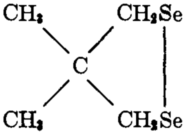
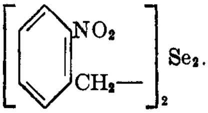
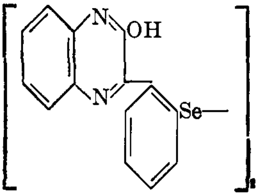
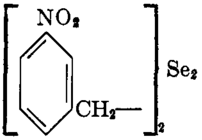
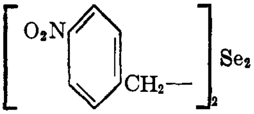
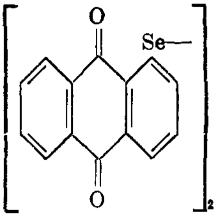
COMPOUND	REFERENCES
	(72, 88)
	(15)
	(15)
$(C_6H_5CH_2)_2Se_2$	(30, 142, 172, 294, 330)
	(142, 294)
	(219)
$(1\text{-}C_{10}H_7Se\text{—})_2$	(332)
$(2\text{-}C_{10}H_7Se\text{—})_2$	(225)
	(294)
	(294)
	(31)

TABLE 6—*Continued*

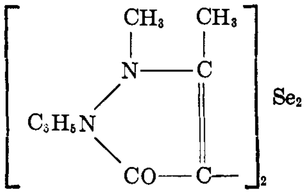
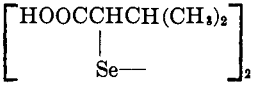
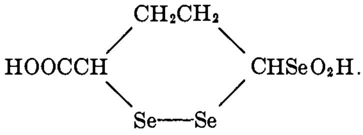
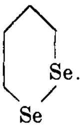
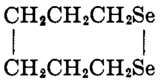
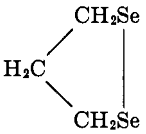
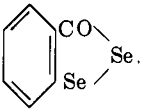
COMPOUND	REFERENCES
	(201)
$[KOOCCH(CH_3)Se]_2$	(11, 120, 121, 133)
$(HOOCCH_2Se)_2$	(13, 35, 129, 279)
$[HOOC(CH_2)_3Se]_2$	(135)
$[HOOCCH(C_3H_7)Se]_2$	(11, 121, 124)
 $\left[\begin{array}{l}HOOCCHCH(CH_3)_2\\ \quad\ \mid\\ \quad\ Se—\end{array}\right]_2$	(121, 124)
$[HOOCCH(CH_3)Se]_2$	(124, 129)
$(4\text{-}HOOCCH_2C_6H_4Se)_2$	(129)
$[HOOCC(CH_3)_2Se]_2$	(121)
$(HOOCCH_2CH_2Se)_2$	(124, 129, 279)
$(HOOCCH(C_2H_5)Se)_2$	(11)
$(C_6H_5NHCOCH_2Se)_2$ (and related compounds)	(136)
	(124, 129)
$2\text{-}O_2NC_6H_4SeSeCN$	(300b)
$4\text{-}Cl\text{-}2\text{-}O_2NC_6H_3SeSeCN$	(300b)
$4\text{-}Br\text{-}2\text{-}O_2NC_6H_3SeSeCN$	(300b)
$4\text{-}CH_3\text{-}2\text{-}O_2NC_6H_3SeSeCN$	(300b)
	(155a)
 $\begin{array}{l}CH_2CH_2CH_2Se\\ \mid \qquad\qquad\quad \mid\\ CH_2CH_2CH_2Se\end{array}$	(155a)
	(260)

TABLE 6—*Concluded*

COMPOUND	REFERENCES
	(222)

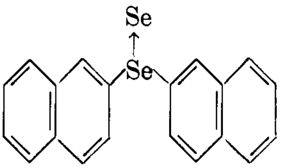
Of the former type, no completely satisfactory methods are known. In certain instances, treatment of a halide with sodium diselenide (15, 26, 30, 172)

$$2RCl + Na_2Se_2 \rightarrow 2NaCl + R_2Se_2 \qquad (10)$$

gives fair yields of diselenide. However, because of the hydrolysis of sodium diselenide, by-products are usually formed which are difficult to remove. Diselenides have been prepared by the Friedel–Crafts reaction from aromatic hydrocarbons and a variety of selenium compounds, such as selenium tetrachloride, selenium dioxide, selenium bromide, etc., or from the Grignard reagent by reaction with selenium bromide:

$$2RMgBr + Se_2Br_2 \rightarrow R_2Se_2 + 2MgBr_2 \qquad (11)$$

The reaction mixtures are quite complex, however, and the yield of any one product is usually low, so it is difficult to say whether the diselenide is produced as a primary product or not (60, 294, 304, 330). Attempts to prepare di-β-naphthyl diselenide by heating the monoselenide with selenium gave a diselenide different from the one obtained by oxidizing β-naphthoselenol. As a result, Loevenich, Fremdling, and Fohr (225) wrote the structure



I

for this new compound. This is the only reported example of this type of structure.

The best method for preparing a normal diselenide is from a compound already containing selenium. Any of the methods listed above for the production of selenols will give diselenides, if the reaction mixture is treated with a mild oxidizing agent, such as air. Thus, under these conditions, the Grignard reaction (7, 71, 72, 285, 333) and alkyl or aryl selenosulfates (294) can be made to give excellent yields of diselenides.

Compounds with selenium in a higher oxidation state can be reduced to diselenides conveniently. Thus, seleninic acids are reducible to diselenides by sodium bisulfite or iodide (234).

Finally, selenocyanates may be converted to diselenides by treating with strong alkali. The reaction is not clean-cut but is experimentally simple, and a reasonably high yield of the desired products can easily be separated. The course of the reaction appears to be open to question. Thus Challenger, Peters, and Halvey (82) write

$$2C_6H_5SeCN + H_2O \xrightarrow{OH^-} 2C_6H_5SeH + 2HCON \qquad (12)$$

$$2C_6H_5SeH + [O] \rightarrow H_2O + C_6H_5SeSeC_6H_5 \qquad (13)$$

while Behagel and Seibert (37) write the following series of equations:

$$2C_6H_5SeCN \rightarrow C_6H_5SeSeC_6H_5 + (CN)_2 \qquad (14)$$

$$(CN)_2 + H_2O \rightarrow HOCN + HCN \qquad (15)$$

then more slowly

$$2C_6H_5SeSeC_6H_5 + 4NaOH \rightarrow 2C_6H_5SeNa + H_2O + 2C_6H_5SeONa \qquad (16)$$

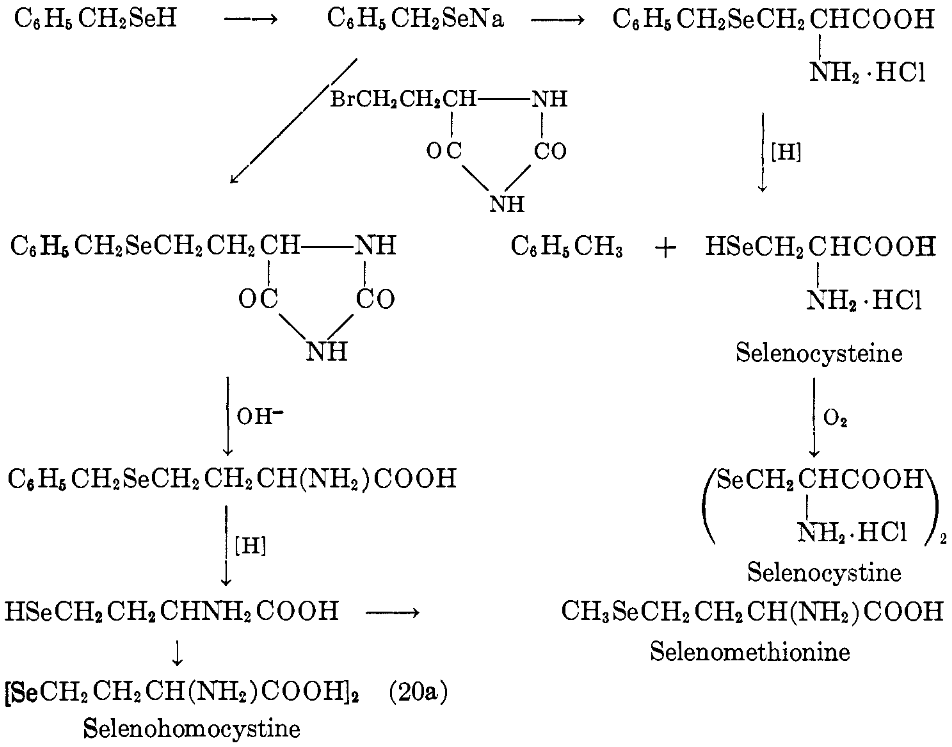
$$\underline{2C_6H_5SeONa \rightarrow C_6H_5SeNa + C_6H_5SeO_2Na} \qquad (17)$$

$$2(C_6H_5Se)_2 + 4NaOH \rightarrow 3C_6H_5SeNa + C_6H_5SeO_2Na + 2H_2O \qquad (18)$$

The formation of the indicated by-products cannot be denied; however, neither scheme is completely satisfactory. In view of the stability of the selenocyanates in solution, it would perhaps be best to await additional experimental data before postulating a complete mechanism.

The selenium analogs of the naturally occurring sulfhydryl and disulfide amino acids have been prepared by adaptations of conventional synthetic methods. Tests by Moxon indicate (268) that selenocystine is the most toxic organoselenium compound reported, when injected intraperitoneally in rats. The lethal dose was found to be of the same order as for sodium selenite, that is, 4 mg./kg. of body weight.

Selenocystine has been prepared directly in low yield from methyl α-amino-β-chloropropionate and a hydroselenide (131, 349). Derivatives of benzyl selenol have been used successfully for the preparation of several selenium analogs. The stable benzyl selenides formed are easily cleaved by reduction (198, 279, 280). For example, the following flow sheet indicates some possible methods of synthesis:



(19)

(20)

Selenomethionine has also been prepared from the ethyl ester of *N*-acetyl-α-amino-δ-chloro-*n*-butyric acid and the sodium derivative of benzyl selenol by similar methods (280). Treatment of benzyl chloromethyl selenide (350) with sodium phthalimidomalonic ester, followed by hydrolysis and reduction, gave a low yield of selenocystine (349). Attempts to use the Strecker synthesis have proven unsatisfactory (107).

The isolation of a protein-like substance containing selenium from plants grown in selenaceous soil has been reported (169). Hydrolysis indicates that all the nitrogen is present as amino nitrogen. The authors consider that their product is a mixture of seleno and thio units, $C_7H_{14}N_2O_4Se$ and $C_7H_{14}N_2O_4S$, present in a ratio of 2:1.

D. Selenenic, seleninic, and selenonic acids

Selenenic acids, RSeOH, are quite rare; only a few examples (see table 7) have been reported (31, 32), all of which were obtained by careful hydrolysis of the corresponding acid halide, RSeX (*vide infra*).

The seleninic acids, $RSeO_2H$ (see table 8), represent the most stable class of oxyselenium acids, and may be prepared by a variety of methods. Thus, hydrolysis of selenide trihalides (obtained from diselenides) gives excellent yields

$$RSeBr_3 + 2H_2O \rightarrow RSeO_2H + 3HBr \qquad (21)$$

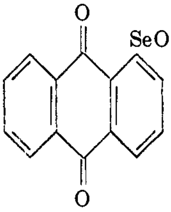
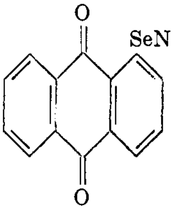
(29, 38, 233), as does oxidation of diselenides by per acids (233a) or peroxides (233, 236).

The seleninic acids are somewhat weaker acids than the corresponding carboxylic acids. Thus, the alkylseleninic acids have ionization constants of the order of magnitude of 5.5×10^{-6} (13, 14), while substituted phenylseleninic acids have a pK_{25° of about 5.0. The pK values of the substituted phenylseleninic acids are a linear function of Hammett's sigma values (236).

Selenonic acids (see table 9), unlike sulfonic acids, are not well known. They are strong acids and strong oxidizing agents. They are formed by direct reaction of an aromatic hydrocarbon with selenonic acid (H_2SeO_4) (3, 4, 103) or by powerful oxidation of seleninic acids with permanganate (295).

TABLE 7

Selenenic acids

COMPOUND	REFERENCES	COMPOUND	REFERENCES
$2,4\text{-}(O_2N)_2C_6H_3SeOH$	(32)	 SeOH	(31, 32)
$2\text{-}O_2NC_6H_4SeOH$	(32)		
$4\text{-}O_2NC_6H_4SeOCOCH_3$	(32)	 $SeNR_2$	(32)
$2\text{-}O_2NC_6H_4SeOCOCH_3$	(32)		

The reaction of aryl hydrocarbons with selenonic acid is not clear-cut. Thus, reaction with toluene gives the *o*-and *p*-isomers, as expected (103), which were characterized by allowing them to react with hydrochloric acid, to give chlorine

$$ArSeO_3H + 2HCl \rightarrow H_2O + Cl_2 + ArSeO_2H \qquad (22)$$

and the corresponding seleninic acid. In addition to the expected products, however, Doughty and Elder isolated some di-*p*-tolyl selenide, $(p\text{-}CH_3C_6H_4)_2Se$, and the following compound:

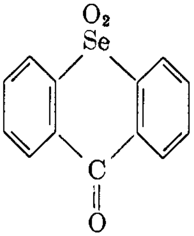
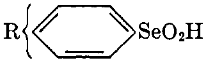


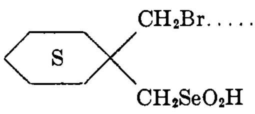
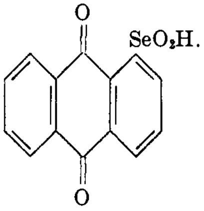
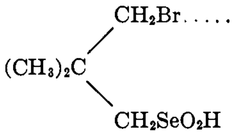
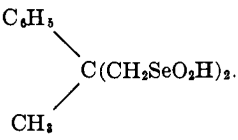
TABLE 8

Seleninic acids:



R	REFERENCES	R	REFERENCES
H	(37, 38, 98, 102, 111, 113, 144, 236, 295, 327)	3-Br	(236)
4-CH_3	(38, 103, 108, 236, 293)	4-F	(236)
3-CH_3	(114, 236, 293)	3-F	(236)
2-CH_3	(103, 114, 293)	4-NO_2	(19, 38)
3,4-$(CH_3)_2$	(293)	3-NO_2	(38, 115, 236, 293)
2,4-$(CH_3)_2$	(293)	2-NO_2	(38)
2-C_2H_5	(29)	2-NO_2-4-CH_3	(81)
4-C_6H_5	(29)	4-CH_3CONH	(19, 295)
2-C_6H_5	(29, 236)	4-C_6H_5CONH	(296)
4-Cl	(38, 112, 236, 265)	4-CH_3COO^-	(192)
3-Cl	(38, 236)	4-CH_3O	(236)
2-Cl	(38)	3-CH_3O	(236)
4-Br	(112, 236, 293)	4-OH-3-NO_2	(192)
		4-OH-3-COOR	(274)

