I. ORGANIC COMPOUNDS OF SELENIUM

W. E. BRADT and M. VAN VALKENBURGH, University of Cincinnati

Introduction. Because selenium and some of its compounds are now available in considerable amounts at reasonable prices, the investigation of the preparation and properties of organic selenium compounds is quite feasible. In order to further this work, the senior author plans a series of papers which, when completed, will present: (a) a classification of the known organic selenium compounds based on the analogous oxygen and sulphur types, (b) a complete list of all known organic selenium compounds, (c) a resume of the chemistry and methods of preparation developed for each class of compounds, and (d) a complete bibliography for each known organic selenium compound.

The physiological action of some of the more common inorganic selenium compounds is well known. Many organic selenium compounds are reported to exhibit valuable therapeutic and tinctorial properties. However, the investigation of these properties has been so incomplete that organic compounds of selenium are still only of scientific interest. It is hoped that a systematic presentation of the chemistry of organic selenium compounds, with a statement of the extent of the synthetic work accomplished to date, will create interest in developing the possibilities of service to mankind (dyes, medicinals etc.), which probably exist in this field. Investigation in this direction lends itself particularly to the worker who has available only limited equipment. The reactions can usually be conducted in apparatus which is always available or which may be easily prepared.

ALIPHATIC SELENOLS

In this group will be discussed compounds, represented by the following formulas, in which "R" is a methyl group, the hydrogen atoms of which may or may not be replaced by other groups.

1. $R-CH_2-SeH$
2. $R_2=CH-SeH$
3. $R_3\equiv C-SeH$
4. $R-Se-SeH$
5. $R_3\equiv Se-SeH$

Aliphatic selenols or seleno mercaptans have been prepared by four methods: (a) the interaction (1) of an alkali acid selenide and an alkyl iodide or bromide, (b) the interaction (2, 3, 4) of an alkali acid selenide or H_2Se and a calcium or potassium alkyl sulphate, (c) aluminum selenide (5) or hydrogen selenide reacting on an aliphatic alcohol at 250-300°C., and (d) the decomposition (6, 7) of a selenocyanate. Air must be excluded when making these preparations

Primary Selenols. Only three primary selenols have been isolated. They are *ethyl selenol*, *n-propyl selenol* and *n-butyl selenol*. They are heavy, colorless liquids with an extremely intense disgusting odor. They are insoluble in water, precipitate with salts of the heavy metals, those with lead and thallium being most characteristic, and form soluble seleno mercaptides (1) with the alkali metals. In air they are quickly converted to diselenides, (1) RSeSeR, and with the Grignard reagent, they yield (1) RSeMgI and hydrocarbons (11) quantitatively.

I. $2RSeH + \frac{1}{2} O_2 \rightarrow R-Se-Se-R + H_2O$.

II. $RSeH + CH_3MgI \rightarrow R-SeMgI + CH4$. Alkyl halides with sodium ethylate convert primary selenomercaptans into selenides, (III) $R-Se-R$.

III. $R-SeH + NaOC_2H_5 + R-Cl \rightarrow R-Se-R + C_2H_5OH + NaCl$. Halogen derivatives, such as $Br-(CH_2)n-Br$, under the same conditions give diselenides such as $C_2H_5Se(CH_2)nSeC_2H_5$; except ethylene bromide, which forms ethylene and diethydiselenide (IV).

IV. $2C_2H_5SeNa + Br-C_2H_4-Br \rightarrow C_2H_5-Se_2-C_2H_5 + C_2H_4 + 2NaBr$.

Secondary Selenols. The only secondary selenol which has been prepared is isopropyl selenol, $CH_3-CHSeH-CH_3$. It was prepared (60% yield) in 1926 (5) by action of Al_2Se_3 at 260-270°C. on isopropyl alcohol (V).

V. $3(CH_3)_2=CHOH + Al_2Se_3 \rightarrow 3(CH_3)_2=CHSeH + Al_2O_3$. Isopropylselenol boils at 70°-75°C.

Aromatic Primary Selenols. The aromatic alcohol, o-nitrobenzyselenol, or *o-nitrobenzylselen mercaptan*, $o\text{-}NO_2-C_6H_4CH_2SeH$, is prepared (6) by dissolving *o*-nitrobenzylselenocyanate (Prepared (VI) from *o*-nitrobenzylchloride and potassium selenocyanate) in aqueous alkali (VII). A red brown solution forms with the evolution of the odor of cyanogen.

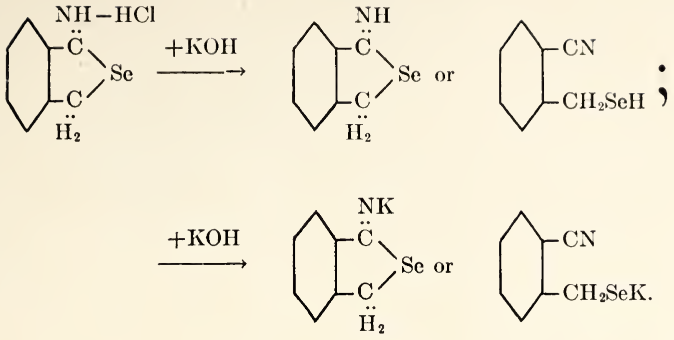
VI. $o\text{-}NO_2-C_6H_4CH_2Cl + KSeCN \rightarrow o\text{-}NO_2-C_6H_4CH_2SeCN + KCl$.

VII. $2o\text{-}NO_2-C_6H_4CH_2SeCN + H_2O + KOH \rightarrow 2o\text{-}NO_2-C_6H_4CH_2SeH + 2CN + O-$. The reaction is probably as indicated by equation (VII). If so, further investigation may demonstrate the formation of other products which would make the accuracy of the equation appear more probable. Since the evolution of oxygen would obviously oxidize the selenol to a diselenide ($R-Se-Se-R$) (I), the presence of the selenol as a final product is indication of the loss of oxygen with the formation of other oxidation products.

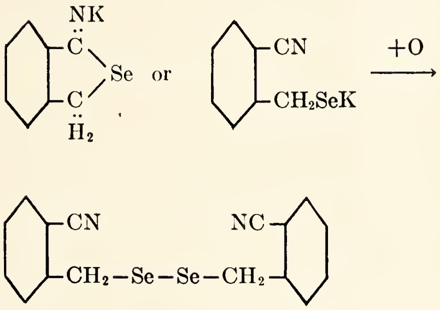
o-Cyanobenzylselenol, o-cyanobenzyl selenomercaptan, $o\text{-}CN-C_6H_4CH_2SeH$, or *selenophthalimidine,* (See Table I.) is prepared (7) by the action of concentrated H_2SO_4 on *o*-cyanobenzylselenocyanate (VIII).

