ORGANIC COMPOUNDS OF SELENIUM, V[1]

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CYCLIC SELENOLS

Introduction. The purpose of this paper is to present a complete list of the cyclic selenols that have been reported in the literature prior to 1931. A complete bibilography and the known methods of preparation are listed (See Tables II and III) for each compound. The equations listed (See Table I) under the methods of preparations are expressed in general terms. In all the equations in this article "R" represents a univalent homocyclic radical unless otherwise stated. The selenols, which are analogues of alcohols and phenols, are represented by the formula R-SeH. Aliphatic selenols, which have been previously described (6), therefore correspond to aliphatic alcohols and mercaptans while the cyclic selenols correspond to phenols and thiols. Mention of 23 cyclic selenols was found in the literature.

Properties. The cyclic selenols like the mercaptans are characterized by a very disagreeable odor. Most of them are colorless compounds. Some have been reported as having a slight yellow color (30). This may be due to a trace of impurity, such as the diselenide, which is formed by oxidation of the selenol. Long exposure to air produces this discolorization. The selenols are generally solids at ordinary temperatures, and become liquids above 100° C. with a specific gravity approximately twice that of water. They are soluble in both alcohol and ether and may be crystallized from these solvents. They are only slightly soluble in water but in an alkaline solution soluble compounds are formed. Phenyl selenol has been separated from an acid solution by steam distillation (17). With soluble salts of the heavy metals the selenols form insoluble seleno mercaptides or selenolates.[2]

$$RSeH + MX = RSeM + HX.$$

(M = Na, K, Hg, Zn, Pb, Ag, or Cu; X = halide or hydroxide.)

With alkyl halides the soluble selenolates react to form selenides.

$$RSeM + RX = RSeR + MX.$$

The zinc salt of *2*-aminophenyl selenol or zinc *2*-aminophenyl selenolate in the presence of ethyl acetate reacts with benzoyl chloride to produce *1*-phenylbenzoselenazole (1).

[1] This paper is the fifth in a series which will ultimately present a classification of the prepared selenium organic compounds and a resume of the chemistry and literature pertaining to them.

[2] Named after the term alcoholate. This nomenclature is preferred to seleno mercaptide because the term seleno should refer only to a divalent selenium, both valences of which are directed to the same carbon atom.

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$$2C_6H_5COCl + (NH_2C_6H_4Se)_2Zn = 2C_6H_4\langle \overset{NH}{\underset{Se}{\quad}} \rangle CPh + ZnCl_2 + 2H_2O.$$

With picryl chloride the zinc salt of *o*-aminophenyl selenol undergoes condensations with the formation of *3-5*-dinitroselenazine.

$$2ClC_6H2(NO_2)_3 + (NH_2C_6H_5Se)_2Zn = 2C_6H_4\langle \overset{NH}{\underset{Se}{\quad}} \rangle C_6H_2(NO_2)_2 + .$$

The selenols are very easily oxidized by contact with air or other mild oxidizing agents to the coresponding diselenides.

$2RSeH + O = R\text{-}Se\text{-}Se\text{-}R + H_2O.$

Stronger oxidizing agents[3] oxidize either the selenol or the diselenide to the seleninic acid. Still stronger oxidation[4] will bring about the formation of the corresponding selenonic acid. In the oxidation of the selenol, the diselenide and the seleninic acid may be formed as intermediate compounds with the selenonic acid as the final product.

$RSeH + O_2 = RSeOOH.$

$R\text{-}Se\text{-}Se\text{-}R + 3(O) + H_2O = 2RSeOOH.$

$RSeOOH + O = RSeO_3H.$

The sodium salt of phenyl selenol or sodium phenyl selenolate has been oxidized electrolytically to the diselenide.

A consideration of the above properties shows a great similarity to the properties of the analagous sulphur compounds. A comparison of the properties of the selenols with those of the phenols show, however, a definite increase in the influence of the more metallic selenium atom. This is best exhibited by the oxidation of the selenols to diselenides and finally to oxygen containing acids.

Methods of Preparation. The following general methods have been used to prepare cyclic selenols:

(a) By the reaction of magnesium alkyl or aryl halides on selenium. The complexes formed yield on treatment with dilute acids, selenols and diselenides.

(b) By the reduction of the corresponding diselenide upon the addition of sodium to the diselenide dissolved in alcohol.

(c) By the hydrolysis of a selenocyanate in an alkaline solution.

(d) By the reduction of the corresopnding seleninic acid with hydrochloric acid and zinc dust.

(e) By the action of sodium selenide or sodium hydrogen selenide on a cyclic halide.

(f) By the reduction of the corresponding selenonic acid with zinc and hydrochloric acid.

(g) By the condensation of an alkali metal selenocyanate with the hydrochloride of *omega*-aminoacetophenones containing substituents in the ring.

[3] The oxidizing agents, that have been used are, alkaline $KMnO_4$ alkaline H_2O_2, HNO_3, and bromine water (7).

[4] The oxidizing agents used to form selenonic acids include aqueous chlorine, alkaline $KMnO_4$, and 30% H_2O_2 in acetic acid.