Miscellaneous seleninic acids

COMPOUND	REFERENCES	COMPOUND	REFERENCES
CH_3SeO_2H	(14, 44)		(10)
$C_2H_5SeO_2H$	(12, 14, 44, 188)	$C_6H_5CH_2SeO_2H$	(172, 173, 222)
$C_3H_7SeO_2H$	(14, 44, 282)		(32)
$C_4H_9SeO_2H$	(14)	4-$O_2NC_6H_4SeONH_2$	(19)
$(CH_3)_2C(CH_2SeO_2H)_2$	(15)	4-$H_2NC_6H_4SeONH_2$	(19)
 $(CH_3)_2C(CH_2Br)(CH_2SeO_2H)$	(10)	4-$CH_3CONHC_6H_4SeONH_2$	(19)
 $C_6H_5C(CH_3)(CH_2SeO_2H)_2$	(15)		

Seleninocarboxy acids

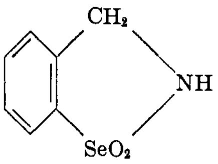
COMPOUND	REFERENCES	COMPOUND	REFERENCES
$HOOCCH_2SeO_2H$	(121, 282)	$HOOCCH(C_2H_5)SeO_2H$	(11, 121)
$HOOCCH_2CH_2SeO_2H$	(11, 282)	$HOOCC(CH_3)_2SeO_2H$	(121)
$HOOC(CH_2)_3SeO_2H$	(135)	$HOOCCH(SeO_2H)CH(CH_3)_2$	(121, 124)
$HOOCCH(CH_3)SeO_2H$	(11, 121)	$HOOCCH(SeO_2H)C_6H_5$	(129)

E. Selenide mono- and trihalides (see table 10)

The selenide halides, $RSeX$ and $RSeX_3$, may be prepared in a variety of ways, from compounds containing other selenium functions. Thus, reaction of a selenol or diselenide with halogen gives either the mono- or the trihalide, depending on the mole ratios of reactants employed:

TABLE 9

Selenonic acids

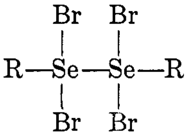
COMPOUND	REFERENCES	COMPOUND	REFERENCES
$C_6H_5SeO_3H$	(102)	Selenosaccharin	(219)
$4\text{-}CH_3C_6H_4SeO_3H$	(103)		
$2\text{-}CH_3C_6H_4SeO_3H$	(103)		
$2,4\text{-}(CH_3)_2C_6H_3SeO_3H$	(3, 4)		
$3,4\text{-}(CH_3)_2C_6H_3SeO_3H$	(3)		
$3\text{-}O_2NC_6H_4SeO_3H$	(295)		
$4\text{-}O_2NC_6H_4SeO_3H$	(19)		
$3\text{-}H_2NC_6H_4SeO_3H$	(295)	CH_3SeO_3K	(29, 30)
$2\text{-}C_{10}H_7SeO_3R$ (esters)	(295)	$C_2H_5SeO_3K$	(29)
		$C_4H_9SeO_3K \cdot HNO_3$	(29)

$$2C_6H_5SeH + 2Br_2 \rightarrow 2HBr + 2C_6H_5SeBr \tag{23}$$

$$C_6H_5SeSeC_6H_5 + Br_2 \rightarrow 2C_6H_5SeBr \tag{24}$$

$$C_6H_5SeBr + Br_2 \rightarrow C_6H_5SeBr_3 \tag{25}$$

It has been reported (330) that reaction of diselenides with halogen gives a compound with the following structure:



$$R-\underset{\displaystyle Br}{\overset{\displaystyle Br}{Se}}-\underset{\displaystyle Br}{\overset{\displaystyle Br}{Se}}-R$$

II

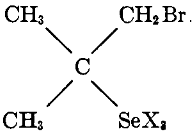
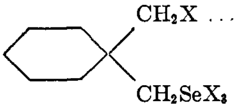
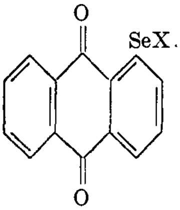
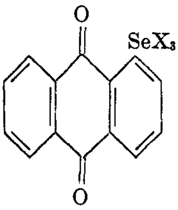
This statement has been refuted by Behagel and Seibert (38), who pointed out that the previous workers were dealing with a mixture of $RSeBr$ and $RSeBr_3$. Although a structure such as II is unlikely, its existence in solutions as a species of low concentration in equilibrium with other species is not impossible.

In addition to the above methods for the preparation of the selenide halides, two others of equal applicability are known. Thus, if one treats a concentrated aqueous solution of a seleninic acid with a strong halogen acid, an immediate precipitation of the selenide trihalide is brought about (71, 111).

$$C_6H_5Se({=}O)OH + 3HBr \rightarrow 2H_2O + C_6H_5SeBr_3 \tag{26}$$

TABLE 10

Selenium halides

 R	REFERENCES		REFERENCES	
	$X_3 = Cl_3$	$X = Cl$	$X_3 = Br_3$	$X = Br$
H	(38, 111, 112)	(38, 112, 187)	(38, 111, 112)	(30, 38, 108)
4-CH_3			(38, 108)	(30)
2-C_2H_5			(29)	(29)
4-Cl	(38, 112)	(112)	(38)	
3-Cl	(38)		(38)	
2-Cl	(38)		(38)	
4-Br			(112)	(112)
2,4,6-Br_3				(32)
4-NO_2	(19, 38)		(38)	(32, 38)
3-NO_2	(38)		(38)	(32)
2-NO_2	(30, 38)	(38)		
2,4-$(NO_2)_2$				(32)
2-NO_2-4-Br				(30)
4-NH_2	(19)			
4-$NHCOCH_3$	(19)		(296)	(296)
4-OH-3-COOR	(274)			
4-C_6H_5	(29)	(29)	(29)	(29)
2-C_6H_5	(29)		(29)	
COMPOUND				
$C_2H_5SeX_3$			(30)	
	(15)		(15)	
	(15)		(15)	
$(CH_3)_2C(CH_2SeX)_2$			(15)	(15)
		(31, 32)		(32, 37)
	(31)			

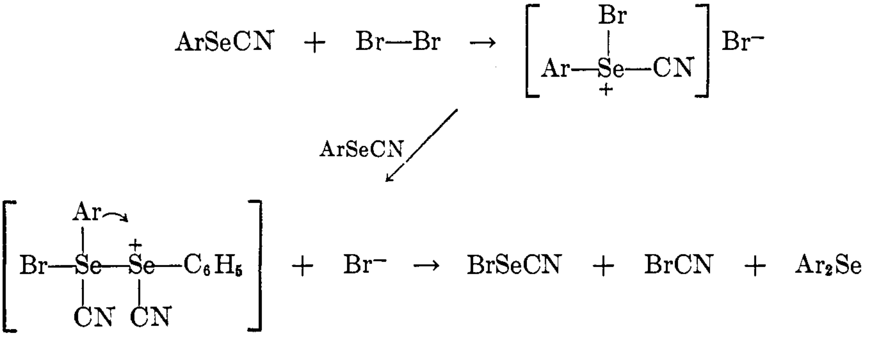
Finally, the selenide halides can be prepared from selenocyanates and halogen (38).

$$ArSeCN + Br_2 \rightarrow ArSeBr + BrCN \qquad (27)$$

This particular reaction is of interest, since the product obtained is completely dependent on the order in which the reactants are mixed (38). To obtain the desired product, i.e., selenide mono- or trihalide, the selenocyanate (in a suitable solvent such as carbon tetrachloride) must be added to the bromine, i.e., *bromine must be in excess.* If the reverse mode of addition is employed (selenocyanate in excess), then the product is *almost exclusively* a diaryl selenide. This observation, for which Behagel and Seibert (38) had no explanation, has been

$$ArSeCN + Br_2 \rightarrow Ar_2Se + \text{unidentified products} \qquad (28)$$

confirmed (233). Since ArSeBr and ArSeCN do not appear to react (71), a possible mechanism for reaction 28 could involve an intermediate ion such as III, which could rearrange, by migration of phenyl, to the observed products.



$$ArSeCN + Br{-}Br \rightarrow \left[Ar{-}\overset{\overset{Br}{|}}{\underset{+}{Se}}{-}CN\right]Br^- \qquad (29)$$

$$\left[Br{-}\overset{\overset{Ar}{|}}{\underset{\underset{CN}{|}}{Se}}{-}\overset{+}{\underset{\underset{CN}{|}}{Se}}{-}C_6H_5\right] + Br^- \rightarrow BrSeCN + BrCN + Ar_2Se \qquad (30)$$

III

Selenide monohalides hydrolyze according to the following scheme (32):

$$C_6H_5SeBr \xrightarrow{H_2O} C_6H_5SeOH \rightarrow ArSeO_2H + ArSeH \qquad (31)$$

$$ArSeH + ArSeOH \rightarrow Ar_2Se_2 + H_2O \qquad (32)$$

the net result being

$$3C_6H_5SeBr + 2H_2O \rightarrow C_6H_5SeO_2H + (C_6H_5)_2Se_2 + 3HBr \qquad (33)$$

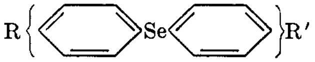
F. Selenides and selenide dihalides (see table 11)

By far the largest class of selenium compounds is that of the selenides. In addition to the synthetic methods described below, they occur as by-products or in nonpreparative yields from other reactions, reference to which will be found in the tables.

For the preparation of aryl selenides, the most useful method appears to be

TABLE 11

Selenides:



R AND R'	REFERENCES		
	Se	$SeCl_2$	$SeBr_2$
H,H	(37, 60, 77, 78, 80, 101, 112, 116, 176, 205, 206, 208, 215, 226, 232, 237, 238, 242, 291, 308, 310, 330)	(112, 116, 176, 202, 205, 208, 215, 227, 238, 318)	(37, 113, 176, 205, 208, 232, 237, 310, 330)
4-CH_3	(30, 143, 216)	(30, 216)	(30, 143, 216)
4,4'-$(CH_3)_2$	(82, 95, 103, 216, 235, 340)	(82, 216, 340)	(235, 340)
3,3'-$(CH_3)_2$	(216, 235)	(216, 235)	(235)
2,2'-$(CH_3)_2$	(226, 235, 340, 356)	(340, 356)	(235, 340)
2,4'-$(CH_3)_2$	(30)		(30)
3,4,4'-$(CH_3)_3$	(30)		(30)
4,4'-Cl_2	(205, 227, 235, 333)		(235)
2,2'-Cl_2	(71, 235)		(71, 235)
4-Br	(108)		
3-Br	(192)		
4,4'-Br_2	(30, 60, 108, 205, 333)		(30, 235)
2-NO_2	(29, 30, 98, 186, 356)	(30, 356)	(30, 356)
4,4'-$(NO_2)_2$	(16, 242, 296)		
2,2'-$(NO_2)_2$	(242)		
2,4,2',4'-$(NO_2)_4$	(34, 340)		
2,4,6,2',4',6'-$(NO_2)_6$	(340)		
2-NO_2-4-Br	(30)		
4-NH_2	(144)		
2-NH_2	(29, 98, 194)		
4,4'-$(NH_2)_2$	(18, 242, 296)		
3,3'-$(NH_2)_2$	(285)		
2,2'-$(NH_2)_2$	(242)		
4,4'-$[N(CH_3)_2]_2$	(29, 148)		
4,4'-$[N(C_2H_5)_2]_2$	(148)		
4-$NHCOCH_3$	(144)	(144)	(144)
4,4'-$(NHCOCH_3)_2$	(18, 242)		
4-NH_2-2-NO_2	(30)		
4-$N(CH_3)_2$-4'-NO_2	(38)		
4-$N(CH_3)_2$-2-NO_2	(38)		
2-C_6H_5-4'-CH_3	(72)	(72)	
3,3'-Cl_2	(71, 235)		(71, 235)
4-Cl-4'-CH_3	(72)	(72)	
4,4'-F_2	(71, 235)		(71, 235)
3-Cl	(72)	(72)	

TABLE 11—*Continued*

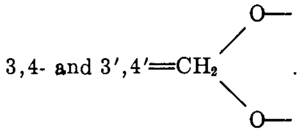
R AND R'	REFERENCES		
	Se	$SeCl_2$	$SeBr_2$
4-OH	(192)		
3-OH	(192)		
2-OH	(194)		
3,4-$(OH)_2$	(195)		
2,6-$(OH)_2$	(195)		
4,4'-$(OH)_2$ (and $OCOCH_3$)	(192, 193, 395)		
4,3'-$(OH)_2$ (and $OCOCH_3$)	(195)		
4,2'-$(OH)_2$ (and $OCOCH_3$)	(195)		
3,3'-$(OH)_2$	(195)		
3,2'-$(OH)_2$	(195)		
2,2'-$(OH)_2$ (and OCOR)	(195)		
4-$OCOCH_3$	(191)		
2-OH-6-OCH_3	(195)		
4-OCH_3	(191, 310)		(310)
4-OC_2H_5	(196)		
3-OCH_3	(196)		
2-OCH_3	(191)		
4,4'-$(OCH_3)_2$	(2, 18, 101, 193, 209)	(2, 18, 209)	(2, 209)
4,4'-$(OC_2H_5)_2$	(2, 193, 209)	(2, 209)	(209)
4,4'-$(OC_3H_7\text{-}n)_2$	(2)	(2)	(2)
4,4'-$(OC_4H_9\text{-}n)_2$	(2)	(2)	(2)
4,3'-$(OCH_3)_2$	(195)		
4,3-$(OCH_3)_2$	(195)		
4,2'-$(OCH_3)_2$	(195)		
4,2'-$(OC_2H_5)_2$	(195)		
3,3'-$(OCH_3)_2$	(195)		
3,2'-$(OCH_3)_2$	(195)		
2,5-$(OCH_3)_2$	(195)		
2,2'-$(OCH_3)_2$	(195, 235)		(235)
2,2'-$(OC_2H_5)_2$	(195)		
4,4'-$(OC_6H_5)_2$	(2, 235)	(2)	(2, 235)
4,4'-$(HOCH_2CH_2O)_2$	(18)	(18)	
4,4'-$(HOCH_2CH_2CH_2O)_2$	(18)	(18)	
 3,4- and 3',4'=$CH_2\begin{matrix}\diagup O\text{—}\\ \diagdown O\text{—}\end{matrix}$	(101)		
4-OH-3-CH_3	(257)		
2-OH-5-CH_3	(257)		
4,4'-$(OCH_3)_2$ 3,3'-$(CH_3)_2$	(2)	(2)	(2)
4,4'-$(OCH_3)_2$ 3,3'-(Br$_2$	(2)	(2)	(2)