VIII. $o\text{-}CN-C_6H_4CH_2SeCN + H_2SO_4 \rightarrow o\text{-}CN-C_6H_4CH_2SeH + CO_2 + NH_3$ The resulting product is an oil which crystallizes gradually. It exhibits both acid and basic properties and is soluble in solution containing an excess of either acid or base. Salts with HBr, HCl, H_2SO_4, H_2PtCl_6 and picric acid were formed which had the following formulas ($C_8H_7NSe=R$): $R-HCl$; $R-HBr$; $R=I_2$; $R-C_6H_3(NO_2)_3OH$; $R=H_2PtCl_6$ and $R_2=H_2SO_4$. The addition of a base to a solution of these salts of selenophthalimidine or *o*-nitrobenzylselenol at first forms a precipitate (IX), which redissolves on the addition of an excess of the base. This basic solution is very easily oxidized by the air (?) to the corresponding diselenide (X).

IX



X



Selenonium Selenols. *Tri-ethylselenomium selenol, tri-ethylselenitine hydroselenide* or *tri-ethylselenonium hydroselenide,* $(C_2H_5)_3=Se-SeH$, was prepared (8) according to the reactions represented by equations (XI) and (XII).

XI. $C_2H_5Br+C_2H_5-Se-Se-C_2H_5 \rightarrow Br.(C_2H_5)_2\equiv Se-Se-C_2H_5$.

XII. $MgBrC_2H_5+Br.(C_2H_5)_2\equiv Se-Se-C_2H_5+HOH \rightarrow C_2H_5OH+MgBr_2+(C_2H_5)_3\equiv Se-SeH$. It is a dense yellow oil with a disagreeable odor, which reacts with alcoholic silver nitrate to form triethylselenonium nitrate and silver selenide (XIII).

XIII. $(C_2H_5)_3\equiv Se-SeH+2AgNO_3 \rightarrow (C_2H_5)_3\equiv Se-NO_3+Ag_2Se+HNO_3$. This reaction demonstrates the properties of the selenol group which is attached to a tetravalent selenium atom. In this respect triethylselenonium selenol is not a true selenol.

Table I lists all of the aliphatic selenols, which have been prepared prior to 1929, with their formulas, boiling points and references to their mention in the literature. It will be noticed that three unsubstituted primary, two substituted primary, only one secondary, and no tertiary selenols have been prepared. Also, no selenide selenol $(R-Se-SeH)$ where the selenol group is attached to a bivalent selenium atom, has been prepared and only one selenonium selenol $(R_3=Se-SeH)$ in which the selenol group is attached to a tetravalent selenium is listed. No unsaturated aliphatic selenols have been prepared.

TABLE I. ALIPHATIC SELENOLS

Name	*Formula*	*B. P. C.*	*Ref. Nos.*
Ethyl selenol	C_2H_5SeH	53.5	1, 2, 3, 4, 5, 9, 10
n-Propyl selenol	C_3H_7SeH	84.	1.
Iso-propyl selenol	$(CH_3)_2=CHSeH$	70.-75.	5.
n-Butyl selenol	C_4H_9SeH	114.	1.
o-Nitrobenzyl selenol	*o*-NO_2-$C_6H_4CH_2SeH$	....	6.
o-Cyanobenzyl selenol	*o*-CN-$C_6H_4CH_2SeH$	....	7.
Tri-ethyl selenonium-hydroselenide	$(C_2H_5)_3\equiv$Se-SeH	....	8.

SELENOALDEHYDES

Selenoaldehydes may be represented by the formula, R−CHSe, in which "R" is hydrogen, an aromatic, or aliphatic organic radical. Unfortunately, no molecular weights have been determined for each of the four members of this group, which have been prepared prior to 1929. Accordingly it is very probable that some of the selenoaldehydes are polymerized. The selenium analogues of formaldehyde, acetaldehyde, isovaleraldehyde, and benzaldehyde have been prepared (11) by the action of hydrogen selenide on the corresponding aldehydes (XIV).

XIV. $R-CHO+H_2S \rightarrow R-CHSe+H_2O$.

Aliphatic Selenoaldehydes. Selenoformaldehyde, (HCHSe)n, which is obtained by passing hydrogen selenide into 36 per cent aqueous formaldehyde mixed with three times its volume of concentrated hydrochloric acid, separates from alcohol as a polymer in columnar crystals melting at about 215°C. It is very sparingly soluble in most organic media and becomes light green on exposure to sunlight.

When hydrogen selenide is passed into a solution of acetaldehyde in three volumes of alcohol, which has been saturated with hydrogen chloride; and the resulting semi-solid mass crystallized from alcohol, *selenoacetaldehyde*, CH_3CHSe, is obtained in slender transparent needles (m.p. = 139°C.). Selenoacetaldehyde separates from acetone in crystals which melt at 123-124°C. If chloroform is used as a solvent, the resulting product melts at 117°C. Selenoacetaldehyde thus apparently exists in several modifications.

The passage of a stream of hydrogen selenide through a solution of isovaleraldehyde in water yields (12) an oily compound, selenoisovalderaldehyde, $(CH_3)_2=CH-CH_2-CHSe$, which on standing in the cold, forms a crystalline mass. This is volatile with steam. A vapor density determination has not been conducted because it is reduced by metallic mercury. Likewisc it has not been successfully crystallized. In a solution of ether, alcohol, or methyl alcohol, it slowly decomposed with the formation of a metallic mirror of selenium. Only through sublimation at ordinary temperature was purification obtained. A beautiful white crystalline crust melting at 56.5°C. was thus formed. It has a terrible odor and those working with it, frequently suffer from palpitation of the heart and difficulty in breathing.

Aromatic Selenoaldehydes. In 1875, Granville Cole (13) prepared *selenobenzaldehyde*, C_6H_5CHSe, by heating an alcoholic solution of potassium selenide with benzylidine chloride, (XV).

XV. $C_6H_5CHCl_2+K_2Se \rightarrow C_6H_5CHSe+2KCl$. It crystallized in yellow needles, which had a very unpleasant odor and dissolved easily in alcohol and ether, but not in water. It resembled its analogue, thiobenzaldehyde, in that its ethereal solution was not affected by dry ammonia, or by a heated mixture of hydrocyanic and hydrochloric acids. Cole found its m.p. to be 70°C., but Vanino and Schinner in 1915 prepared (11) crystallized "alpha"-selenobenzaldehyde in clusters of yellow transparent columns, melting at 83-84°C. They, apparently in ignorance of Cole's work, prepared it, by passing hydrogen selenide for 3-4 hours into an alcoholic solution of benzaldehyde, (XVI).

XVI. $C_6H_5CHO+H_2Se \rightarrow C_6H_5CHSe+H_2O$. When the alcohol was previously saturated with hydrogen chloride, a mixture of "beta" and "gamma" selenobenzaldehyde was obtained, which was resolved into its constitutents by taking advantage of their different solubilities in benzene. "Beta"-selenobenzaldehyde, the more sparingly soluble form, crystallized from benzene in lustrous, golden needles m.p. about 205°C., of the composition $3C_6H_5CHSe.C_6H_6$. The benzene mother liquors yielded on evaporation "gamma"-selenobenzaldehyde, which crystallized in slender pale yellow needles, (m.p. = 166°C.). When distilled with copper powder "beta"-selenobenzaldehyde was converted into stilbene.