TABLE I

THE PREPARATION OF SELENOLS

Method No.	*Equation*	*Ref. No.*
1.	$Se + RMgX + Et_2O; + H_2O + HCl = R_2Se_2 + R_2Se +$ RSeH + $Se + RMgX = RSeMgX, + HCl = RSeH + MgXCl +$ $2Se + 2RMgX = RSeH + Se(MgX)_2.$ $3Se + 3RMgX = R_2Se_2 + Se(MgX)_2.$ (X = Br, I.)	14, 20, 22. 28, 29, 30, 31
2.	$MSe + RX = RSeH + MX +$ (R = Homo- or Heterocyclic.) ($M = K_2, Na_2, NaH.$) (X = Br, Cl.)	4, 13, 23
3.	$MSeCN + RX = RSeCN; + MOH = MX + RSeH +$ HOCN + $MSeCN + RX = RSeCN + MX.$ $RSeCN + MOH = RSeH + HOCN.$ (M = Na, K.)	3, 4, 15, 20, 24
4.	$MSeCN + RN{=}NX; + MOH = RSeH + RSeCN + MX +$ $N_2 + HOCN +$ $MSeCN + RN{=}NX = RSeCN + MX + N_2.$ $RSeCN + MOH = RSeH + HOCN.$ (R = Homo- or Heterocyclic; M = K, Na; X = Cl, Br.)	1, 2, 3, 15 16, 20.
5.	$MSeCN + RCOCH_2NH_2{\cdot}HX = R\text{-}C(=N\text{-})CH(\text{-}NH\text{-})C\text{-}SeH + H_2O + MX.$ (M = K; X = Cl.)	26
6.	$R\text{-}Se\text{-}Se\text{-}R + H_2 = 2RSeH$	1, 5, 17, 18, 19, 20
7.	$RSeOOH + 2H_2 = RSeH + 2H_2O.$ (H = SO_2)	27
8.	$RSeO_3H + 3H_2 = RSeH + 3H_2O.$ (H = Zn + HCl)	12
9.	Reported but not now considered to have been prepared.	8, 9, 10
10.	Methods not affecting the Se atom.	1, 2

TABLE II.

LIST OF HOMOCYCLIC SELENOLS

Selenol	*Formula*	*M. P. or B. P. °C.*	*Methods of Prep.*	*Reference Numbers*
Phenyl-	C_6H_5SeH	$B_{16}=183$	1, 6, 7, 8, 9.	8, 9, 10, 12, 14, 17, 19, 21, 27, 28, 29, 30, 31.
2-Nitrophenyl	*2*-NO_2-C_6H_4SeH	..	4.	1, 14.
4-Nitrophenyl-	*4*-NO_2-C_6H_4SeH	..	4.	1, 14.
2-4-Dinitro-phenyl-	*2-4*-$(NO_2)_2=C_6H_3SeH$	..	3.	15.
2-Aminophenyl-	*2*-NH_2-C_6H_4SeH	..	6, 10.	1, 2, 5, 11.
Picrate of 2-Aminophenyl-	*2*-NH_2-$C_6H_4SeH\cdot C_6H_2(NO_2)_3$	..	10.	1, 2.
2-Sulfonic acid-*5*-Aminophenyl-	*2*-HO_3S-(*5*-NH_2-)-C_6H_3SeH	..	..	25.
4-Bromophenyl-	*4*-Br-C_6H_4SeH	M=75-7	1.	28, 29.
4-Chlorophenyl-	*4*-Cl-C_6H_4SeH	M=55	1, 3.	24, 28, 29.
4-Methylphenyl-	*4*-CH_3-C_6H_4SeH	M=46-7	1.	28, 29.
4-Ethoxyphenyl-	*4*-C_2H_5O-C_6H_4SeH	$B_{24}=156$	1.	28, 29.
2-Carboxyphenyl-	*2*-HOOC-C_6H_4SeH	..	6.	18.
Cyclohexanyl-	$C_6H_{11}SeH$	B=170-2	1.	22.

TABLE II—Continued

Selenol	*Formula*	*B. P. or M. P. °C.*	*Methods of Prep.*	*Reference Numbers*
1-Naphthyl-	$C_{10}H_7SeH$	B=165-7	1.	20, 28, 29, 30.
2-Naphthyl-	$C_{10}H_7SeH$	M=72-4	4, 6.	4, 6, 20.
1-Anthra-quiononyl-	$C_6H_4(CO)_2C_6H_3$-SeH-*1*	M=212	2, 4.	3, 4, 16.
2-Anthra-quinonyl-	$C_6H_4(CO)_2C_6H_3$-SeH-*2*	..	2.	4.
5-Sulfonic acid-anthraquinonyl-	*5*-HSO_3-$C_6H_3(CO)_2C_6H_3$-SCH-*1*	..	4.	3.
8-Sulfonic acid-*2*-nitroanthraquinonyl-	*8*-HO_3S-$C_6H_3(CO)_2C_6H_2(NO_2$-*2*$)$SeH-*1*	..	2.	4.

Table III.

List of Heterocyclic Selenols

Selenol	*Formula*	*M. P. °C.*	*Methods of Prep.*	*Reference Numbers*
5-Acridinyl-	$C_6H_4=C(SeH)-N=C_6H_4$	238	2.	13.
1-Ph-3-Me-4-Bz-pyrro-(a)monazolyl-*5*- (2 modifications)	Ph-N-N=C(Me)CBz-CSeH	96 and 116	2.	23.
3-(*3'*-*4'*-Dimethoxy Ph)-pyrro(b)monazolyl-*5*-	$(MeO)_2=C_6H_3-C=CH-NH-C(SeH)=N$	115-7	5.	26.
3-(*4'*-*5'*-Dimethoxy-2'-tolyl)-pyrro(b)monazolyl-5-	$(MeO)_2=C_6H_2(Me)-C=CH-NH-C(SeH)=N$	159-63	5.	26.

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