TABLE 11—*Continued*

R AND R'	REFERENCES		
	Se	$SeCl_2$	$SeBr_2$
4,4'-$(HOCH_2CH_2O)_2$ 3,3'-$(NH_2)_2$	(18)		
4,4'-$(HOCH_2CH_2O)_2$ 3,3'-$(NO_2)_2$	(18)	(18)	
4,4'-$(HOCH_2CH_2CH_2O)_2$ 3,3'-$(NO_2)_2$	(18)	(18)	
4,4'-$(CH_3CO)_2$	(101)		
4,4'-$(C_6H_5CH{=}CHCO)_2$	(101)		
4,4'-$(C_6H_5CH{=}CHCH{=}CHCO)_2$	(101)		
4,4'-$(C_6H_5CO)_2$	(101)		
4,4'-$(C_6H_5CHOH)_2$	(101)		
4,4'-$[(C_6H_5)_2CCl]_2$	(101)		
4-COOH	(143)		
4,4'-$(COOH)_2$	(101)		
2,2'-$(COOH)_2$	(219, 308)		
4-COOH-4'-OH	(194)		
3-COOH-4-OH	(257)		
3-COOR-4-OH	(18, 274, 276)	(18, 274, 276)	(18, 274, 276)
4-$COOCH_3$-4'-$OCOCH_3$	(196)		
3-$COOCH_3$-4'-$OCOCH_3$	(196)		
4-C_5H_5	(30)	(30)	(30)
4,4'-$(C_6H_5)_2$	(30)		(30)
2,2'-$(C_5H_5)_2$	(30)	(30)	(30)
4-C_6H_5-4-CH_3	(30)		(30)
2-$SeCH_3$	(190)		
2-SeC_2H_5	(190)		
2-$SeCH_3$-5-CH_3	(189)		
2-$SeCH_3$-3-CH_3	(189)		
2-$SeCH_3$-2'-CH_3	(190)		
2-$SeCH_3$-3,4'-$(CH_3)_2$	(189)		
2-$SeCH_3$-3,2'-$(CH_3)_2$	(189)		

Selenides: $R\{C_6H_4SeCH_2COOH$ *or* $R_2\{C_6H_3SeCH_2COOH$

R	REFERENCES		
	Se	$SeCl_2$	$SeBr_2$
H	(108, 266)		(108, 266)
4-CH_3	(34, 36, 108, 266)		(108)
2-CH_3	(34, 36, 293)		
3,4-$(CH_3)_2$	(293)		
2,4-$(CH_3)_2$	(293)		
4-Cl	(34, 36)		
2-Cl	(34, 36)		
4-Br	(266)		(266)

TABLE 11—*Selenides—Continued*

R	REFERENCES		
	Se	$SeCl_2$	$SeBr_2$
4-NO_2	(34, 36)		
3-NO_2	(36)		
2-NO_2	(33, 34, 36)		
4-NH_2	(36)		
4-CH_3O	(34, 36)		
2-CH_3O	(34, 36)		
2-COOH	(219)		
4-CH_3S	(34, 36)		(266)
4-$HOOCCH_2S$	(36)		

Miscellaneous selenides in which selenium is not part of a heterocyclic system

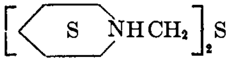
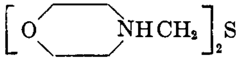
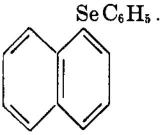
COMPOUND	REFERENCES		
	Se	$SeCl_2$	$SeBr_2$
$(CH_3)_2Se$	(45, 173, 174)	(174)	(174)
$CH_3SeC_2H_5$	(44, 339)		
$C_2H_5SeC_2H_5$	(180, 244)		
$CH_3SeC_3H_7(n)$	(44, 339)		
$CH_3SeC_4H_9(n)$	(339)		
$(n\text{-}C_3H_7)_2Se$	(339)		
$C_2H_5Se(CH_2)_3SeC_2H_5$	(339)		
$(HOCH_2CH_2)_2Se$	(317)		
$(CH_3OCH_2CH_2)_2Se$	(317)		
$(C_6H_5CH_2)_2Se$	(142, 174, 282)	(330)	(330)
$(4\text{-}ClC_6H_4CH_2)_2Se$	(321)		
$(3\text{-}ClC_6H_4CH_2)_2Se$	(321)		
$(2\text{-}ClC_6H_4CH_2)_2Se$	(321)		
$(2,5\text{-}Cl_2C_6H_3CH_2)_2Se$	(321)		
$(3\text{-}O_2NC_6H_4CH_2)_2Se$	(321)		
$(2\text{-}O_2NC_6H_4CH_2)_2Se$	(321)		
$(2\text{-}NCC_6H_4CH_2)_2Se$	(106)		
 Se	(43)		
 Se	(43)		
$C_6H_5SeCH_2CH_2OH$	(239)		
$C_6H_5CH_2SeCH_2CH_2OH$	(239)		
$C_6H_5SeCH_2CH_2(OC_2H_5)_2$	(239)		
	(72)	(72)	

TABLE 11—*Continued*

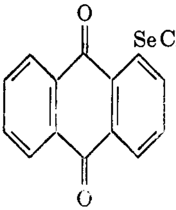
COMPOUND	REFERENCES		
	Se	$SeCl_2$	$SeBr_2$
$Se(CH_2COOH)_2$	(35, 129, 282)		
$Se(CH_2CH_2COOH)_2$	(35, 282)		
$Se(CH_2CH_2CH_2COOH)_2$	(135)		
$Se[CH(C_2H_6)COOH]_2$	(129, 282)		
$Se[C(CH_3)_2COOH]_2$	(129)		
$Se[CH(CH_3)COOK]_2$	(89, 128, 129)		
$Se(CH_2CONHC_6H_5)_2$	(136)		
$Se(CH_2CONHC_6H_4Cl\text{-}2)_2$	(136)		
$Se(CH_2CONHC_6H_4Cl\text{-}4)_2$ (also 2-, 3-, and 4-CH_3 and 4-OC_2H_5)	(129)		
$Se(CH_2C_6H_5)COOH$	(130)		
$CH_2(SeCH_2COOH)_2$	(130)		
$(CH_2SeCH_2COOH)_2$	(130)		
$(CH_2)_3(SeCH_2COOH)_2$	(130)		
$C_6H_5CH_2SeCH_2COOH$	(130)		
$C_6H_5CH_2Se(CH_2)_2COOH$	(130)		
$C_6H_5CH_2Se(CH_2)_3COOH$	(134)		
$HOOCCH_2Se(CH_2)_2COOH$	(130)		
$CH_3Se(CH_2)_2CHNH_2COOH$	(280)		
$HOOCCH(CH_3)SeCH_2COOH$	(134)		
1-$C_{10}H_7SeCH_2COOH$	(266)		
 $SeCH_2COOH$	(32)		
(1-$C_{10}H_7)_2Se$	(205, 230)	(230)	(230)
(2-$C_{10}H_7)_2Se$	(225, 230)	(230)	
2-$CH_3CONHC_6H_4SeCH_3$	(185, 188)		
2-$CH_3CONHC_6H_4SeC_2H_5$	(185)		
2-$H_2NC_6H_4SeR$	(188)		
4-$CH_3CONHC_6H_4SeCH_3$	(185)		
2-O_2N-4-$CH_3C_6H_3SeCH_3$	(185)		
2-H_2N-4-$CH_3C_6H_3SeCH_3$	(185)		
2-CH_3CONH-4-$CH_3C_6H_3SeCH_3$	(185)		
2-CH_3-5-$O_2NC_6H_3SeCH_3$	(185, 188)		
2-CH_3-5-$H_2NC_6H_3SeCH_3$	(185, 188)		
2-CH_3-5-$CH_3CONHC_6H_3SeCH_3$	(185, 188)		
1,4-$C_6H_4(SeCH_3)_2$	(186)		
1,3-$C_6H_4(SeCH_3)_2$	(186)		
2-$CH_3OC_6H_4Se$(Alkyl)	(195)		
2-HOC_6H_4Se(Alkyl)	(195)		
4-$CH_3OC_6H_4Se$(Alkyl)	(195)		

TABLE 11—*Continued*

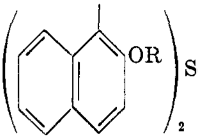
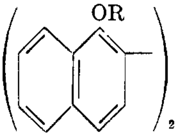
COMPOUND	REFERENCES		
	Se	$SeCl_2$	$SeBr_2$
4-HOC_6H_4Se(Alkyl)	(195)		
1,4-$ROOCC_6H_4SeCH_3$ (also 1,2- and 1,3-)	(195)		
1-$C_{10}H_7SeC_6H_4R$ (R = CH_3O and OH in ortho, meta, and para positions)	(195)		
 Se	(247)		
 Se	(247)		
$(CH_3COCH_2)_2Se$		(247)	
2-$O_2NC_6H_4SeCH_3$	(185)		
2-$H_2NC_6H_4SeCH_3$	(185)		
4-$H_2NC_6H_4SeCH_3$	(188)		
$C_6H_5CH_2SeC_2H_5$	(30)		
$C_6H_5CH_2SeC_6H_5$	(30)		
$C_6H_5CH_2SeC_6H_4NO_2$-2	(30)		
$C_6H_5SeCH_3$	(16, 108, 116, 185, 291, 347)		(108, 116)
$C_6H_5SeC_5H_{11}$	(113, 116)		(113, 116)
3-$O_2NC_6H_4Se(C_1$ to $C_7)$	(115)		(115)
3-$H_2NC_6H_4Se(C_1$ to $C_7)$	(115)		
$C_6H_5SeC_4H_9(n)$	(113)		(113)
$(CCl_3CHOH)_2Se$	(224)		
4-$ClC_6H_4SeC_2H_5$	(112)	(112)	
4-$BrC_6H_4SeC_2H_5$	(112)		(112)
4-$HOOCC_6H_4SeCH_3$	(143)		(143)
$C_6H_5SeC_6H_{13}$	(113)		(113)
$(C_6H_5CH_2SeCH_2)_2$	(142)		
$(C_6H_5COCH_2)_2Se$		(247)	
1-$C_{10}H_7Se$(Alkyl)	(225)		
(1-$C_{10}H_7Se$—$)_2CR_2$	(225)		
(2-$C_{10}H_7Se$—$)_2CR_2$	(225)		
2-$C_{10}H_7Se$(Alkyl)	(225)		
4-$CH_3C_6H_4SeCH_2C_6H_5$	(333)		
4-$O_2NC_6H_4SeCH_3$	(16, 185)		
4-$(CH_3)_2NC_6H_4SeCH_3$	(82)		

TABLE 11—*Continued*

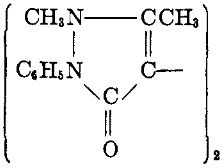
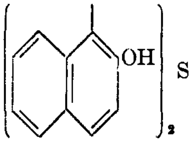
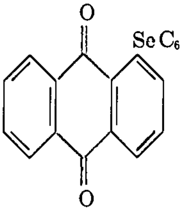
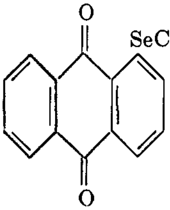
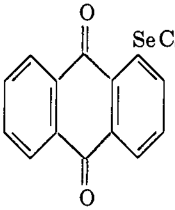
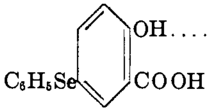
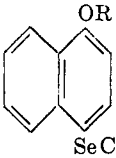
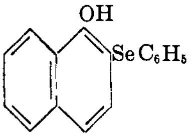
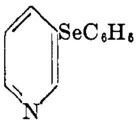
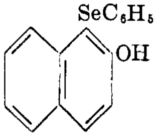
COMPOUND	REFERENCES		
	Se	$SeCl_2$	$SeBr_2$
 Se	(184, 201)		
$C_6H_5SeC_2H_5$	(30, 38, 111, 113, 116, 185)		(30, 108, 111, 116, 185)
 Se	(54, 257, 325)		
 $SeC_6H_4N(CH_3)_2$-4	(31)		
 $SeC_6H_4N(C_2H_5)_2$-4	(32)		
 SeC_6H_5	(31)		
	(195)		

TABLE 11—*Concluded*

COMPOUND	REFERENCES		
	Se	$SeCl_4$	$SeBr_2$
 (R = H, C_2H_5, or CH_3CO)	(195)		
	(195)		
	(195)		
	(195)		

the reaction of a diazonium salt with potassium selenide, prepared by fusing selenium and potassium hydroxide (191–196, 221, 242, 308):

$$ArN_2^+ + Se^{--} \rightarrow (ArN_2)_2Se \rightarrow Ar_2Se + N_2 \qquad (34)$$

A variation of this technique, which allows for the preparation of unsymmetrical selenides, ArSeR′, employs a potassium selenolate instead of potassium selenide (192):

$$ArN_2^+ + SeR^- \rightarrow ArN_2SeR \rightarrow ArSeR \qquad (35)$$

Alkali selenolates will also react with reactive halides to give selenides (10, 16, 30, 36, 98, 116). This synthesis is particularly useful in the aliphatic series,

$$RSeNa + R'Br \rightarrow NaBr + RSeR' \qquad (36)$$

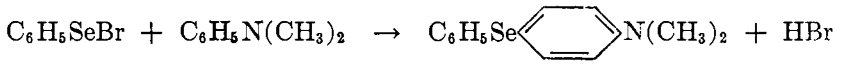
or for the preparation of mixed aromatic-aliphatic selenides, as in the preparation of selenoanisole, $C_6H_5SeCH_3$, from phenyl selenolate and a methyl halide. A method useful for the preparation of derivatives of activated aromatic nuclei involves the reaction of a compound such as dimethylaniline or anisole with selenium oxychloride. This leads directly to the selenide dihalide in good yield, which is easily converted to the selenide (2, 18, 71, 148, 209, 247).

$$\begin{array}{l} CH_3OC_6H_5 + SeOCl_2 \rightarrow (4\text{-}CH_3OC_6H_4)_2SeCl_2 + H_2O \\ \qquad\qquad\qquad\qquad\qquad\qquad \downarrow \text{Zn dust} \\ \qquad\qquad\qquad\qquad\qquad (4\text{-}CH_3OC_6H_4)_2Se \end{array} \quad (37)$$

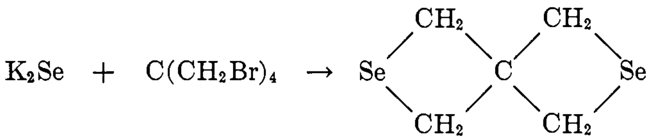
Selenium oxychloride also reacts with ketones to give unstable products (275).

$$SeOCl_2 + RCOCH_3 \rightarrow (RCOCH_2)_2SeCl_2 + H_2O \quad (38)$$

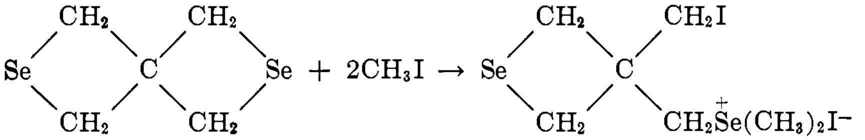
A similar reaction occurs with dimethylaniline and phenylselenium bromide (38):


(39)