SELENOKETONES

A few compounds which are listed in the literature (14) under names indicating a selenoketone structure, are misnamed and are in reality selenides of oxygen ketones. The name selenoketone should indicate the replacement of the oxygen of the ketonic carbonyl group by selenium to give a compound of the type (R = organic carbon radical) $R_2=C=Se$. Each (15) member of this group prepared prior to 1929 has been isolated in a polymerized condition in which the selenoketone contains two of the original ketone structures.

Aliphatic Seleno Ketones. *Diselenoacetone,* $(CH_3CSeCH_3)_2$, was prepared (15) by conducting hydrogen selenide through a cooled mixture of equal volumes of acetone and concentrated hydrochloric acid until no further reaction was noticeable (XVII).

XVII. $2CH_3COCH_3+2H_2Se \rightarrow (CH_3CSeCH_3)_2+H_2O$. From the turbid mixture, a heavy red oil separated with a yield of fifty per cent by volume. After washing with water and distilling with steam at a temperature of 45-60°C., diselenoacetone, a clear red oil of unpleasant garlic odor was isolated. It is not miscible with water, only slightly soluble in glacial acetic acid, and is miscible in benzol and chloroform without decomposition. The solution on standing in 95 per cent alcohol precipitates red selenium. When benzene or chloroform solutions of any of the known seleno ketones are subjected to the action of chlorine, decomposition occurs with separation of selenium tetrachloride.

Diselenomethylethyl ketone, $(CH_3-CSe-C_2H_5)_2$, is prepared (15) from methyl-ethyl-ketone in a similar manner (XVI). The product is a dark red oil, which when washed, steam distilled under atmospheric pressure, and dried in a vacuum, is a clear, red, mobile oil, resembling diselenoacetone in its appearance and odor. It is volatile with steam without decomposition at ordinary pressures.

Aromatic Seleno Ketones. As yet only one aromatic ketone, *diselenoacetophenone,* $(CH_3CSeC_6H_5)_2$, has been prepared. This was prepared (15) from acetophenone according to the general procedure described above (XVI). A red oil not volatile in steam was obtained. The remaining unchanged acetophenone and other volatile contaminations were removed by treatment of the crude product with steam. The non-volatile part was then dried and identified as diselenoacetophenone. It is a red, viscous oil, which possesses an odor similar to that of diselenoacetone.

BIBLIOGRAPHY

1. Tschugaeff, L. Ueber Selenomercaptane und einige Derivate derselben. Ber. **42**: 49-54 (1909); also J. Chem. Soc. **46**: Ai, 129-30 (1909).

2. Lowig, C. Organische Chemie, **2**: 432 (1846).

3. Siemens, C. Ueber Selenmercaptan. Ann. **61**: 360-62 (1847).

4. Shaw, E. H. Jr. & Reid, E. E. Some Derivatives of Ethyl Selenomercaptan. J. Am. Chem. Soc. **48**: 520 (1926).

5. Natta, G. Einwirkung von Aluminiumselenid, -tellurid und-arsenid und von Magnesiumarsenid auf Alkahole und Äther. Chem. Zentr. **98**: (i), 415 (1927); also Giorn. chim. ind. applicata. **8**: 367-70 (1926).

6. Fromm, E. & Martin, K. Versuche zur Einführung von Selen in organische Verbindungen. Ann. **401**: 177-88 (1913); also J. Chem. Soc. **104**: Ai, 1323-24 (1913).

7. Drory, A. Zur Kenntniss des *o*-Cyanbenzylchlorides und des *o*-Cyanbenzalchlorides. Ber. **24**: 2563 (1891); also J. Chem. Soc. **60**: Aii, 1460 (1891).

8. Pieroni, A. & Coli, C. Azione del bromuro di selenio sui magnesioalchili. Gazz. chim. ital. **44**: ii, 349 (1914); also J. Chem. Soc. **106**: Ai, 1198 (1914).

9. Pieverling, L. von. Beitrag zur Kenntniss der Selenverbindungen. Ann. **185**: 331-39 (1877); also J. Chem. Soc. **34**: 129-30 (1878).

10. Hilditch, T. P. & Smiles, S. Aromatic selenonium bases. J. Chem. Soc. **93**: T. ii. 1384-87 (1908).

11. Vanino, L. & Schinner, A. Ueber Selenaldehyde. J. pr. Chem. (2), **41**: 116-127 (1915); also J. Chem. Soc. **108** Ai, 117-118 (1915).

12. Schröder, A. Untersuchungen ueber den Valeraldehyd. Ber. **4**: 403 (1871).

13. Cole, G. Ueber Benzselenaldehyd. Ber. **8**: 1165 (1875); also J. Chem. Soc. **29**: Ai, 397 (1876).

14. Kunckell, F. & Zimmermann, R. Ueber Selenderivate aromatischer Ketone. Ann. **314**: 281-295 (1901); also J. Chem. Soc. **80**: Ai, 214-215 (1901).

15. Lyons, R. E. & Bradt, W. E. Ueber die Darstellung von Seleno-ketonen. Ber. **60**: 824-26 (1927)

II*. ORGANIC COMPOUNDS OF SELENIUM

W. E. BRADT and M. VAN VALKENBURGH, University of Cincinnati

ORGANIC SELENIUM ACIDS

Organic selenium acids may have any of five formulas. These are (R = any organic carbon radical):

1. Selenol acids, $R-C=O-SeH$.
2. Seleno acids, $R-C=Se.OH$.
3. Selenol-seleno acids or diseleno acids, $R-C=Se.SeH$.
4. Seleninic acids, $R-Se=O.OH$.
5. Selenonic acids, $R-SeO_2.OH$.

Only one selenol acid and only derivatives of the seleno and selenol-seleno acids have been prepared prior to 1929. However, numerous examples of the seleninic and selenonic acids are known. The seleninic and selenonic acids which are analogous respectively to sulfinic and sulfonic acids, may be considered as derivatives of the inorganic selenious and selenic acids.

Selenol Acids. The only known selenol acid, *selenol benzoic acid*, C_6H_5COSeH, was called "*alpha*-selenobenzoic acid" by Mingoia. He prepared it (1) by the interaction at 100° C. of magnesyl selenhydrate and an ether solution of benzoyl chloride (I).

I. $BrMgSeH+C_6H_5COCl \rightarrow C_6H_5COSeH+MgBrCl$. After acidification of the product with H_2SO_4, extraction with ether, and crystallization from methyl alcohol, lustrous rose colored crystals were obtained which melted at 133°C. Selenol benzoic acid is soluble in aqueous alkali hydroxides, carbonates and NH_4OH with formation of salts. Ammonium selenol benzoate, $C_6H_5COSeNH_4$ is easily decomposed by oxygen and by water. The acid, however, is more stable than the sulfur analogue.

