CCCCXXXVII.—*Interactions of Selenium Oxychloride and Phenols.*

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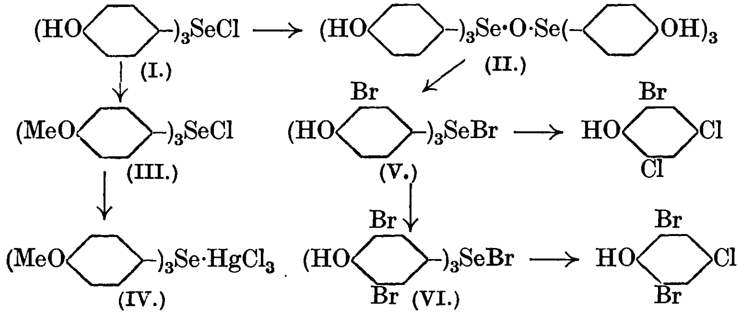
IN two communications on organic selenium compounds formerly published from the Rostock Laboratories, Michaelis and Kunckell described certain reactions between selenium oxychloride or tetrachloride and the phenols and phenolic ethers (*Ber.*, 1895, **28**, 609; 1897, **30**, 2823). The second of these publications contains a short description of condensations effected in ethereal solution between selenium oxychloride and phenol, β-naphthol and resorcinol, wherein the two monohydric phenols are stated to give selenides of the type $Se(R{\cdot}OH)_2$, R being C_6H_4 or $C_{10}H_6$, whilst resorcinol is alleged to yield a selenyl derivative, $SeO[C_6H_3(OH)_2]_2$.

On repeating the condensations we have been able to confirm these statements only in the case of β-naphthol, which gives the selenide, $Se(C_{10}H_6{\cdot}OH)_2$, in ethereal or preferably in chloroform solution.

The interactions of selenium oxychloride with phenol, the cresols, resorcinol, β-naphthol, and salicylic acid have now been investigated with the following results:

1. *Phenol.* When condensed with selenium oxychloride either in ethereal or in chloroform solution, phenol yields two isomeric *selenonium chlorides*, $[(HO{\cdot}C_6H_4)_3Se]Cl$, each containing ionisable chlorine precipitable as silver chloride and replaceable by other acidic radicals. The complex kation of these selenonium chlorides includes three phenolic hydroxyl groups which confer acidic properties on the chlorides so that these salts dissolve in aqueous caustic alkalis. From such solutions carbonic or acetic acid precipitates the amphoteric *oxide*, $[(HO{\cdot}C_6H_4)_3Se]_2O$, which redissolves in alkalis and reacts with acids to furnish the corresponding *bromide*, *nitrate*, *sulphate* and *chloroplatinate*.

The less soluble of the two selenonium chlorides, which is the main condensation product, is proved to be *tri-4-hydroxytriphenylselenonium chloride* (I) by progressive halogenation, for when neutralised with acetic acid, an alkaline solution of selenonium chloride deposits the *oxide* (II), which on bromination yields successively a tribrominated bromide (V) and a hexabrominated bromide (VI). With chlorine water the former of these bromides gives 2 : 4-dichloro-6-bromophenol, whereas the latter furnishes 4-chloro-2 : 6-dibromophenol.

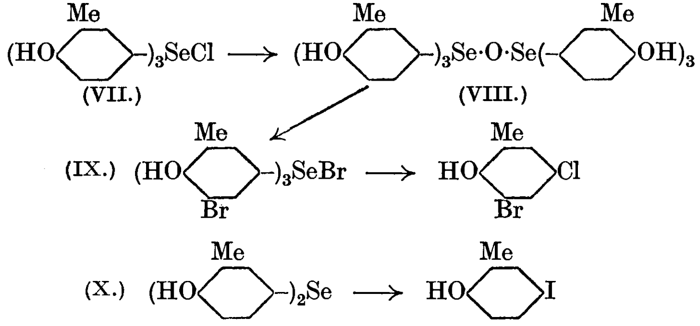


With the orientation of selenium and hydroxyl radicals established in these compounds it becomes possible to determine the constitution of trianisylselenonium chloride formerly prepared by Hilditch and Smiles (J., 1908, **93**, 1384), who, on employing a modified Friedel–Crafts reaction, obtained only selenonium salts from anisole, phenetole and resorcinol dimethyl ether.

Tri-4-hydroxytriphenylselenonium chloride is methylated to the oily *tri*-4-*methoxytriphenylselenonium chloride* (III), which is converted into crystalline *mercurichloride* (IV). This complex salt is compared with a specimen prepared from trianisylselenonium chloride obtained by the method of Hilditch and Smiles. Both mercurichlorides melt as one compound at 68—70°.