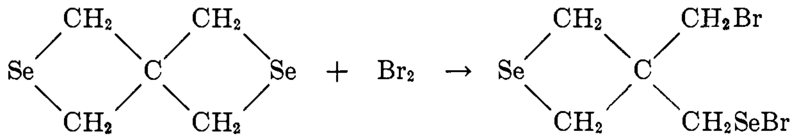
From aliphatic halides (or activated aromatic halides) and potassium selenosulfate, K_2SeSO_3, (340) (or potassium selenide) good yields of symmetrical selenides can be obtained. This reaction has been used to advantage for the preparation of some spiro derivatives in good yield (10), for example:


(40)

These compounds react with methyl iodide to open the ring and give a selenonium salt:


(41)

Similar reactions occur with halogen:


(42)

From a Grignard reagent and selenide halide can be obtained in poorer yield either symmetrical or unsymmetrical selenides (30, 333).

$$RMgCl + R'SeCl \rightarrow MgCl_2 + R'SeR \quad (43)$$

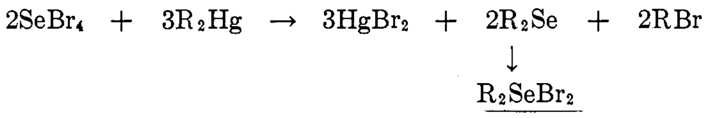
Other general methods which offer few, if any, advantages include the reaction of selenium with a sulfone, for example (208),

$$4\text{-}CH_3C_6H_4SO_2C_6H_5 + Se \rightarrow 4\text{-}CH_3C_6H_4SeC_6H_5 + SO_2 \tag{44}$$

and the reaction of selenium with a diarylmercury (206):

$$Se + (C_6H_5)_2Hg \rightarrow Hg + (C_6H_5)_2Se \tag{45}$$

For the direct preparation of relatively small amounts of pure selenides, certain reactions of organometallic compounds can be recommended. Thus, selenium tetrabromide reacts quantitatively with diarylmercury to give selenides (213), which can be isolated directly and easily as their dibromides, which are quite insoluble in the reaction medium:



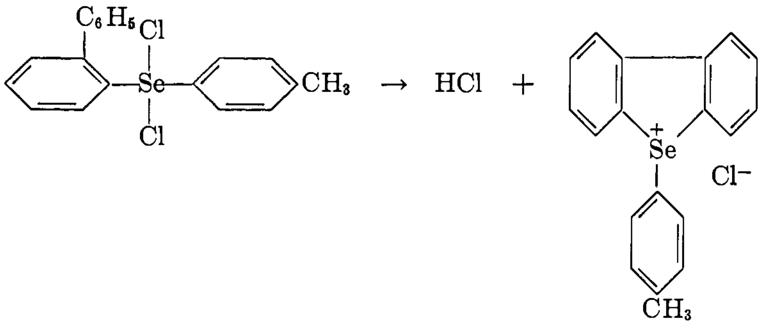
$$2SeBr_4 + 3R_2Hg \rightarrow 3HgBr_2 + \underset{\displaystyle\underline{R_2SeBr_2}}{\underset{\downarrow}{2R_2Se}} + 2RBr \tag{46}$$

A variation of this synthesis allows for the synthesis of selenides with dissimilar groups (72):

$$2RSeBr + R'_2Hg \rightarrow HgBr_2 + 2R'SeR \tag{47}$$

Diselenides react with lithium compounds (310) and with the Grignard reagent (72) to give quantitative yields of selenides. For example, di-*o*-biphenylyl diselenide reacts with *p*-tolylmagnesium bromide to give 2-phenyl-4′-methyldiphenyl selenide (72). The dichloride of this latter compound loses hydrogen chloride to give a selenonium salt (72, 233):

$$\begin{aligned} &4\text{-}CH_3C_6H_4MgBr + 2\text{-}C_6H_5C_6H_4SeSeC_6H_4C_6H_5\text{-}2 \\ &\qquad \rightarrow 2\text{-}C_6H_5C_6H_4SeMgBr + 2\text{-}C_6H_5C_6H_4SeC_6H_4CH_3\text{-}4 \end{aligned} \tag{48}$$



(49)

The selenium analogs of the mustard gases have been prepared by conventional methods. Thus, if ethylene is passed into selenium monochloride, bis(β-chloroethyl) selenide is produced, which is converted to the selenide dihalide in the presence of excess selenium chloride (28, 53).

$$Se_2Cl_2 + CH_2{=}CH_2 \rightarrow (ClCH_2CH_2)_2Se + Se \tag{50}$$

$$(ClCH_2CH_2)_2Se + Se_2Cl_2 \rightarrow 2Se + (ClCH_2CH_2)_2SeCl_2 \tag{51}$$

Similar reactions may be carried out using selenium tetrachloride (40, 317) or selenium oxychloride (137).

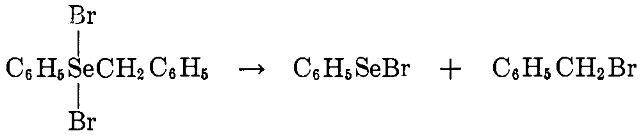
The reaction of higher 1,2-olefins with these reagents leads to bis(β-chloro-*n*-alkyl) selenides (40, 53). Vinyl chloride reacts with selenium tetrachloride to give bis(β,β-dichloroethyl) selenide (317).

$$SeCl_4 + CH_2{=}CHCl \rightarrow (Cl_2CHCH_2)_2Se \qquad (52)$$

Hydrogen selenide reacts with formaldehyde and an amine to give bis(alkylaminomethyl) selenides (43).

$$2RNH_2 + 2CH_2O + H_2Se \rightarrow RNHCH_2SeCH_2NHR + 2H_2O \qquad (53)$$

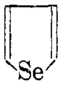
Selenide dihalides are invariably prepared by treating the appropriate selenide with a slight excess of halogen. The dichlorides and dibromides are stable, while the diiodides are not. The fluorides have not been reported, though diphenyltellurium difluoride exists (109). The partially or wholly aliphatic dihalides are unstable (30):



$$C_6H_5\overset{\displaystyle Br}{\underset{\displaystyle Br}{Se}}CH_2C_6H_5 \rightarrow C_6H_5SeBr + C_6H_5CH_2Br \qquad (54)$$

G. Selenophene and related heterocycles (see table 12)

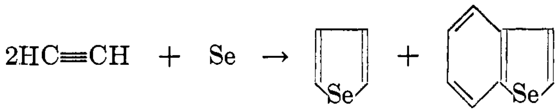
The parent compound, selenophene (IV), is a stable liquid boiling at 110°C.,



IV

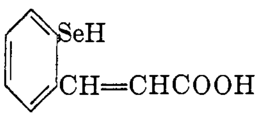
Selenophene

and its reactions are similar to those of thiophene. It has been prepared by the reaction of sodium succinate (347a) or succinic acid (109a) with phosphorus pentaselenide or by the reaction of acetylene and selenium at elevated temperatures (65, 66). This reaction also produces selenonaphthene (benzoselenophene),



(55)

C_8H_6Se (200, 243). This latter compound has also been synthesized (342) by allowing potassium ferricyanide to react with *o*-selenolcinnamic acid (V).



V

TABLE 12

Miscellaneous selenides: heterocycles in which selenium is the only hetero atom

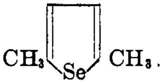
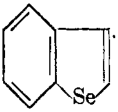
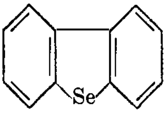
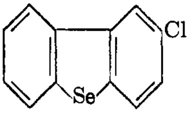
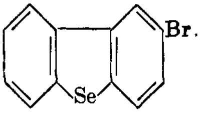
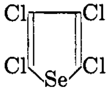
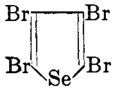
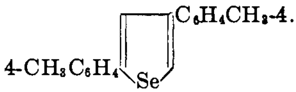
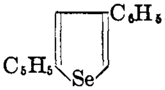
COMPOUND	REFERENCES		
	Se	$SeCl_2$	$SeBr_2$
	(157, 240, 355)		
	(50, 278, 357)		
	(94, 157)		
	(29, 30, 93, 98, 233a)	(29, 30)	(29, 30, 93)
			(29, 30)
	(29, 30)		(30)
	(65, 67)		
	(65, 67)		
	(50)		
	(50)		

TABLE 12—*Continued*

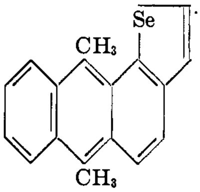
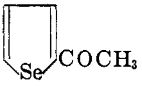
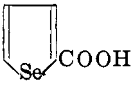
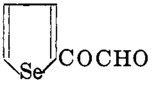
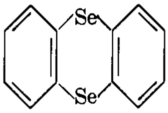
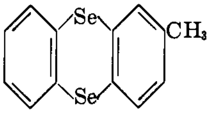
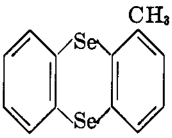
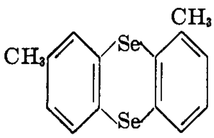
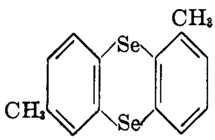
COMPOUND	REFERENCES		
	Se	SeCl$_2$	SeBr$_2$
	(159)		
	(341)		
	(341)		
	(341)		
	(98, 187, 190, 204)		
	(187, 189)		
	(187, 189)		
	(189)		
	(189)		

TABLE 12—*Continued*

COMPOUND	REFERENCES		
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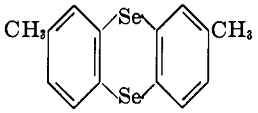
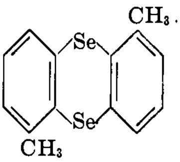
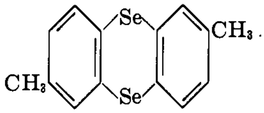
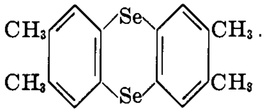
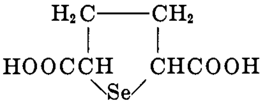
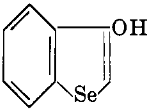
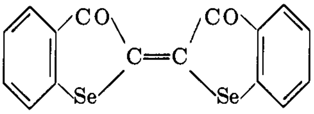
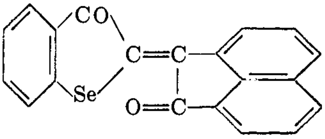
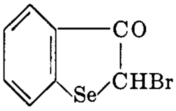
	(189)		
	(187, 189)		
	(187, 189)		
	(189)		
 (*cis* and *trans*)	(122, 125, 129)		
	(219)		
	(217, 219)		
	(219)		
	(217)		

TABLE 12—*Continued*

COMPOUND	REFERENCES		
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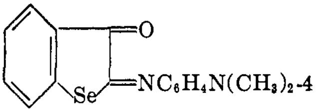
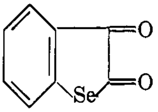
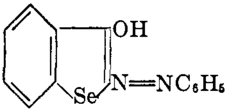
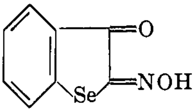
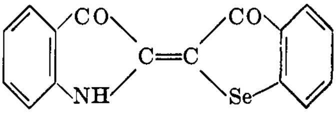
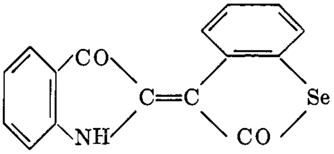
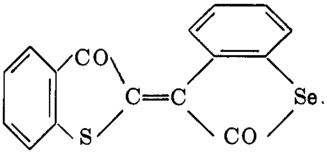
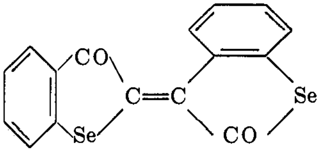
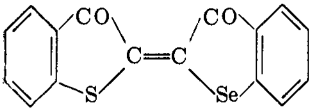
	(217)		
	(217)		
	(217)		
	(217)		
	(219)		
	(217)		
	(217)		
	(217)		
	(217)		

TABLE 12—*Continued*

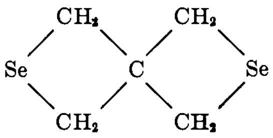
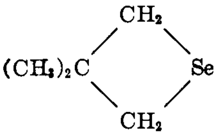
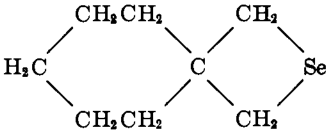
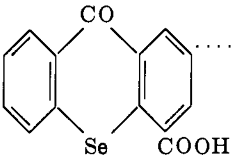
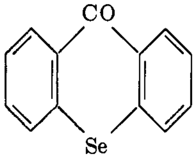
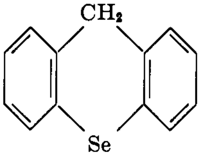
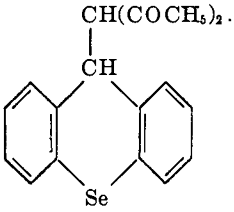
COMPOUND	REFERENCES		
	Se	$SeCl_2$	$SeBr_2$
	(15)		
	(15)		
	(15)		
	(221)		
	(222)		
	(117)		
	(119)		

TABLE 12—*Continued*

COMPOUND	REFERENCES		
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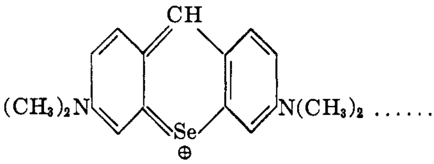
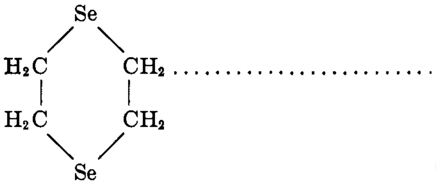
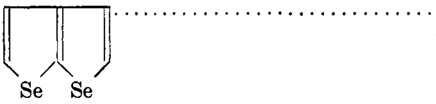
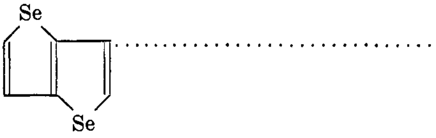
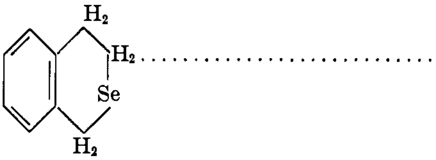
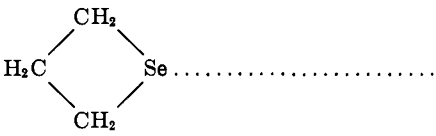
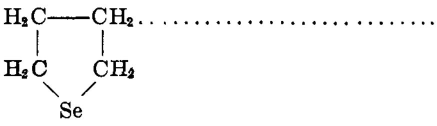
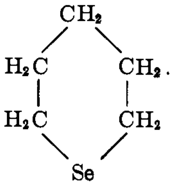
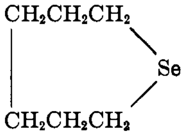
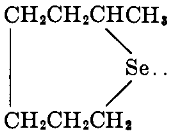
 (and related compounds)	(22, 23, 24)		
	(148a)		(148a)
	(337)		
	(337)		
	(236)		
	(168)	(168)	(168)
	(260)		
	(155a, 355)	(155a)	(155a)

TABLE 12—*Continued*

COMPOUND	REFERENCES		
	Se	$SeCl_2$	$SeBr_2$
	(155a, 355)	(155a)	(155a)
	(261)	(261)	(261)
	(261)	(261)	(261)