Seleno Acids. Although none of the acids of this group have been isolated, five of the acid amides have been prepared. These will be discussed as acid amides of selenium acids.

Selenol-Seleno Acids. The only known representative of this group is the ethyl ester of *selenol-seleno carbonic acid* (2), (3). The potassium salt, which has been isolated, is better known as an analogue of potassium zanthogenate, and is therefore called *potassium seleno xanthogenate*. It has been prepared by the action of carbon diselenide on potassium alcoholate (II).

II. $C_2H_5OK+CSe_2 \rightarrow C_2H_5OCSeSeK$. The potassium selenoxanthogenate separates as yellow needles which are easily soluble in alcohol and in water. It is very easily decomposed. No free acid of this group has been isolated.

Seleninic Acids. Seleninic acids contain tetravalent selenium and accordingly may be considered as analogues of either sulfinic or carboxylic acids. They

---

*This paper is the second 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.

are, moreover, correctly considered as derivatives of selenious acid, H_2SeO_3. Seleninic acids were among the organic selenium compounds first discovered. Because of this fact, there is some confusion in the literature (2, 4, 5) regarding the formula for one or two compounds placed in this group. The authors have endeavored to reinterpret this early data in the light of information which is now available regarding the general properties and methods of preparation of these compounds.

A total of twenty seleninic acids has been reported in the literature. Five are derivatives of aliphatic compounds, while in the remaining fifteen, the selenium atom is attached to a cyclic carbon atom. The methods of preparation include the oxidation of diselenides, $R-Se-Se-R$, by nitric acid, alkaline permanganate or alkaline hydrogen peroxide; the oxidation of selenols, $R-SeH$, by nitric acid or alkaline permangante; the action of nitric acid on selenocyanates, $R-SeCN$; the action of hydrogen peroxide on aryl "selenoglycollic" acids, $R-Se-CH_2COOH$; the action of nitric acid or H_2O_2 on the diethylselenomercaptoles, $R_2=C=(Se-C_2H_5)_2$, of a few ketones; and finally by the reduction of the corresponding selenonic acid, $R-SeO_3H$, with concentrated hydrochloric acid.

A complete list of the seleninic acids prepared prior to 1929, with melting points, formula, and references to their mention in the literature is given in Table I.

In 1856 Wohler and Dean (4) reported the formation (III) of a crystalline compound, melting at 122°C., by the interaction of dimethyldiselenide and nitric acid.

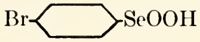
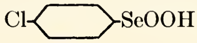
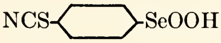
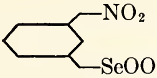
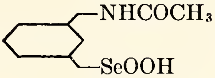
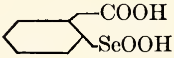
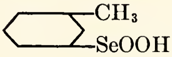
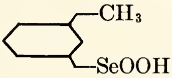
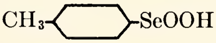
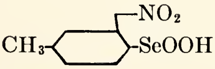
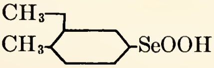
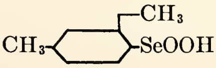
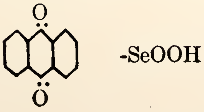
III. $CH_3-Se-Se-CH_3+4HNO_3 \rightarrow 2CH_3-SeOOH.HNO_3+2NO$. This substance, of which the nitric acid solution formed a white precipitate upon the addition of HCl, probably (6) was the nitric acid compound of *methyl seleninic acid*, $CH_3-SeOOH.HNO_3$. Their analysis of the hydrochloride derivative, from which the formula, $(CH_3-SeO(OH)Cl)_2$, was derived was found by Rathke (2) to indicate the hydrochloride of the acid, $CH_3SeOOH.HCl$. Since similar compounds result on the addition of HCl to solutions of most seleninic acids, this is assumed to be the product obtained. Methyl seleninic acid forms compounds with hydrochloric acid, $CH_3SeOOH\text{-}HCl$, and with nitric acid, $CH_3SeOOH\text{-}HNO_3$. The latter is soluble in water and in alcohol, and crystallizes in colorless prisms melting at 122°C. The ammonium, barium, and silver salts have been prepared.

Methane diseleninic acid. In 1874 Proskauer (5) reported that the action of nitric acid on methane diselenocyanate formed the diselenonic acid. If this is true, the reaction is quite unusual. Other examples of the oxidation of the selenocyanate group by nitric acid have uniformly given seleninic acid. Also it is known (25) that oxidation of organic selenium by fuming nitric acid in the Carious treatment stops with the formation of selenious acid. No hexavalent selenium is formed. Because of these facts, the writers assume that the product formed was methane diseleninic acid (IV).

IV. $CH_2(SeCN)_2+2HNO_3 \rightarrow CH_2(SeOOH)_2+2NO+(CN)_2$. In 1852 Joy (8) treated diethyldiselenide with strong nitric acid but was not able to isolate the product which was certainly the nitric acid compound of *ethyl seleninic acid*, $C_2H_5SeOOH.HNO_3$, m.p. = 80°C. (V).

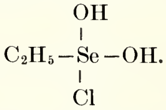
V. $C_2H_5-Se-Se-C_2H_5+4HNO_3 \rightarrow 2C_2H_5SeOOH\text{-}HNO_3+2NO$. The addition of HCl to a solution of this product made possible the isolation of a crystalline product, reported by Joy to be $2C_2H_5-SeO-OH-Cl$, and considered by Rathke (2) who repeated this work in 1869 to be the hydrochloride of ethyl

TABLE I. SELENINIC ACIDS

Names	*Formula*	*M.P.°C*	*Ref. Nos.*
Methyl-	$CH_3-SeOOH$	......	6, 2, 4.
Methane-di-	$HOOSe-CH_2-SeOOH$	......	5.
Ethyl-	$C_2H_5-SeOOH$	......	6, 2, 7, 8.
Ethane-di-	$HOOSe-CH_2-CH_2-SeOOH$	......	5.
Benzyl-	$C_6H_5CH_2-SeOOH$	122-3	9, 10, 11.
Phenyl-	$C_6H_5-SeOOH$	124-5	12, 13, 14, 15.
p-Bromophenyl-		187 (?)	16, 17.
p-Chlorophenyl-		178 (?)	17, 18.
p-Thiocyanophenyl-		154	17.
m-Nitrophenyl-		156	12, 19.
m-Acetaminophenyl-		209	12, 19.
o-Carboxyphenyl-		228	20, 21.
o-Toluene-		126-7	22, 23.
m-Toluene-		119-20	22.
p-Toluene-		171	22, 23.
2-Nitro-*p*-toluene-		151	17.
o-Xylene-4-		125	22.
m-Xylene-4-		146-7	22.
2-Anthraquinone-		......	24.

seleninic acid, $C_2H_5SeOOH\text{-}HCl$. That this was correct, was established by Shaw and Reid (6) who prepared the same substance (m.p. = 100 − 107°C. with decomposition) by the oxidation of ethylselenol with nitric acid (VI); and subsequent addition of HCl; as well as by the oxidation (by nitric acid, or by a 3 per cent solution of H_2O_2) of the diethylseleno-mercaptoles of acetone (VII), methylethyl ketone and diethyl ketone.