Owing to the comparatively small yield of the more soluble selenonium chloride, the constitution of this salt was not determined; it is evident, however, that one, two, or three of its hydroxyl groups must be in the ortho-position with respect to selenium.

2. o-*Cresol.* The main product of the selenium oxychloride condensation is *tri*-4-*hydroxytri*-3-*methyltriphenylselenonium chloride* (VII), the constitution of which is ascertained by progressive halogenation, starting with the corresponding *oxide* (VIII), which

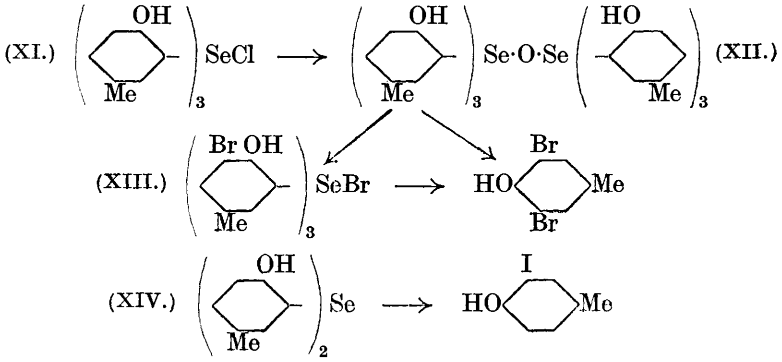


yields a tribrominated bromide (IX) decomposed by chlorine water to furnish 5-chloro-3-bromo-*o*-cresol.

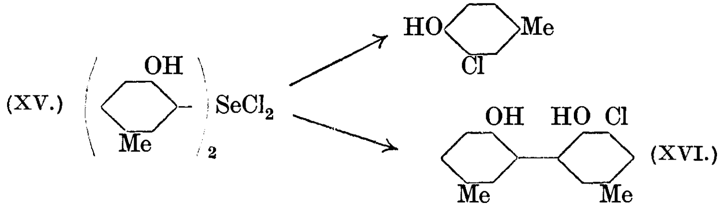
Di-4-*hydroxydi*-3-*methyldiphenyl selenide* (X), which arises as a by-product in the condensation of *o*-cresol and selenium oxychloride, is decomposed on boiling with hydriodic acid to yield 5-iodo-*o*-cresol.

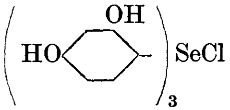
3. p-*Cresol.* A similar halogenation suffices to characterise *tri*-2-*hydroxytri*-5-*methyltriphenylselenonium chloride* (XI), a product of the selenium oxychloride condensation with *p*-cresol. Its *oxide* (XII) furnishes a tribrominated bromide (XIII) with anhydrous bromine, whereas with bromine water this bromide or the original oxide gives rise to 3 : 5-dibromo-*p*-cresol. In addition to the foregoing selenonium chloride, *p*-cresol yields a considerable pro-

portion of *di-2-hydroxydi-5-methyldiphenyl selenide* (XIV), which on treatment with hydriodic acid gives 3-iodo-*p*-cresol.



The phenols have not in the condensations under review yielded chlorinated selenium derivatives of the type $Cl_2Se(R\cdot OH)_2$, although analogous compounds, $Cl_2Se(R\cdot OX)_2$, with $X = CH_3$ or C_2H_5, were obtained by Kunckell (*loc. cit.*) from anisole and phenetole. The absence of such chlorinated derivatives in the phenolic condensations is probably due to the readiness with which the phenols undergo chlorination. The mother-liquors from the selenide (XIV) contain 3-chloro-*p*-cresol and also a chlorinated dicresol (XVI). These substances may arise from the autochlorination of the hypothetical dichloroselenide (XV).



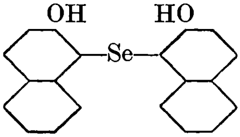
4. *Resorcinol.* In its condensation with selenium oxychloride resorcinol resembles phenol in giving rise to a selenonium chloride having the constitution  (XVII).

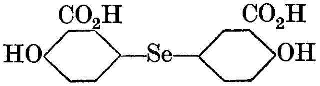
5. β-*Naphthol.* This condensation proceeds quantitatively in the sense of the equation

$$3C_{10}H_7\cdot OH + SeOCl_2 = Se(C_{10}H_6\cdot OH)_2 + C_{10}H_6Cl\cdot OH + HCl + H_2O.$$

*Di-2-hydroxydi-*1-*naphthyl selenide* (XVIII) is decomposed by warm hydriodic acid into 1-iodo-β-naphthol and selenium, and a similar attack by bromine furnishes 1-bromo-β-naphthol.

(XVIII.)





(XIX.)