Miscellaneous selenides: heterocycles containing selenium together with nitrogen, sulfur, or oxygen in the same ring

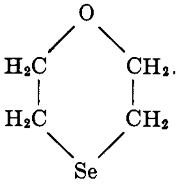
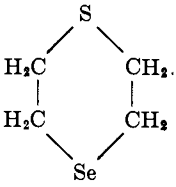
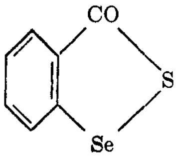
COMPOUND	REFERENCES		
	Se	$SeCl_2$	$SeBr_2$
	(145)		
	(146)		
	(222)		

TABLE 12—*Continued*

COMPOUND	REFERENCES		
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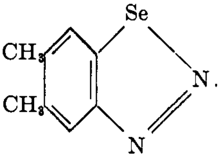
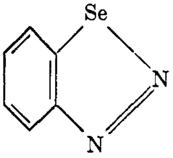
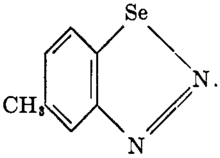
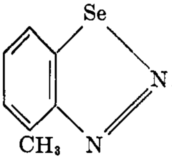
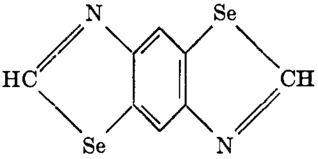
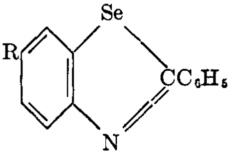
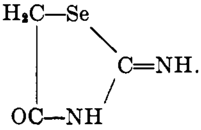
	(190)		
	(187)		
	(187)		
	(187)		
 (and derivatives)	(51)		
 (R = H, NO_2, NH_2, CN, *or* COOH)	(27, 49, 142)		
	(167)		

TABLE 12—*Continued*

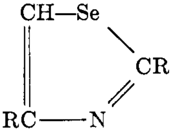
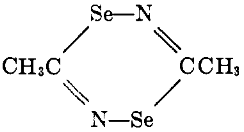
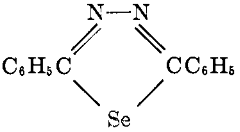
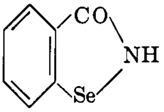
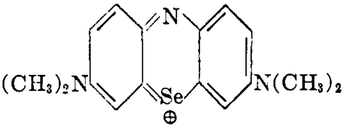
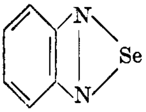
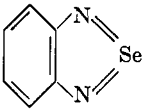
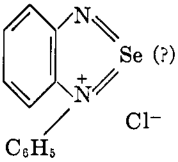
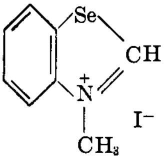
COMPOUND	REFERENCES		
	Se	$SeCl_2$	$SeBr_2$
 (R = alkyl, aryl, H, NH_2, etc.)	(167)		
	(167)		
	(328)		
	(222)		
	(182, 196)		
 or  and analogs	(25, 161, 162, 163, 164, 165, 166, 306)		
	(25)		
	(84, 85)		

TABLE 12—*Continued*

COMPOUND	REFERENCES		
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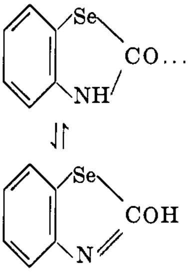
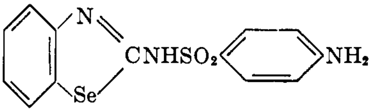
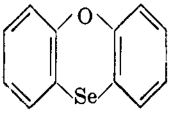
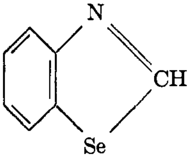
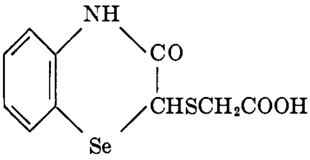
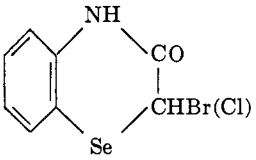
	(100)		
	(153)		
	(105, 353)		
	(91, 92)		(92)
	(33)		
	(33)		

TABLE 12—*Continued*

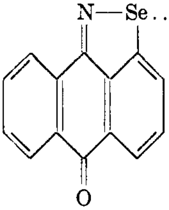
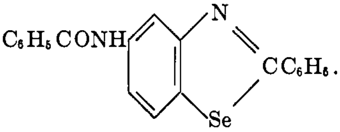
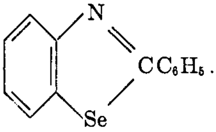
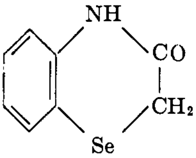
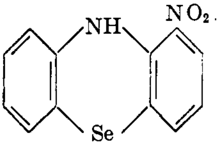
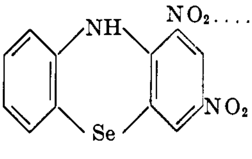
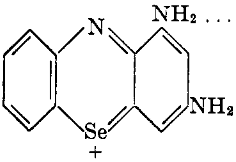
COMPOUND	REFERENCES		
	Se	$SeCl_2$	$SeBr_2$
	(32)		
	(142)		
	(26, 142)		
	(33, 36)	(33)	(33)
	(27)		
	(27)		
	(27)		

TABLE 12—*Concluded*

COMPOUND	REFERENCES		
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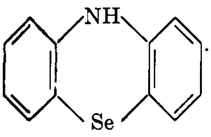
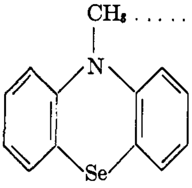
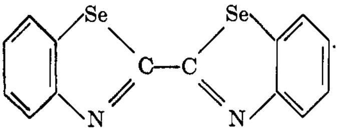
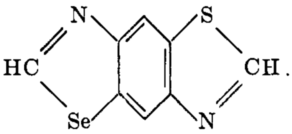
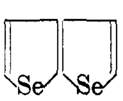
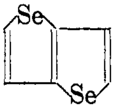
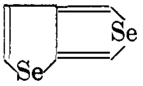
	(90)		
	(90)		
	(52)		
 and derivatives	(51)		

The reaction of acetylene and selenium leads to other products as well; thus,

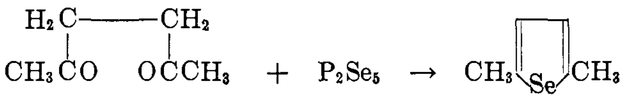

VI


VII


VIII

the isomeric isoselenonaphthenes (VI, VII, VIII) have been isolated (342), as well as higher unidentified fractions.

The condensation between 1,4-dicarbonyl compounds and phosphorus pentaselenide readily gives substituted selenophenes. Thus, acetonylacetone gives 2,5-dimethylselenophene (47, 278, 357).

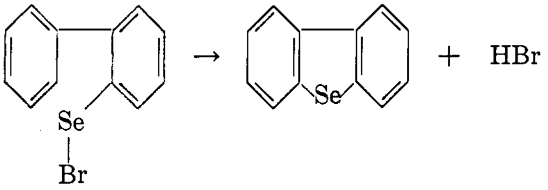


$$\begin{array}{ccc} H_2C & \text{——} & CH_2 \\ | & & | \\ CH_3CO & & OCCH_3 \end{array} + P_2Se_5 \rightarrow \tag{56}$$

2,5-Dimethylselenophene

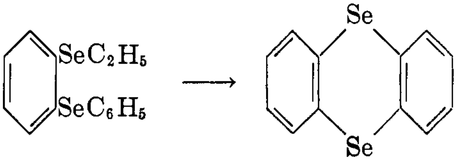
The Hinsberg reaction between $Se(CH_2COOCH_3)_2$ and benzil in methanol in the presence of sodium gives a mixture of 3,4-diphenylselenophene-2,5-dicarboxylic acid and 3,4-diphenyl-2-carboxyselenophene, either of which may be decarboxylated to 3,4-diphenylselenophene (8).

Dibenzoselenophene has been prepared in a variety of ways, most of which give unsatisfactory yields. A recent paper (233a) describes a simple method of synthesis, based on previous work of Behagel and Hoffman (29), wherein *o*-biphenylylselenium bromide is cyclized quantitatively to dibenzoselenophene.



(57)

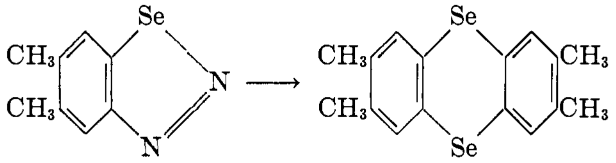
Selenanthrene (IX) and its analogs have been obtained in low yield from phenylselenium chloride and phosphorus pentoxide in chloroform (187), from diphenylene sulfone and selenium (125), and in better yields by refluxing *o*-(selenoethyl) diphenyl selenide with zinc and acetic acid (190),



(58)

IX
Selenanthrene

also by heating a selenoazo compound (189).



(59)

It is beyond the scope of this review to discuss the multitudinous syntheses which lead to heterocycles containing selenium and another element, usually nitrogen. It is sufficient to say that the selenium analogs of most of the sulfur heterocycles have been prepared, by much the same reactions. A partial tabulation of these heterocycles will be found in the last section of table 12; the reader is referred to the references quoted there for additional information.

H. Selenoxides and selenones (see table 13)

Selenoxides and selenones are commonly prepared by the oxidation of sele-

$$\underset{\text{O}}{\underset{\downarrow}{\text{RSeR}}}$$

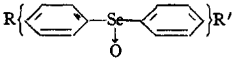
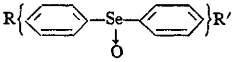
Selenoxides

$$\underset{\text{O}}{\underset{\|}{\overset{\overset{\text{O}}{\|}}{\text{RSeR}}}}$$

Selenones

TABLE 13

Selenoxides and selenones

 R AND R'	REFERENCES	 R AND R'	REFERENCES
H	(93, 108, 113, 116, 177, 205, 298, 299, 300)	4,4'-$(NHCOCH_3)_2$	(18)
		4,4'-$(CH_3O)_2$	(2, 17, 144)
		4,4'-$(C_2H_5O)_2$	(2, 113, 144)
4-CH_3	(143)	4,4'-$(C_3H_7O)_2$	(2)
4,4'-$(CH_3)_2$	(113, 340, 356)	4,4'-$(C_4H_9O)_2$	(2)
2,2'-$(CH_3)_2$	(340)	4,4'-$(C_6H_5O)_2$	(2)
2,4'-$(CH_3)_2$	(30)	4,4'-$(CH_3O)_2$-3-Br	(2)
4,3',4'-$(CH_3)_3$	(30)	4,4'-$(CH_3O)_2$-3-CH_3	(2)
4-CH_3-4'-C_6H_5	(30)	4,4'-$(HOCH_2CH_2O)_2$	(18)
4-C_6H_5	(30)	4,4'-$(HOCH_2CH_2CH_2O)_2$	(18)
2,2'-$(C_6H_5)_2$	(30)	4,4'-$(CH_3CHOHCH_2O)_2$	(18)
2-NO_2	(30)	4,4'-$(HOOCCH_2O)_2$	(335)
4,4'-$(NO_2)_2$	(242)	4-COOH	(143)
4-NH_2	(144)	4,4'-$(COOH)_2$	(101)
4-$NHCOCH_3$	(144)		

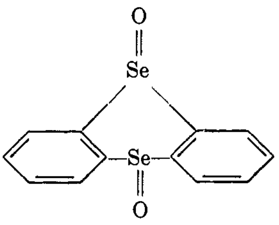
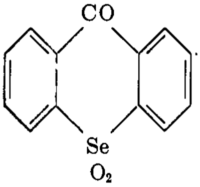
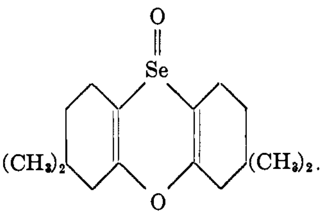
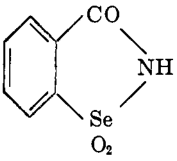
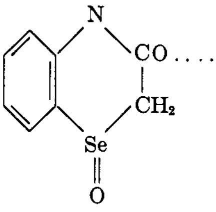
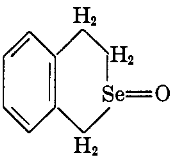
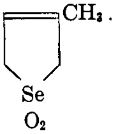
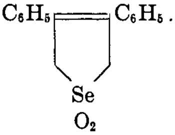
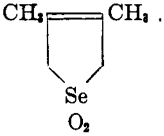
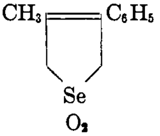
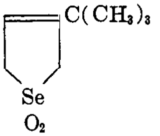
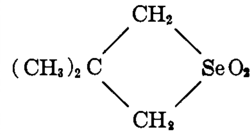
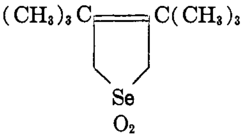
COMPOUND	REFERENCES	COMPOUND	REFERENCES
$(CH_3)_2Se{=}O$	(44)		
$(Cl_2C{=}CH)_2Se{=}O$	(64)		
$(ClCH_2CH_2)_2Se{=}O$	(317)		
$(HOCH_2CH_2)_2Se{=}O$	(317)		
$(BrCH_2CH_2)_2Se{=}O$	(317)		
$(CHCl_2CH_2)_2Se{=}O$	(64)		
$(C_6H_5)_2SeO_2$	(202, 298, 299, 300)		(204)
$(1\text{-}C_{10}H_7)_2SeO_2$	(225)		
$(2\text{-}C_{10}H_7)_2SeO_2$	(225)		
$(4\text{-}HOOCC_6H_4)_2SeO_2$	(103)		
	(103)		(325)
	(219)		(33)
$C_6H_5Se({=}O)CH_3$	(108, 113, 116)		(168)
$4\text{-}BrC_6H_4Se({=}O)C_2H_5$	(113)		
$4\text{-}HOOCC_6H_4Se({=}O)CH_3$	(143)		
$(1\text{-}C_{10}H_7)_2Se{=}O$	(225)		
$(2\text{-}C_{10}H_7)_2Se{=}O$	(225)		
$(C_6H_5CH_2)_2Se{=}O$	(330)		

TABLE 13—*Concluded*

Selenoxides or selenium dihydroxides

COMPOUND	REFERENCES	COMPOUND	REFERENCES
	(9)		(9)
	(9)		(9)
	(9)		(10)
	(9)		

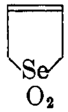
nides. Thus, a selenide may be converted to a dihalide, which is treated with aqueous alkali, preferably bicarbonate, to give the selenoxide (2, 18, 30, 233):

$$(C_6H_5)_2Se \xrightarrow{Br_2} (C_6H_5)_2SeBr_2 \xrightarrow{H_2O} (C_6H_5)_2SeO + 2HBr \qquad (60)$$

Other oxidizing agents may be used, such as 30 per cent hydrogen peroxide (233, 300) and peracetic acid (233a).