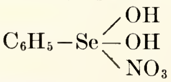
VI. $3C_2H_5SeH + 7HNO_3 \rightarrow 3C_2H_5SeOOH - HNO_3 + 4NO + 2HOH$.

VII. $(CH_3)_2C = (SeC_2H_5)_2 + 4H_2O_2 \rightarrow 2C_2H_5SeOOH + CH_3COCH_3 + 3HOH$. Shaw and Reid found that the action of HBr on the nitrate of ethyl seleninic acid formed ethylselenonium tribromide, $C_2H_5SeBr_3$, which they state (6) is a "new type of compound." However, the literature mentions more than seventy selenonium compounds, several of which are very similar to ethylselenonium tribromide. The formation of this tribromide and the corresponding tri-iodide led Shaw and Reid to propose a selenonium formula for the hydrochloride of the acid,  $C_2H_5-\underset{\underset{\displaystyle Cl}{|}}{\overset{\overset{\displaystyle OH}{|}}{Se}}-OH$. This is further supported by Karve (7), who reported data indicating that ethyl seleninic acid is a "pseudo acid" even in aqueous solution.

Ethane diseleninic acid. In 1874 Proskauer (5) treated $(NCSe-CH_2-)_2$ with nitric acid and reported the formation of ethane *alpha-beta* diselenonic acid. He prepared the lead, barium and silver salts. In view of the usual action (25) of nitric acid on selenium the product was probably a diseleninic acid (VIII). No analysis was reported.

VIII. $C_2H_4(SeCN)_2 + 2HNO_3 \rightarrow CH_2)SeOOH)_2 + (CN)_2 + 2NO$. Jackson (10, 11) and Lesser and Weiss (9) formed benzyl seleninic acid by treating dibenzyldiselenide with fuming nitric acid (IX).

IX. $C_6H_5CH_2-Se-Se-CH_2C_6H_5 + 2HNO_3 \rightarrow 2C_6H_5CH_2-SeOOH + 2NO$. It crystallizes from the acid liquid on cooling in stellate groups of needles which may be purified by recrystallization from hot water or alcohol. It melts at 122-123°C., (Jackson reported 85°C.,) has a strong acid reaction, and expells carbonic acid from carbonates. The ammonium salt, formed by neutralizing the acid with ammonia, is a white substance which crystallizes with difficulty and is very freely soluble in water. The silver salt, $C_6H_5CH_2SeOOAg$, is obtained as a curdy precipitate on adding silver nitrate to the ammonium salt. Benzyl seleninic acid is converted by PCl_5 into dibenzyl selenonium dichloride, $(C_7H_7)_2SeCl_2$, (m.p. = 134-135°C.). It is insoluble in cold water, alcohol, and ether, but easily soluble in nitric acid. The sodium and barium salts formed by neutralizing the acid with the respective carbonates, are freely soluble in water. The lead salt, precipitated by lead nitrate from the ammonium salt, is a white crystalline powder, nearly insoluble in water.

In 1896 Krafft & Lyons (13) dissolved one part by weight of diphenyl diselenide in forty parts of concentrated nitric acid and heated. On cooling the well-crystallized nitrate of *phenylseleninic acid* separated (m.p. = 112°C.) The nitrate exhibits properties of both an acid and a base, indicating a selenonium structure,  $C_6H_5-Se\begin{matrix}\diagup OH\\ -OH\\ \diagdown NO_3\end{matrix}$ which may be in equilibrium with the form, $C_6H_5SeOOH\text{-}HNO_3$. In 1906 Stoecker and Krafft (15) prepared the free acid as white crystals melting at 122-124°C, by treating the silver salt with HCl. They reported the formation of a hydrate, $C_6H_5SeOOH.H_2O$, which decomposed on heating. However, Doughty, (14) who prepared phenyl seleninic acid by the reduction of phenyl selenonic acid with concentrated HCl, (X), and Pymen (12) in 1919, showed that phenyl seleninic acid crystalized as the anhydrous acid, C_6H_5SeOOH, and that heating formed the acid anhydride (XI).

X. $C_6H_5SeOOH+HCl \rightarrow C_6H_5SeOOH+H_2O+Cl_2$.

XI. $2C_6H_5SeOOH \rightarrow C_6H_5SeO-O-OSeC_6H_5+H_2O$. The Ag, Ba, Cu, and Na salts have been described. Phenyl seleninic acid is soluble in water and is reduced by zinc and HCl to phenyl selenol (XII).

XII. $C_6H_5SeOOH+2H_2 \rightarrow C_6H_5SeH+2H_2O$. The nitrate and copper salt detonate on heating.

p-Bromophenyl seleninic acid was first prepared (16) in 1925 by treatment of *p*-bromophenyl selenoglycollic acid, $p-Br-C_6H_5-Se-CH_2COOH$, with H_2O_2 (XIII).

XIII. $p\text{-}Br-C_6H_4-Se-CH_2COOH+H_2O_2 \rightarrow p\text{-}Br-C_6H_4SeOOH+\ldots\ldots$ The product was at first considered to be a selenoxide but in 1927 Porritt (22) established the fact that it was a seleninic acid. The same acid was prepared in 1928 (17) by treatment of $p\text{-}Br-C_6H_4-SeCN$ with HNO_3 (XIV).

XIV. $2p\text{-}Br-C_6H_4-SeCN+2HNO_3 \rightarrow 2p\text{-}Br-C_6H_4SeOOH+2NO+(CN)_2$. *p*-Bromophenylseleninic acid is soluble in $CHCl_3$, alcohol, hot water, slightly soluble in cold water and forms crystals from water melting at 113°C. An insoluble copper salt and soluble salts of ammonia and the alkali metals have been described.

A well cooled aqueous solution of *p*-chlorobenzenediazonium chloride, sodium acetate, and alcoholic potassium selenocyanate gives *p*-chlorophenylselenocyanate (XV). With aqueous alkali this substance forms the corresponding selenol which is oxidized to the diselenide by hydrogen peroxide. Oxidation of either of these compounds with alkaline permaganate gives (18) the sodium salt of *p-chlorophenylseleninic* or *p-chlorophenylselenious acid.* This acid (colorless needles from hot water, m.p. = 178°C.) is produced by boiling the sodium salt with hydrochloric acid.

XV. $2p\text{-}Cl-C_6H_4-N=N-Cl \rightarrow 2p\text{-}Cl-C_6H_4-SeCN \rightarrow 2p-Cl-C_6H_4-SeH \rightarrow (p\text{-}Cl-C_6H_4-Se-{}_2) \rightarrow 2p\text{-}Cl-C_6H_4-SeOONa \rightarrow 2p\text{-}Cl-C_6H_4-SeOOH$. The nitration (17) at 3°C. of *p*-chlorophenyl selenocyanate yields mainly the diselenide with some *p*-chlorophenyl seleninic acid (XVI).

XVI. $4p\text{-}Cl-C_6H_4-SeCN+2HNO_3 \rightarrow (p\text{-}Cl-C_6H_4-Se-)_2+2p\text{-}Cl-C_6H_4SeOOH+NO+(CN)_2$. It is an amphoteric substance, giving rise to metallic *p*-chlorophenylselenites and to salts of the mineral acids, such as the nitrate and hydrochloride.

When *p*-thiocyanophenylselenocyanate, is nitrated at 3°C., *p-thiocyanophenylseleninic acid* is formed (17) by a reaction similar to (XVII).

Although aniline sulfate and arsenate readily yield sulfanilic acid and arsanilic acid, respectively, at an elevated temperatrue, no similar selenium compound could be obtained by Pyman. However, by the nitration of phenylseleninic acid, he (12, 19) prepared a 20% yield of *m-nitrophenylseleninic acid* (XVII).

XVII. $C_6H_5-SeOOH+HNO_3 \rightarrow m\text{-}NO_2-C_6H_4-SeOOH+H_2O$. This acid forms yellow needles (m.p. = 156-7°C.). It is reduced successively (XVIII) to *m*-nitrophenyl diselenide, yellow spears, m.p. =83°C., then to *m*-aminophenyldiselenide, and is oxidized by $KMnO_4$ to the selenonic acid.

XVIII. $m\text{-}NO_2-C_6H_4-SeOOH \rightarrow (m\text{-}NO_2-C_6H_4-Se-)_2 \rightarrow m\text{-}NH_2-C_6H_4-Se-Se-C_6H_4-NH_2\text{-}m$. The dihydrochloride of the amine forms yellow grains melting at 291-2°C. *m*-Nitrophenyl seleninic acid is fairly soluble in hot and sparingly soluble in cold water. It crystallizes from the latter in prismatic needles.

Di-*m*-aminophenyldiselenide gives on acetylation di-*m*-acetylaminophenyldiselenide, from which *m-acetylaminophenylseleninic acid* is obtained (12, 19) by oxidation with nitric acid. *m*-Acetylaminophenylseleninic acid melts with decomposition at 209°C. and is sparingly soluble in hot water. The nitrate (m.p.= 146°C.), the ammonium salt and sodium salt have been isolated.

An aqueous solution of *o*-carboxyphenyl selenonic acid is transformed (21) (XIX) by hydrochloric acid into *o-carboxyphenyl seleninic acid*, or *o-seleninbenzoic acid*, $o\text{-}HOOSe-C_6H_4COOH$. (See below.) This acid is also obtained (20, 21) by the oxidation of diphenyldiselenide-di-*o*-carboxylic acid by nitric acid or by alkaline H_2O_2 (XX).

XIX. $o\text{-}HOOC-C_6H_2-SeO_3H+HCl \rightarrow o\text{-}HOOC-C_6H_4-SeOOH+H_2O+Cl_2$.

XX. $2o\text{-}HOOC - C_6H_4 - Se - Se - C_6H_4 - COOH\text{-}o + 2H_2O + 3O_2 \rightarrow 4o\text{-}HOOC-C_6H_4-SeOOH$. When heated at 130-140°C. until constant in weight this acid is transformed into the anhydride without change in melting point. It crystallizes from water in long glistening needles which melt at 228-29°C.

On reduction (23) of a concentrated mixture of *o* and *p*-tolueneselenonic acids with hydrogen chloride, *p-tolueneseleninic acid*, $CH_3C_6H_4SeOOH.H_2O$, was precipitated in long silky white needles melting at 160°C.; while the mother-liquor yielded *o-tolueneseleninic acid* with ½ H_2O in nodules of short, white needles with a m.p. of 99-101°C. Analysis indicated the presence of water of crystallization but its presence was not definitely established. Porritt also prepared (22) each of these acids and *m-tolueneseleninic acid* (m.p.= 119-120°C.) by oxidation of the corresponding toluene selenoglycollic acids (XXI) with cold H_2O_2.

XXI. $CH_3-C_6H_4-Se-CH_2COOH+H_2O \rightarrow CH_3-C_6H_4-SeOOH+\ldots$. He obtained each in anhydrous form as colorless needles. The *o*-toluene seleninic acid prepared by him melted at 126-127°C. while the *para* compound melted at 171°C. *o*-Toluene seleninic acid is soluble in alcohol, $CHCl_3$, H_2O and is slightly soluble in ether. The action of nitric acid (17) on p-toluene selenocyanate caused both oxidation of the selenium and nitration, forming *2-nitro-p-toluene seleninic acid* which melts at 151°C. (XXII).

XXII. $p\text{-}CH_3-C_6H_4-SeCN+HNO_3 \rightarrow p\text{-}CH_3-(NO_2)-C_6H_4-SeOOH+NO+H_2O$. Other seleninic acids mentioned in the literature are *o-xylene-4-seleninic acid* and *m-xylene-4-seleninic acid*, (See Table II). They were prepared (22) by oxidation of the corresponding selenoglycollic acids with H_2O_2. (See equation XXI). The former melts with decomposition at 125°C. and the latter at 146-147°C. *2-Anthraquinone seleninic* acid results (24) from the action of concentrated HNO_3 on 2-anthraquinone selenol. It separates as colorless crystals.

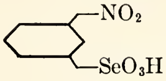
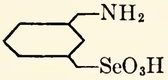
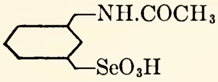
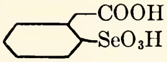
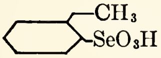
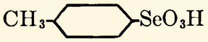
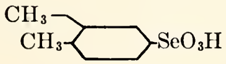
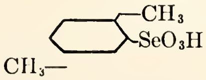
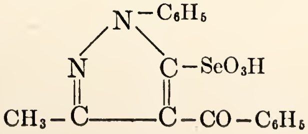
Selenonic Acids. Selenonic acids, $R-SeO_3H$ may be prepared by two general methods: (a) the action of concentrated selenic acid on a hydrocarbon (XXIII), and (b) the oxidation of tetravalent organic selenium (XXIV).

XXIII. $R-H+HO-SeO_3H \rightarrow R-SeO_3H+H_2O$.

XXIV. $2R-Se-Se-R+5O_2+2H_2O \rightarrow 4R-SeO_3H$. Variations of the second method include the oxidation of diselenides by aqueous chlorine, alkaline permanganate and 30% H_2O_2 in acetic acid; and oxidation of the corresponding seleninic acid by permanganate.