Selenones are generally prepared by the use of more powerful oxidizing agents, such as potassium permanganate. For example, diphenyl selenone may be prepared from diphenylselenium by heating with alkaline permanganate (103, 202, 225). Certain cyclic selenones may be prepared from conjugated dienes and selenium dioxide (9):

$$CH_2{=}CHCH{=}CH_2 + SeO_2 \longrightarrow$$



(61)

I. Selenonium salts (see table 14)

Selenium forms a well-defined series of -onium compounds, $RR'R''Se^+ A^-$, which may be prepared by the conventional methods used to produce ammonium and sulfonium salts from the corresponding bases. For example, phenyl methyl

TABLE 14

Selenonium salts

$RR'R''Se^+ X^-$

R	R'	R″	REFERENCES
CH_3	CH_3	CH_3	(109, 172)
C_6H_5	C_6H_5	C_6H_5	(109, 215)
4-$CH_3C_6H_4$	C_6H_5	C_6H_5	(95, 216)
3-$CH_3C_6H_4$	C_6H_5	C_6H_5	(216)
$C_6H_5CH_2$	C_6H_5	C_6H_5	(142)
4-HOC_6H_4	C_6H_5	C_6H_5	(257)
2,4-$(HO)_2C_6H_3$	C_6H_5	C_6H_5	(257)
4-$CH_3OC_6H_4$	C_6H_5	C_6H_5	(160, 257)
4-$C_2H_5OC_6H_4$	C_6H_5	C_6H_5	(160)
4-HO-3-BrC_6H_3	C_6H_5	C_6H_5	(257)
4-HO-3-$CH_3C_6H_3$	C_6H_5	C_6H_5	(257)
5-CH_3-4-Br-2-HOC_6H_2	C_6H_5	C_6H_5	(257)
3,5-Br_2-4-HOC_6H_2	C_6H_5	C_6H_5	(257)
4-$O_2NC_6H_4$	CH_3	CH_3	(16)
3-$O_2NC_6H_4$	CH_3	CH_3	(16)
2-$O_2NC_6H_4$	CH_3	CH_3	(16)
$C_6H_5CH_2$	CH_3	CH_3	(16)
C_6H_5	CH_3	CH_2COOH	(108)
4-$CH_3C_6H_4$	CH_3	CH_2COOH	(108)

Selenonium salts

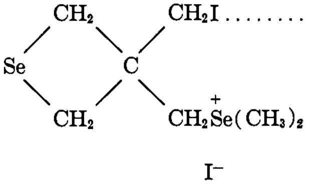
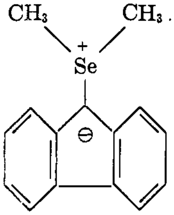
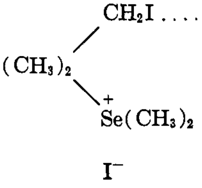
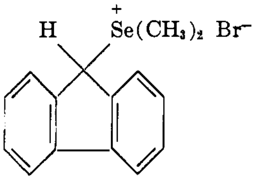
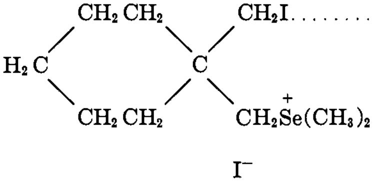
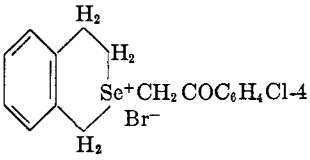
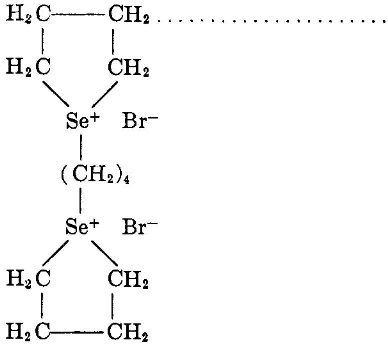
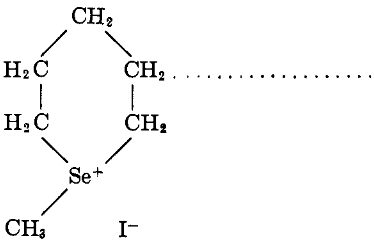
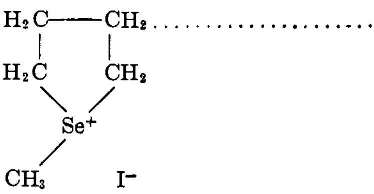
COMPOUND	REFERENCES	COMPOUND	REFERENCES
	(15)		(170)
	(15)		(170)
		$[(C_6H_5CH_2)_3Se]^+ NO_3^-$	(142)
		$(4\text{-}CH_3OC_6H_4)_3Se^+ Cl^-$	(160)
		$(4\text{-}C_2H_5OC_6H_4)_3Se^+ Cl^-$	(160)
		$(4\text{-}HOC_6H_4)_3Se^+ Cl^-$ (and derivatives)	(257)
	(15)		(168)

TABLE 14—*Concluded*

Miscellaneous selenonium salts

COMPOUND	REFERENCE	COMPOUND	REFERENCE
	(155a)		(155a)
			(155a)

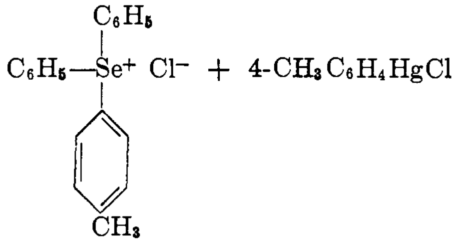
selenide reacts with methyl iodide or methyl sulfate to give phenyldimethylselenonium iodide or sulfate (16, 108, 170). Other less common methods which lead to selenonium salts include the reaction of a selenide dichloride and an aromatic hydrocarbon in the presence of aluminum chloride (215). Thus, triphenylselenonium chloride may be prepared from diphenylselenium dichloride and benzene (216).

$$(C_6H_5)_2SeCl_2 + C_6H_6 \xrightarrow{AlCl_3} (C_6H_5)_3Se^+Cl^- + HCl \qquad (61a)$$

This method is straightforward and gives good yields of product.

Selenide dihalides also react with diarylmercury compounds to give selenonium salts. This reaction is particularly useful for small batches of product, since the yield is excellent and the product easily recovered (212, 216):

$$(C_6H_5)_2SeCl_2 + (4\text{-}CH_3C_6H_4)_2Hg \rightarrow$$

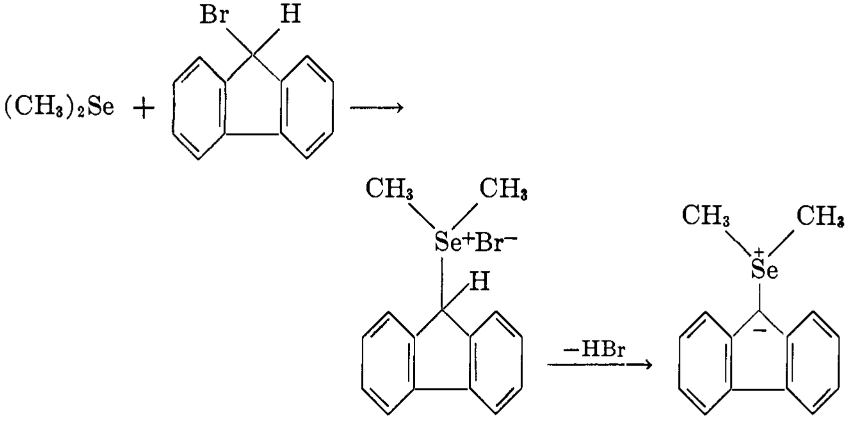


$$C_6H_5-\underset{C_6H_4CH_3}{\overset{C_6H_5}{Se^+}}\ Cl^- + 4\text{-}CH_3C_6H_4HgCl \qquad (62)$$

Finally, phenols and other very reactive molecules give selenonium salts with selenium oxychloride (257). This reaction, however, in other cases leads to

$$C_6H_5OH + SeOCl_2 \rightarrow (4\text{-}HOC_6H_4)_3Se^+Cl^- + H_3O^+ + Cl^- \qquad (63)$$

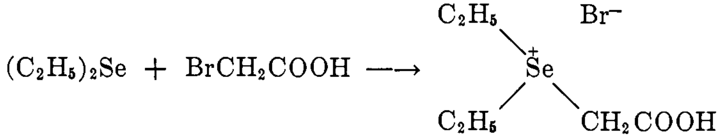
other products; see, for example, Section IV, E. An interesting selenonium salt has been prepared by Hughes and Kuriyan (170). They allowed dimethyl selenide to react with 9-bromofluorene to give dimethylfluorenylselenonium bromide, which then gave, on loss of hydrogen bromide, the compound dimethylselenoniumfluorenylidide, a black precipitate, soluble in organic solvents to give a purple solution.



(64)

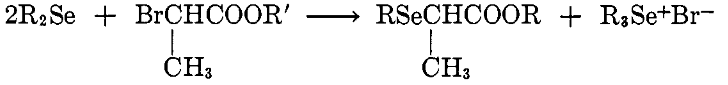
A number of optically active selenonium salts have been prepared (*vide infra*). Some examples are $RR'Se^+CH_2COOH\ Br^-$.

It is interesting to note that while Carrara (75) was able to react diethyl selenide and bromoacetic acid to give the corresponding selenonium salt,



$$(C_2H_5)_2Se + BrCH_2COOH \longrightarrow (C_2H_5)_2\overset{+}{Se}CH_2COOH\ Br^- \qquad (65)$$

Biilman and Jensen (41) found an anomalous reaction between R_2Se and alkyl α-bromopropionate:



$$2R_2Se + \underset{\displaystyle CH_3}{BrCHCOOR'} \longrightarrow \underset{\displaystyle CH_3}{RSeCHCOOR} + R_3Se^+Br^- \qquad (66)$$

J. Selenocarbonyl compounds (see table 15)

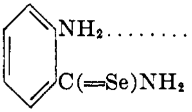
The selenocarbonyls (RCSeR') have been prepared by treatment of aldehydes and ketones with hydrogen selenide in the presence of concentrated hydrochloric acid (311) or alcoholic hydrogen chloride (343). The products are vile-smelling compounds, which are probably not monomeric (57). Selenobenzaldehyde exists in three modifications, α, β, and γ (343). Selenoketals may be prepared by the action of a selenomercaptan with a carbonyl compound in the presence of hydrochloric acid (313). Oxidation of the ketals fails to give products analogous to the sulfone ketals of the sulfur series.

The preparation of selenobenzoic acid has been reported (255) from the reaction of BrMgSeH and benzoyl chloride. The acid so obtained was unstable to prolonged heating in water, but was more stable than the corresponding thio analog.

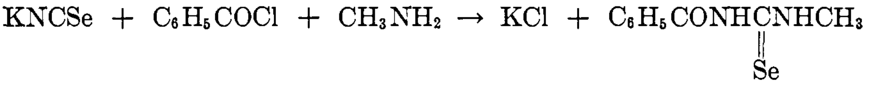
Carbon diselenide may be prepared in 50 per cent yield from hydrogen selenide and carbon tetrachloride at 500°C. (297). It has a melting point of 45.5°C. and boils without decomposition at 124°C. (760 mm.). Treatment of carbon diselenide with alcohol in the presence of alkali leads to the formation of sodium selenoxanthogenate in fair yield. Carbon diselenide is apparently polymerized by ammonia to low-molecular-weight substances which do not, however, contain nitrogen.

TABLE 15

Selenocarbonyl compounds

COMPOUND	REFERENCES	COMPOUND	REFERENCES
$(2\text{-}C_{10}H_7)_2Se \rightarrow Se$	(225)	$C_6H_5CH_2C(=Se)NH_2$	(197a)
$HC(=Se)H$	(343)	$CH_3C(=Se)NH_2$	(197a)
$CH_3C(=Se)H$	(343)		
$C_6H_5C(=Se)H$ (α, β, and γ forms)	(343)		
$C_6H_5C(=Se)NH_2$	(199)		(49)
C_6H_5COSeH	(224)		
$RCONHC(=Se)NHR'$	(109)		
$C_6H_5NHC(=Se)CONHC_6H_5$	(136)		

The selenoureas have been prepared by several methods. Hydrogen selenide may be added to substituted cyanamides to give selenoureas (5), while the reaction of hydrogen selenide and dicyanamide in the presence of strong hydrochloric acid gives selenourea itself. Unsymmetrical aroylalkylselenoureas have been prepared by the reaction of an aroyl acid chloride, potassium selenocyanate, and an aliphatic or aromatic amine (104).



$$KNCSe + C_6H_5COCl + CH_3NH_2 \rightarrow KCl + C_6H_5CONH\underset{\underset{\text{Se}}{\|}}{C}NHCH_3 \quad (67)$$

Symmetrical selenoureas may be made by the reaction of amines with carbon diselenide (297).

V. PHYSICAL PROPERTIES OF ORGANOSELENIUM COMPOUNDS

Table 16 contains a compilation of data on the physical properties of the selenium compounds considered above. The comments are necessarily of a general nature; where feasible, exceptions have been noted, though by no means have all exceptions been considered.

The properties listed are for pure compounds. This should be borne in mind especially with regard to odor. Impure samples of compounds listed as odorless may have atrocious odors.