Selenonic acids are reduced by concentrated HCl to the corresponding seleninic acid and to selenols by H_2S, SO_2, or Zn and HCl. Table II includes a

TABLE II. SELENONIC ACIDS

Name	*Formula*	*M.P.°C.*	*Ref. Nos.*
Methyl-	CH_3SeO_3H	not isolated	4.
Phenyl-	$C_6H_5SeO_3H$	142	14,15,26
m-Nitrophenyl-		.....	12.
m-Aminophenyl-		229	12, 19
m-Acetaminophenyl-		......	12, 19.
o-Carboxyphenyl-		......	19, 27
p-Carboxyphenyl-		not identified	23.
o-Toluene		......	23.
p-Toluene		......	23.
o-Xylene-4- (?)-		108-110	28, 29.
m-Xylene-4-(?)-		130-130.5	28.
p-Xylene-2-(?)-		95-96	28, 29.
4-Benzoyl-1-phenyl-3-methyl-pyrazole-5-		152	30.

list of the selenonic acids found in the literature with formulas, melting points and references. It will be seen that no aliphatic selenonic acid has been isolated.

In 1856, Woehler and Dean (4) precipitated the hydrochloride of methyl seleninic acid by adding HCl to a dilute nitric acid solution of methyl seleninic acid. They observed however, that addition of HCl to a concentrated nitric acid solution failed to give a precipitate of $CH_3SeOOH.HCl$. It is quite possible that the selenium was oxidized with formation of a soluble *methyl selenonic acid.*

Methane diselenonic acid and *ethane diselenonic acid* were reported by Proskauer (5) in 1874. However, since his methods of preparation indicate the probable formation of seleninic acids, these compounds have been considered under that heading.

The *"ethyl selenonic acid"* which Fabian (31) reported in 1861 was in reality an ethyl ester of selenic acid $C_2H_5O-SeO_3H$, and was erroneously named by him.

In 1889, Chabrie (26) obtained an acid by the interaction of H_2SeO_4 and benzene. This acid, which formed a soluble barium salt was probably *phenyl selenonic acid,* $C_6H_5SeO_3H$. Doughty (14) later prepared *phenylselenonic acid,* by this method and isolated it as colorless needles. Stoecker and Krafft (15) prepared (XXV) it by the oxidation of diphenyl diselenide with moist chlorine at 50°C.

XXV. $C_6H_5SeSeC_6H_5+5Cl_2+6H_2O \rightarrow 2C_2H_5SeO_3H+10HCl$. It was isolated in the form of its white crystalline silver salt. This detonated feebly when heated. Phenyl-selenonic acid deposits red selenium when exposed to light, and may be reduced to the selenol by HCl and zinc, H_2S or SO_2. The Cu, Ag, Ba, and Cd salts have been prepared. The free acid crystallizes from the water in anhydrous crystals which melt at 142°C., and decompose above 180°C., with the formation of CO_2 and H_2O. It is soluble in water, alcohol and insoluble in ether and benzene.

Pyman (12, 19) prepared *m-nitrophenyl selenonic acid,* $m\text{-}NO_2-C_6H_5.SeO_3H$, by oxidation of the corresponding seleninic acid with alkaline $KMnO_4$. He crystallized the acid from water in colorless plates containing two molecules of water which were lost at 100°C. The anhydrous acid melted at 142°C. He also prepared (12, 19) salts of *m-acetaminophenyl selenonic acid,* $m\text{-}CH_3CO-C_6H_4-SeO_3H$, by the same method. Boiling the barium salt with aqueous H_2SO_4 caused hydrolysis and *m-aminophenyl selenonic acid* separated from the cold filtered solution in colorless needles which melted at 229°C.

o-Carboxyphenyl selenonic acid, or *"o-selenonbenzoic acid,"* $o\text{-}HOOC-C_6H_4-SeO_3H$ is prepared (21, 27) by the oxidation of di-*o*-carboxyphenyldiselenide with alkaline potassium permanganate solution (XXVI).

XXVI. $o\text{-}HOOC-C_6H_4-Se-Se-C_6H_4-COOH\text{-}o+H_2O+5(O) \rightarrow 2o\text{-}HOOC-C_6H_4-SeO_3H$. It is a very strong acid, the salts of which are not decomposed by dilute nitric acid. It has not been obtained in the crystalline state but yields a barium salt which separates from water in colorless, anhydrous needles (9). It is reduced by concentrated HCl to the corresponding seleninic acid.

In 1912, Doughty and Elder (23) treated *p*-toluene seleninic acid with potassium permanganate and obtained a dibasic acid which was possibly *p*-carboxyphenyl seleninic acid, but which more probably was *p-carboxyphenyl selenonic acid.* The potassium salt melted at 264°C. At the same time (23) the formation of a mixture of *o-toluene selenonic acid* and *p-toluene selenonic acid* was obtained by the action of concentrated selenic acid on toluene. Neither was isolated, but both were reduced by HCl to the corresponding seleninic acids and identified.

The action of H_2SeO_4 on *o*-, *m*- and *p*-xylene yielded (28, 29) respectively products partially identified as *o-xylene-4-selenonic acid*, *m-xylene-4-selenonic acid* and *p*-xylene-2-selenonic acid. In each case, although the location of the selenonic acid group has not been definitely established, it is probably in the position indicated. Each was prepared in good yield by adding 96% H_2SeO_4 dropwise to the xylene in the presence of an equal volume of acetic anhydride. Salts of NH_3, K, Na, Ba, Mg, Zn, Ni, Co, Cu and Ag, have been described for each acid. *o*-Xylene-4-selenonic acid melts at 108-110°C., *m*-xylene-4-selenonic acid at 130-130.5°C., and *p*-xylene-2-selenonic acid at 95-96°C.

2-Anthraquinone selenonic acid, is found in the literature (24) due to an error. The original article, refers to the seleninic acid, which has been previously described.

The only selenonic acid of a heterocyclic compound mentioned (30) in the literature is *4-benzoyl-1-phenyl-3-methyl pyrazole-5-selenonic acid*. This acid (See Table II), which melts at 152°C., is obtained by the oxidation of the corresponding diselenide in acetic acid by thirty per cent H_2O_2 according to (XXIV). It may be crystallized as colorless needles from benzene and ligroin, is soluble in NH_4OH, aqueous alkalis, ether and $CHCl_3$, and sparingly soluble in water. Treatment with halogens yields tetra-halides of the type $R-Se_2X_4-R$.

ACID ANHYDRIDES

Carbon diselenide, which may be considered as the anhydride of selenolseleno carbonic acid, HO–CSeSeH, has been prepared (2, 3) in poor yield by the treatment of carbon tetrachloride with either CdSe or P_2Se_5 (XL).

XXVII. $7CCl_4+3CdSe \rightarrow CSe_2+SeCl_4+3CdCl_2+3C_2Cl_6$. Not more than three ccm. have been prepared at one time. It possesses a very disagreeable odor which when diluted, resembles that of carbon di-sulfide. Its reaction with sodium alcoholate has been previously described.

The anhydride of phenyl seleninic acid, has been prepared (28) (XXVIII) by heating the acid at 130°C.