TABLE 16

Properties of organoselenium compounds

TYPE OF COMPOUND	PHYSICAL STATE (AT ROOM TEMPERATURE)	COLOR	ODOR	SOLUBILITY	REMARKS
Selenocyanates:					
Aliphatic	Liquid	Colorless	Vile	Soluble in all organic solvents; immiscible with water	Usually yellow because of diselenide contaminant
Aromatic	Crystalline solids, except phenyl	Colorless	Bad	Soluble in all organic solvents; immiscible with water	Any yellow or orange color due to diselenide
Selenols:					
Aliphatic	Liquid	Colorless	Vile	Soluble in all organic solvents and in aqueous alkali	Usually yellow, owing to impurity of diselenide
Aromatic	Crystalline solids	Colorless	Vile		
Diselenides:					
Aliphatic	Liquid	Bright yellow	Bad	Soluble in all organic media; insoluble in water	Diselenide linkage is a characteristic yellow chromophore
Aromatic	Crystalline solids	Bright yellow	Slight; not necessarily bad		
Selenium acids:					
—SeOH	Crystalline solids	Colorless	None	Soluble in polar organic media, water, and alkali	Selenonic acids are strong acids and strong reducing agents; seleninic acids are stable and of moderate strength; selenenic acids are weak and unstable
—SeO_2H					
—SeO_3H					
Selenide halides (aliphatic and aromatic):					
Mono-Cl	Solids	Colorless to pale yellow	Odor of the halogen	Soluble in organic media; hydrolyzed by water	Easily hydrolyzed, the chlorine derivative more rapidly than the bromine
Tri-Cl					
Mono-Br	Solids	Orange to deep red	Odor of the halogen	Soluble in alkali	Se—Br is an orange chromophore
Tri-Br					
Selenocarbonyl derivatives	Usually solids	Yellow to orange	Usually vile	Soluble in organic media	C=Se is a yellow chromophore
Selenides, R_2Se:					
Aliphatic	Liquids	Colorless	Bad	Soluble in all organic media; insoluble in water	Colors due to impurities
Aromatic	Crystalline solids, except the phenyl and *o*-tolyl derivtives, which are liquids	Colorless	No odor or a slight *pleasant* odor, such as that of diphenyl ether	Soluble in all organic media; insoluble in water	Colors due to impurities

TABLE 16—*Concluded*

TYPE OF COMPOUND	PHYSICAL STATE (AT ROOM TEMPERATURE)	COLOR	ODOR	SOLUBILITY	REMARKS
Selenide dibromides.	Crystalline solids	Light orange to ruby red	Slight odor of halogen	Soluble in organic media, except strongly nonpolar ones, such as hexane; hydrolyzed by water	Partially dissociated in solution to bromine and selenide; aliphatic derivatives are unstable
Selenide dichlorides.	Crystalline solids	Colorless to lemon yellow	Slight odor of halogen	Soluble in organic media except strongly nonpolar alkanes, such as hexane; hydrolyzed by water	Partially dissociated in solutions
Selenoxides	Crystalline solids	Colorless	None	Soluble in organic media; partially soluble in water	Very soluble in benzene
Selenones	Crystalline or amorphous solids; high melting	Colorless	None	Solubility is slight; usually may be recrystallized from acetic acid	
Selenonium salts	Crystalline solids	Colorless	None	Soluble in polar organic media and in water	

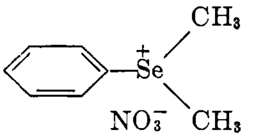
VI. CERTAIN ASPECTS OF THE CHEMISTRY OF ORGANOSELENIUM COMPOUNDS OF INTEREST TO THEORETICAL CHEMISTRY

A. Orientation effects

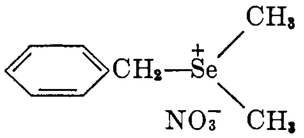
No thorough study has been made of the orienting influences of a selenium atom attached to an aromatic ring. The nitration of diphenylselenium gives *m*-nitrodiphenyl selenoxide (86). This reaction appears to take place in two steps; the first step consists of oxidation to a selenoxide, which is then nitrated. As the dipole of the Se—O group is directed strongly away from the benzene ring, meta orientation predominates, as it does in the case of nitro or carbonyl groups.

On the other hand, phenyl selenocyanate is converted smoothly to the *p*-nitro compound without intermediate oxidation (57).

Nitration of phenyldimethylselenonium nitrate (X) gives 100 per cent meta nitration, while nitration of benzyldimethylselenonium nitrate (XI) gives 16 per cent meta and 84 per cent ortho–para derivatives.



X



XI

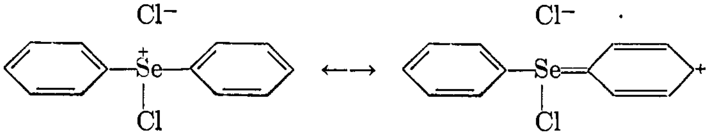
Halogenation of diphenylselenium, brought about by heating a diphenylselenium dihalide above its melting point, gives predominantly para substitution (30).

Attempts to metalate methyl phenyl selenide with butyllithium gave, after carbonation, benzoic acid and butyl methyl selenide (266a).

$$C_6H_5SeCH_3 + n\text{-}C_4H_9Li \xrightarrow{CO_2} C_6H_5COOH + C_4H_9SeCH_3 \qquad (67a)$$

B. Electric moments

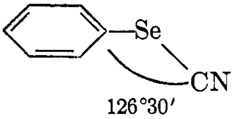
The electric moments of selenium derivatives have been covered in several papers (77, 176, 177, 303, 318, 319). Smyth, Grossman, and Ginsburg (318) have measured the electric moments of diphenylselenium dichloride (3.47 D in benzene) and selenium tetrachloride (2.54 D in benzene). Since the latter compound has a finite moment, it cannot be tetrahedral (sp^3 bonds) or square (sp^2d bonds). They have suggested that the tetravalent selenium compounds form a trigonal bipyramid; additional evidence for this type of structure has been shown quite clearly in a series of crystal structure studies by McCullough and Hamburger (237, 238). Smyth, Grossman, and Ginsburg also attributed considerable ionic character to the selenide halides, to account for the high moment observed. Thus they consider structures such as XII, stabilized by resonance, to contribute to the overall structure:



XII

Similar arguments have been put forward by Jensen (176), who found the moment of diphenylselenium dichloride to be 3.21 D, while that of diphenylselenium dibromide was found to be 3.40 D. Smyth, Lewis, Grossman, and Jennings (319) have measured the moments of selenium oxychloride (2.62 D) and selenium dichloride (Se_2Cl_2, 2.1 D). Diphenyl selenoxide has a dipole moment of 4.44 (177). The magnitude of this moment has been interpreted by Phillips, Hunter, and Sutton (283) to indicate that the selenium-oxygen bond is semipolar.

Rogers and Campbell (73, 303) have measured the electric moments of a number of selenium compounds, which are listed in table 17. From these data, it was concluded that the C—Se—C angle in selenides is about 115°, while the C—Se—Se bond angle in diselenides is 110°. The selenocyanate group in aromatic compounds was calculated to make an angle of 126°30′ with the axis of the benzene ring, if free rotation around the bond between the selenium atom and the aromatic ring was assumed.



The dipole moments of selenophene (336) and some higher ring systems have been measured. The data are given in table 18.

TABLE 17

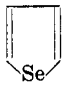
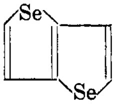
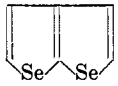
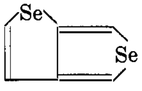
Molar refractions, molar polarizations, and dipole moments

SUBSTANCE	MR_D	P_∞ AT 25°C.	μ
			Debyes
Diphenyl diselenide	75.7	133	1.67
Di-*p*-tolyl diselenide	84.7	192	2.29
Dibenzyl diselenide	84.7*	133	1.54
Di-*p*-bromophenyl diselenide	91.8	102	0.70
Di-*p*-tolyl selenide	72.6	140	1.81
Di-*p*-chlorophenyl selenide	72.6*	84.7	0.77
Benzyl selenocyanate	47.3	372	3.98
p-Tolyl selenocyanate	47.8*	434	4.35
p-Chlorophenyl selenocyanate	48.5	269	3.28
p-Aminophenyl thiocyanate	47.0	592	5.16
p-Dimethylaminophenyl thiocyanate	54.0	720	5.70
p-Nitrophenyl thiocyanate	46.0	243	3.10
p-Aminophenyl selenocyanate	43.0	600	5.22
p-Dimethylaminophenyl selenocyanate	57.0	708	5.64
p-Methoxyphenyl selenocyanate	48.1	450	4.42
p-Nitrophenyl selenocyanate	50.5	312	3.58
p-Selenocyanophenyl thiocyanate	55.4	385	4.02

* Estimated from the empirical constants of Eisenlohr (Z. physik. Chem. **75**, 585 (1910)), along with the value 12.6 for selenium and 26.21 for benzene. The value for selenium is an average calculated from mole refractions of aromatic selenium compounds. Tschugaeff (339) gives the following atomic refractions: for RSeH, 10.78; for RSeR, 10.91; for R_2Se_2, 11.94.

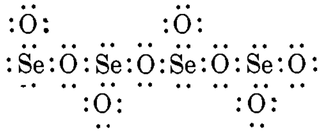
TABLE 18

The electric moments of selenophene and some related compounds

COMPOUND	MOMENT	COMPOUND	MOMENT
	Debyes		*Debyes*
	0.78		0.0
	1.52		1.07

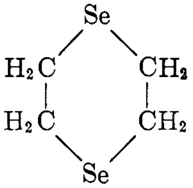
C. Studies of the crystalline state

Mixed crystal studies (298, 299, 300) have been carried out on a large number of pairs of sulfur and selenium compounds. The data have been interpreted by Rheinboldt and Giesbricht to indicate that the steric configurations of sulfones, sulfoxides, selenones, and selenoxides are all essentially the same. This should mean that optically active selenoxides could be obtained (see, however, Section IV, D). The crystal structure of selenium dioxide has been worked out by McCullough (231). His data show that selenium dioxide in the solid state is polymeric.



$$\begin{array}{cccccccc} :\ddot{\mathrm{O}}: & & & & :\ddot{\mathrm{O}}: & & & \\ :\ddot{\mathrm{Se}}: & \ddot{\mathrm{O}}: & \ddot{\mathrm{Se}}: & \ddot{\mathrm{O}}: & \ddot{\mathrm{Se}}: & \ddot{\mathrm{O}}: & \ddot{\mathrm{Se}}: & \ddot{\mathrm{O}}: \\ & & :\ddot{\mathrm{O}}: & & & & :\ddot{\mathrm{O}}: & \end{array}$$

The compound 1,4-diselenane (XIII) has been shown by Marsh and McCullough (241a), using x-ray methods, to exist in the "chair" form in the solid state. They also made the rather unexpected observation that the Se—C bond length in this compound is extraordinarily long, 2.01 ± 0.03 Å.; this is 0.07 Å. longer than the sum of the single-bond covalent radii for selenium and carbon.

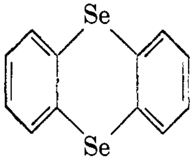


XIII

1,4-Diselenane

The crystal structures of selenanthrene (352, 354) and phenoxaselenin (353) have been determined. From the data Wood and Williams (354) have calculated that the angle of fold in selenanthrene is about 127°.

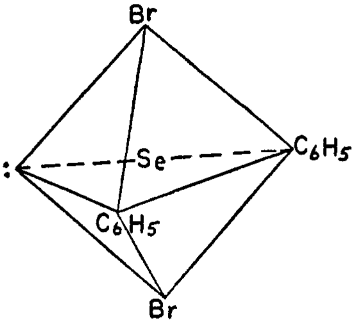
Similar studies have been carried out by Campbell, LeFèvre, LeFèvre, and Turner (70), who calculated that the molecule of selenanthrene (XIV) is "folded" and not planar.



XIV

Selenanthrene

Diphenylselenium dichloride (238) and diphenylselenium dibromide (237) have been examined crystallographically by McCullough and Hamburger, who showed that these molecules exist as trigonal bipyramids, with an unshared pair of electrons at one vertex (XV). The corresponding di-*p*-tolyl derivatives have been examined by McCullough and Marsh (238b).



XV

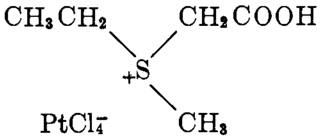
To attain this configuration, it should be noted, selenium must expand its outer shell to contain ten electrons.

The structure of triphenylselenonium chloride has been partially elucidated (238a). The configuration of the phenyl groups has not been determined, but the experimental value of 3.60 Å. for the selenium–chlorine bond distance indicates clearly that this bond is ionic.

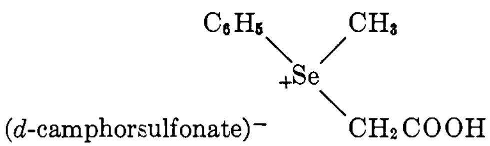
D. Optical activity of organoselenium compounds

The theory of optical activity requires the existence of a center of asymmetry. Usually, one thinks of the tetrahedral carbon atom with four unlike groups as such an asymmetric center. This familiar concept can be extended to other elements, such as nitrogen, sulfur, arsenic, etc. In particular, it is of interest to consider the selenium atom as a center of asymmetry.

As early as 1899, Pope and Peachey (291) were able to resolve methylethylthetine platinchloride (XVI) into optically active forms. In 1902 Pope and Neville (290) separated phenylmethylselenetine bromide (XVII) by means of its *d*-camphorsulfonate:

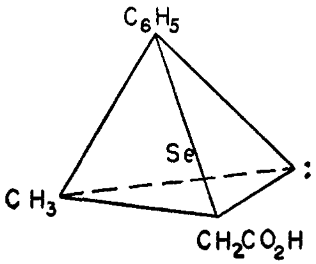


XVI



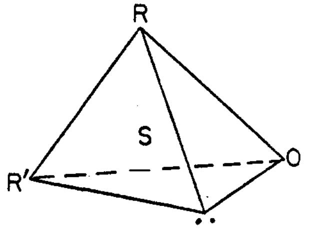
XVII

In the selenonium (and sulfonium) salts, the optical activity results from a configuration such as that shown in XVIII for the ion:



XVIII

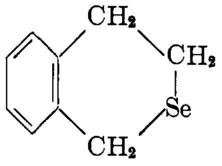
It has been shown by Harrison, Kenyon, and Phillips (157) that sulfoxides (RR′S→O) also are resolvable, the fourth corner of the tetrahedron again being occupied by an unshared pair of electrons:



XIX

Thus, 4-methyl-4′-aminodiphenyl sulfoxide has $[\alpha]_{5461}^{25°} = \pm 123°$ in ethanol, and *m*-carboxyphenyl methyl sulfoxide has $[\alpha]_{5461}^{25°} = \pm 135$ in the same solvent. In an attempt to extend this analogy to selenium, Gaythwaite, Kenyon, and Phillips (143, 144) prepared phenyl tolyl selenoxide and *p*-carboxyphenyl methyl selenoxide, which they were unable to separate into stereoisomers, using standard procedures which worked well with the sulfoxides.

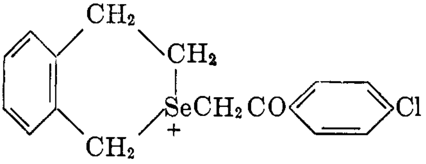
Thompson and Turner (338) have prepared some selenium-containing analogs of the suitably substituted optically active phenoxarsines, but were unable to resolve them, even though the molecules should be bent in the same manner and should exhibit similar properties. Holliman and Mann (168) have prepared



XX

Selenoisochroman

selenoisochroman, but were unable to resolve its oxide; however, the selenonium salt with *p*-chlorophenacyl bromide was readily resolved with *d*-camphorsulfonic acid.



XXI

There appears to be no apparent reason why selenoxides cannot be resolved whereas sulfoxides can. Since the problem is of considerable interest from the theoretical point of view, some further attempts should be made to resolve selenoxides. One possibility has occurred to the present authors: namely, that the resolution of selenoxides may require strictly anhydrous conditions, as it appears likely that selenoxides may form relatively stable hydrates of the type $RR'Se(OH)_2$, while sulfoxides do not. This point could be checked relatively easily, by comparing the rate of exchange of O^{16} in analogous selenoxides and sulfoxides for O^{18} in solvents containing O^{18}-enriched water.

E. Oxidation by selenium dioxide

The use of selenium dioxide as an oxidizing agent has been reviewed recently by Waitkins and Clark (344a). This reagent is specific for certain types of structures. Thus, methylene groups alpha to a carbonyl are oxidized to carbonyl, so that the method offers probably the best synthetic route for many dicarbonyl compounds.

$$RCH_2COR' + SeO_2 \rightarrow RCOCOR' + Se + H_2O \qquad (68)$$

Similarly, methylene groups alpha to carbon–carbon double bonds are oxidized,

$$CH_3CH{=}C(CH_3)_2 \rightarrow CH_3CH{=}C(CH_3)CH_2OH \qquad (69)$$

as is a methyl group activated by an aromatic ring (331a).

$$C_6H_5CH_3 + SeO_2 \rightarrow C_6H_5CHO + C_6H_5COOH \qquad (70)$$

The mechanism of the reaction between selenium dioxide and an olefin has been examined by Guillemonat (154), who proposed the following sequence of changes:

$$4RCH_3 + SeO_2 \rightarrow (RCH_2)_4Se + 2H_2O \qquad (71)$$

$$(RCH_2)_4Se + H_2O \rightarrow (RCH_2)_2Se + RCH_3 + RCH_2OH \qquad (72)$$

$$(RCH_2)_2Se + H_2O \rightarrow RCH_2OH + RCH_3 + Se \qquad (73)$$

This "mechanism" is completely unsatisfactory, since aside from the fact that it explains nothing, it requires intermediates and reactions of a completely unproven nature. Indeed, the overwhelming bulk of the evidence is against even the transient existence of tetraalkylselenium compounds and against the hydrolysis indicated in equation 73.

A more logical approach to the mechanism of this reaction has been made by Mel'nikov, Rokitskaya, and Cherkasova (244, 245). (For additional references see Waitkins and Clark (344a), who postulate an intermediate selenite ester.)

We should like to point out that the reaction between selenium dioxide and organic molecules is identical in its specificity to certain reactions such as bromination with *N*-bromosuccinimide and autoxidation with molecular oxygen, which are known to be free-radical reactions. It appears reasonable, then, to guess that selenium dioxide reacts with organic molecules by a free-radical mechanism; beyond that, it is difficult to postulate any sequence of reactions without considerable additional experimental data.

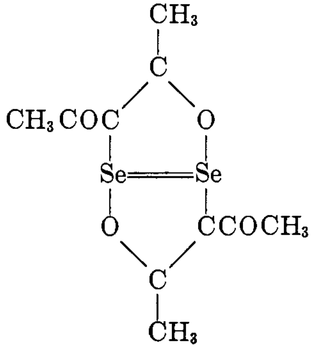
F. Reaction between β-diketones and selenium halides

Certain selenium halides react with copper salts of β-diketones by replacing copper to form a series of compounds with interesting proposed structures (139, 262, 264, 267a).

The reaction between selenium tetrachloride and copper acetylacetone may be represented by the overall equation:

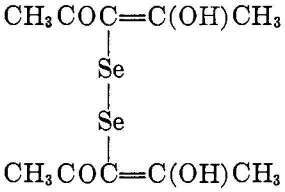
$$2SeCl_4 + 2Cu(C_5H_7O_2)_2 = Se_2(C_5H_6O_2)_2 + 2C_5H_7O_2Cl + 2HCl \quad (74)$$

The diselenide is nonenolic. It has been represented as having the following structure:



XXII

Treatment of this compound with hydriodic acid gives diselenium biacetylacetone, to which the following structure has been assigned:

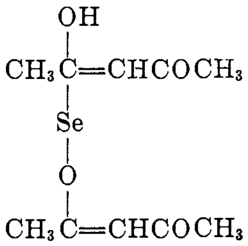


$$\begin{array}{c} CH_3COC{=}C(OH)CH_3 \\ | \\ Se \\ | \\ Se \\ | \\ CH_3COC{=}C(OH)CH_3 \end{array}$$

XXIII

This product is enolic; it is produced also by allowing copper acetylacetone and selenium chloride to react.

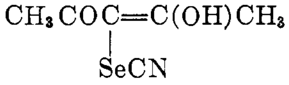
When selenium acetylacetone is treated with acetylacetone, selenium *O,C*-bisacetylacetone is produced.



$$\begin{array}{l}\text{OH}\\ |\\ CH_3C{=}CHCOCH_3\\ |\\ \text{Se}\\ |\\ \text{O}\\ |\\ CH_3C{=}CHCOCH_3\end{array}$$

XXIV

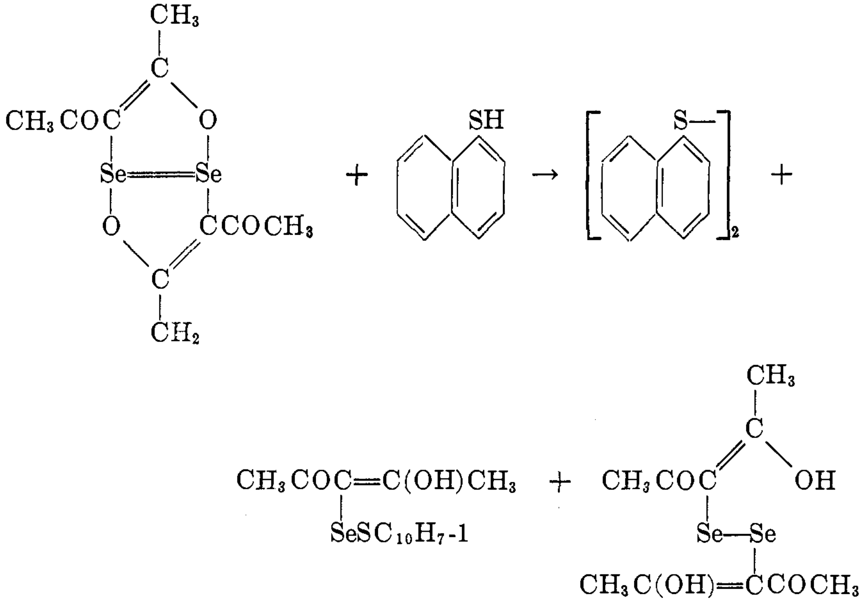
This reaction is reversed by heat or hydrolysis. Treatment of selenium acetylacetone with hydrogen cyanide yields 2 moles of 3-selenocyanoacetylacetone:



$$\begin{array}{l}CH_3COC{=}C(OH)CH_3\\ |\\ \text{SeCN}\end{array}$$

3-Selenocyanoacetylacetone

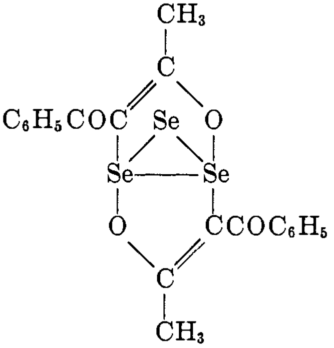
If selenium acetylacetone and α-naphthyl mercaptan are allowed to react, three products are formed. The reaction has been represented as follows:



XXV

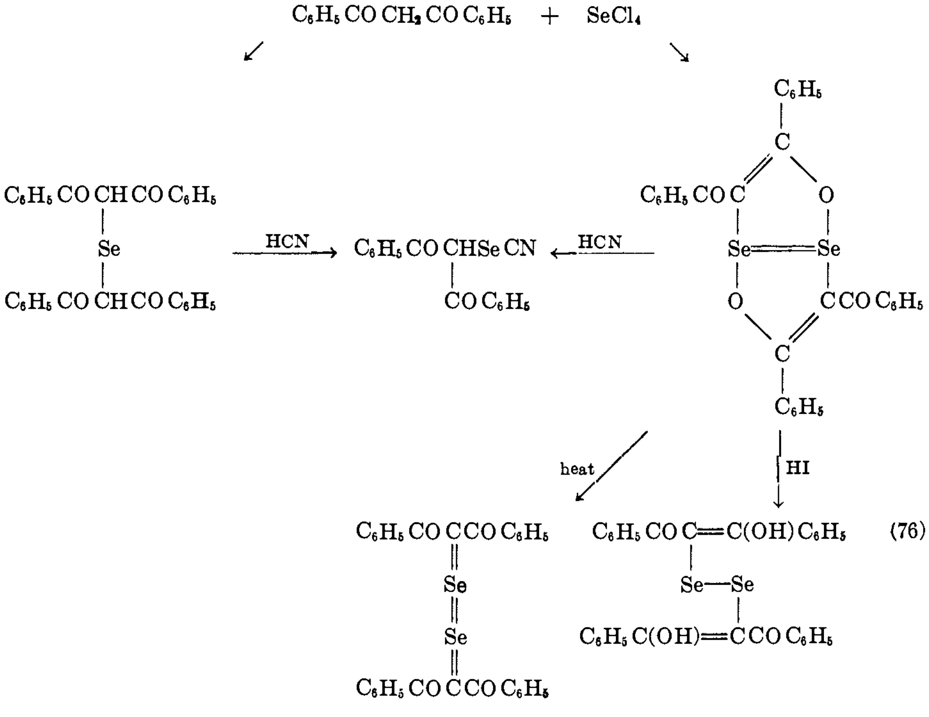
(75)

Copper benzoylacetone and selenium tetrachloride give a product similar to that from acetylacetone. In addition, a second compound can be isolated if an excess of selenium tetrachloride is used. This latter compound has the empirical formula $C_{10}H_8O_2Se_3$; the unusual and improbable structure below has been proposed for it:



XXVI

Interaction of dibenzoylmethane and selenium tetrachloride leads essentially to the same results as those obtained with other β-diketones, with formation of one additional compound of different composition, $Se(C_{15}H_{11}O_2)_2$. The following schematic representation of the reactions of dibenzoylmethane and selenium tetrachloride, and of the relationship of the compounds in their subsequent reactions, has been proposed:



(76)

G. Miscellaneous considerations

(1) Dissociation of diarylselenium dihalides

Diarylselenium dibromides and dichlorides dissociate appreciably in solution (232, 232a, 235).

$$Ar_2SeBr_2 \rightleftharpoons Ar_2Se + Br_2 \qquad (77)$$

McCullough and Eckerson (235) and McCullough and Barsh (232a) have measured the extent of dissociation of a series of symmetrically and unsymmetrically ring-substituted diphenylselenium dihalides (table 19) and found that the data could be correlated by use of Hammett's rho–sigma treatment.

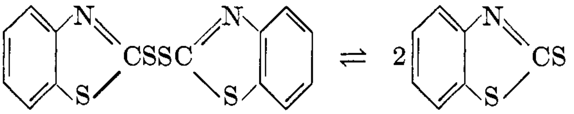
TABLE 19

Dissociation constants of diarylselenium dibromides

R	K (25°C.)	R	LOG K
H	4.8×10^{-4}	4-CH_3O	−4.19
2,2′-Cl_2	8.5×10^{-2}	4-CH_3	−3.68
3,3′-Cl_2	1.1×10^{-2}	3-CH_3	−3.64
4,4′-Cl_2	2.1×10^{-3}	4-CH_3-4′-Cl	−3.26
2,2′-$(CH_3)_2$	7.0×10^{-3}	4-Cl	−2.96
3,3′-$(CH_3)_2$	1.4×10^{-4}	3-Cl	−2.64
4,4′-$(CH_3)_2$	3.6×10^{-5}		
4,4′-F_2	1.2×10^{-3}		
4,4′-Br_2	2.8×10^{-3}		
4,4′-$(CH_3O)_2$	2.7×10^{-5}		
4,4′-$(C_6H_5O)_2$	1.1×10^{-4}		

(2) Dissociation of diselenides into free radicals

It has been shown by Schönberg, Rupp, and Gumlich (309) that solutions of diphenyl diselenide and various disulfides do not obey Beer's law and that they exhibit chemical characteristics which indicate that they are probably partially dissociated into free radicals. This has been confirmed recently by Cutforth and Selwood (98a), who determined magnetically the degree of dissociation of 2,2′-benzothiazyl disulfide at different temperatures (table 20). The probability that diselenides exhibit similar characteristics is very great. Thus a simple experiment has been done (71) showing that temperature has an effect on the color of diselenides. A solution of diphenyl diselenide in xylene was divided equally among three colorimeter tubes. One was heated to boiling, one kept at room temperature, and one cooled to −80°C. A distinct loss of color occurred in the cold sample, and a distinct increase occurred in the heated sample; on regaining room temperature, the solutions in all three tubes were



(78)

again the same color. This color change may be connected with dissociation of the molecule into free radicals.

Other reactions of diselenides which may be interpreted as reactions of a radical type include the halogenation to RSeBr, the facile reaction with mercury and silver ions (133), and the thermal decomposition to R_2Se, which may take the following course:

TABLE 20

Degree of dissociation of 2,2'-benzothiazyl disulfide

Solvent, toluene; molality of disulfide, 0.0148

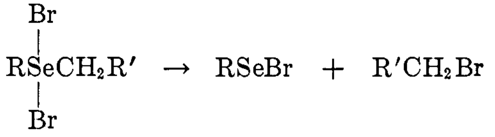
TEMPERATURE	α (DEGREE OF DISSOCIATION)	TEMPERATURE	α (DEGREE OF DISSOCIATION)
°C.		°C.	
25	(0.0)	125	0.151
100	0.032	150	0.350

$$C_6H_5SeSeC_6H_5 \rightleftharpoons 2C_6H_5Se\cdot \rightarrow C_6H_5\cdot + Se \tag{79}$$

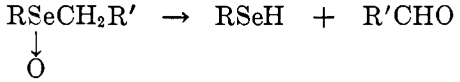
$$C_6H_5Se\cdot + C_6H_5\cdot \rightarrow C_6H_5SeC_6H_5 \tag{80}$$

(3) Decomposition of alkyl selenide dihalides and alkyl selenoxides

Compounds of this type derived from selenides containing the structural unit —$SeCH_2$— decompose readily (30, 108).

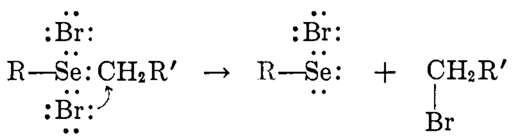


$$R\overset{\overset{Br}{|}}{\underset{\underset{Br}{|}}{Se}}CH_2R' \rightarrow RSeBr + R'CH_2Br \tag{81}$$

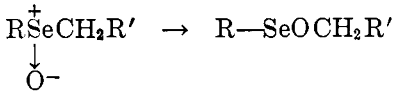


$$R\underset{\underset{O}{\downarrow}}{Se}CH_2R' \rightarrow RSeH + R'CHO \tag{82}$$

This reaction appears to require a transfer of an atom from selenium to the alpha carbon atom:



$$R{-}\overset{:\ddot{Br}:}{\underset{:\underset{\cdot\cdot}{Br}:}{\ddot{Se}}}{:}CH_2R' \rightarrow R{-}\overset{:\ddot{Br}:}{\underset{\cdot\cdot}{\ddot{Se}}}{:} + \underset{\underset{Br}{|}}{CH_2R'} \tag{83}$$



$$R\overset{+}{\underset{\underset{O^-}{\downarrow}}{Se}}CH_2R' \rightarrow R{-}SeOCH_2R' \tag{84}$$

$$RSeOCH_2R' \rightarrow RSeH + RCHO \tag{85}$$

Reaction 85 is analogous to the formation of an alcohol and an aldehyde by the "disproportionation" of a peroxide.

$$\mathrm{ROOCH_2R'} \rightarrow \mathrm{RO\cdot} + \mathrm{R'CH_2O\cdot} \rightarrow \mathrm{ROH} + \mathrm{R'CHO} \qquad (86)$$

A similar reaction occurs with alkylseleninic acids.

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