XXVIII. $2C_6H_5-SeOOH \rightarrow (C_6H_5SeO)=O+H_2O$. It sublimes at about 130°C., melts at 164°C., and decomposes at 200°C. Stoecker and Krafft, (15) reported the acid as a hydrate, $C_6H_5SeOOH.\ H_2O$, melting at 122°C., which when heated at 130°C., gave the acid. Doughty concluded that the compound melting at 122°C. was the acid and that Stoecker and Krafft, had prepared the acid anhydride. The anhydride of *o-carboxyphenyl seleninic acid* or *o-seleninbenzoic acid* has been obtained (21) free by heating the acid at 130-140°C., until constant in weight. It is transformed into the anhydride, $(o\text{-}HOOC-C_6H_4-SeO)_2=O$, without change in the melting point, which remains 228-229°C. The anhydride is stable in dry air.

BIBLIOGRAPHY

1. Mingoia, Q. Sull'acido *alpha* selenobenzoico Gazz. chim. ital. **56**: 835-9 (1926); also C. A. **21**, 1104 (1927).

2. Rathke, B. Beitrage zur Kenntniss des Selens. Ann. **152**: 181-220 (1869); also Beilstein 3d. ed. I, 906 (1893).

3. Bartal, A. von. Ueber Selenkohlenstoff. Chem. Ztg. **30**: 1044-1045 (1906).

4. Woehler, F. & Dean, J. Versuche ueber Telluramyl und Selenmethyl. Ann. **97**: 1-9 (1856).

5. Proskauer, B. Ueber Selencyanäthylen und Selencyanmethylen. Ber. **7:** 1279-82 (1874); also J. Chem. Soc. **28:** 144 (1875).

6. Shaw, E. H. Jr. & Reid, E. E. Some derivatives of ethyl selenomercaptan. J. Am. Chem. Soc. **48:** 520 (1926).

7. Karve, D. D. Acid nature of some derivatives of sulfur, selenium and tellurium. J. Indian Chem. Soc. **2:** 128-141 (1925) also J. Chem. Soc. **128:** Aii. 1188 (1925).

8. Joy, C. A. Ueber das selenäthyl. Ann. **86:** 35-39 (1853).

9. Lesser, R. & Weiss, R. Ueber selenhaltige aromatische Verbindungen. Ber. **57:** Ab.B, 1077-1082 (1924); also J. Chem. Soc. **126:** Ai, 1004-5 (1924).

10. Jackson, C. L. Ueber einige Methyl-und Benzylselenverbindungen. Ann. **179:** 1-20 (1875); also J. Chem. Soc. **28:** 553 (1875) and **29:** 581 (1876).

11. Jackson, C. L. Ueber einige neue organische Selenverbindungen: Dibenzyldiselenid und Trimethylselenin. Ber. **7:** 1277-79 (1875); also J. Chem. Soc. **28:** 154 (1875).

12. Pyman, F. L. *meta*-Substituted aromatic selenium compounds. J. Chem. Soc. **115:** T, 166-75 (1919); also C. A. **13:** 1299-1300 (1919).

13. Krafft, F. and Lyons, R. E. Ueber Diphenylselenon. Ber. **29:** 424-428 (1896); also J. Chem. Soc. **70:** Ai, 304 (1896).

14. Stoecker, M. & Krafft, F. Ueber Oxydation von Diphenyldiselenid. Ber. **39:** 2197-2201 (1906); also J. Chem. Soc. **90:** Ai, 568 (1906).

15. Doughty, H. W. Benzeneselenonic acid and related compounds. Am. Chem. J. **41:** 326-337 (1908); also J. Chem. Soc. **96:** Ai, 296-297 (1909).

16. Morgan, G. T. & Porritt, W. H. Aryl selenoglycollic acids. J. Chem. Soc. Tii, 1757 (1925).

17. Challenger, F. & Peters, A. T. Nitration of aromatic thiocyanates and selenocyanates. J. Chem. Soc. 1364-75 (1928); also C. A. **22:** 3152 (1928).

18. Morgan, G. T. & Elliott, J. E. *p*-Chlorophenylselenious acid. Proc. Chem. Soc. **30:** 248-9 (1914).

19. Pyman, F. L. Aromatic selenium compounds. Proc. Chem. Soc. **30:** 302-3 (1914); also C. A. **9:** 2889-90, (1915)

20. Schoeller, A. Ueber eine einfache und bequeme methode zur Darstellung aromatischer selenverbindungen. Ber. **52:** Ab. B. 1517-18 (1919); also J. Chem. Soc. **118:** Ai, 41, (1920).

21. Lesser, R. & Weiss, R. Ueber selenhaltige aromatische Verbindungen. Ber **46:** 2640-2658 (1913); also J. Chem. Soc. **104:** Ai, 1184 (1913).

22. Porritt, W. H. Arylseleninic acids, J. Chem. Soc. Ti, 27 (1927).

23. Doughty, H. W. & Elder, F. R. Reaction between selenic acid and toluene. Eighth Inter. Cong. App. Chem. **6:** 93-101 (1912); also J. Chem. Soc. **104:** Ai, 962 (1913).

24. D. R. P. Nr. 26494 (1913). Elberfeld. Verfahren zur Darstellung von selenophenolen und Diseleniden der anthrachinonreihe; also Chem. Zentr. **84:** (2) 1351 (1913).

25. Lyons, R. E. & Shinn, F. L. The quantitative determination of selenium in organic compounds. J. Am. Chem. Soc. **24:** 1087-1093 (1902); also J. Chem. Soc. **84:** Aii, 326 (1903).

26. Chabrie, M. C. Premiers essais de synthese de composes organiques sélénies dans la série aromatique. Bull. Soc. Chim. **50**, (2), 133-137 (1888) and **2**, (3), 796 (1889); also J. Chem. Soc. **56:** Ai, 41 (1889).

27. Lesser, R. & Weiss, R. Ueber den "Selen-indigo" (Bis-seleno-naphthen-indigo) und selenhaltige aromatische Verbindungen I. Ber. **45**: 1835-41 (1912).

28. Anschuetz, R. & Teutenberg, F. Ueber aromatische selenosäuren, ii: *m*-Xylol-selenosäure. Ber. **57**: Ab.B., 1018-1023 (1924); also J. Chem. Soc. **126**: Ai, 889 (1924).

29. Anschuetz, R., Kallen, J. and Riepenkroger, K. Ueber eine Methode zur Darstellung aromatischer Selenosaüren: *p*-Xylol-und *o*-Xylol-selenosäure. Ber. **52**: 1860-75 (1919); also J. Chem. Soc. **118**: Ai, 24 (1920).

30. Michaelis, A. and Langenkamp, P. Ueber ein Selenopyrazolon und ueber das Selenopyramidon. Ann. **404**, 21-36 (1914); also J. Chem. Soc. **106**: Ai, 582-84 (1914).

31. Fabian, Chr. Ueber das Verhalten der Selensäure zum Aethylalkohol. Ann. Spl. 1, 241-250 (1861).