6. *Salicylic acid.* The condensation, effected preferably in the absence of solvent, leads to a disalicylyl selenide (*di-4-hydroxydiphenyl selenide di-3-carboxylic acid,* XIX).

The foregoing results indicate that between selenium oxychloride and the phenols two modes of reaction may take place, one manifested by phenol and resorcinol :

1. $3H{\cdot}R{\cdot}OH + SeOCl_2 = (HO{\cdot}R)_3SeCl + HCl + H_2O$,

and another exemplified by β-naphthol and salicylic acid :

2. $3H{\cdot}R{\cdot}OH + SeOCl_2 = Se(R{\cdot}OH)_2 + Cl{\cdot}R{\cdot}OH + HCl + H_2O$.

With *o*- and *p*-cresols both interactions occur concurrently.

EXPERIMENTAL.

1. *Phenol and Selenium Oxychloride.*—On adding selenium oxychloride (33·2 g.; 1 mol.), diluted with 50 c.c. of chloroform, to a well-stirred solution of phenol (56·4 g.; 3 mols.) in 500 c.c. of the same solvent, the mixture darkened rapidly and became opaque owing to separation of insoluble matter; meanwhile heat was generated and hydrogen chloride evolved. After an hour the yellow solution containing in suspension a deep red oil was refluxed until the insoluble product adhered to the containing vessel as a semi-solid, yellow gum. The chloroform was decanted and the residue triturated with acetone; the selenonium chloride then separated as a white powder which crystallised from alcohol–ether in small, white prisms, m. p. 232° (decomp.) (Found : C, 53·9; H, 4·0; Se, 19·8, 20·4; Cl, 9·2. $C_{18}H_{15}O_3ClSe$ requires C, 54·85; H, 3·8; Se, 20·1; Cl, 9·0%).

Tri-4-hydroxytriphenylselenonium chloride (I), a stable salt, dissolved readily in hot water to an almost neutral solution (p_H 5·7); it separated on cooling from hot water or alcohol in an anhydrous condition as a microcrystalline powder. It was insoluble in the other organic media. Cold, concentrated sulphuric acid dissolved it to a colourless solution with evolution of hydrogen chloride; on warming, yellow to green tints were developed. Aqueous ferric chloride gave a reddish-purple coloration, and aqueous caustic soda dissolved the selenonium chloride to a pale yellow solution from which carbon dioxide or the calculated amount of dilute acetic acid precipitated white, amorphous *tri-4-hydroxytriphenylselenonium oxide* (II), decomp. 240° (Found: C, 58·2; H, 4·2; Se, 21·9, 21·7. $C_{36}H_{30}O_7Se_2$ requires C, 59·0; H, 4·1; Se, 21·6%).

This complex amphoteric oxide was insoluble in neutral organic media but furnished salts with mineral acids. The sulphate and bromide, decomposing respectively at 269—270° and 237°, are prepared by adding the appropriate acid to alkaline solutions of the oxide. The bromide crystallised from alcohol–ether in white needles. With an alcoholic solution of the selenonium chloride, silver nitrate gave a quantitative deposition of silver chloride; the filtrate on evaporation and addition of ether yielded the white, crystalline, water-soluble *nitrate*, m. p. 138—139° (decomp.) (Found: N, 3·4. $C_{18}H_{15}O_6NSe$ requires N, 3·3%).

From a hot aqueous solution of selenonium and platinic chlorides an orange *chloroplatinate* crystallised, on cooling, in lustrous needles, decomp. 244° (Found: Pt, 17·4. $C_{36}H_{30}O_6Cl_6Se_2Pt$ requires Pt, 17·4%).

Tri-4-methoxytriphenylselenonium chloride (III). Five g. of methyl iodide were added to a solution of tri-4-hydroxytriphenylselenonium chloride (3·9 g.) and sodium methoxide (1 g. of sodium in 200 c.c. of methyl alcohol), the mixture being refluxed until acid to litmus. After being acidified strongly with hydrochloric acid, the mixture was distilled in steam, and the residue was dissolved in chloroform, dried, and evaporated to a yellow, uncrystallisable gum which, however, yielded *tri-4-methoxytriphenylselenonium mercurichloride* (IV), m. p. 68—70°, identical with the mercurichloride obtained from trianisylselenonium chloride prepared by the method of Hilditch and Smiles (*loc. cit.*) (Found: Cl, 14·4. $C_{21}H_{21}O_3Cl_3SeHg$ requires Cl, 15·05%).

Tri-3-bromotri-4-hydroxytriphenylselenonium bromide (V). Tri-4-hydroxytriphenylselenonium oxide was stirred gradually into excess of bromine and when the vigorous reaction had subsided the mixture was evaporated to dryness; the dry residue after trituration with ether left a white, brominated product which was dissolved in hot alcohol. This solution deposited a crop of impure hexabrominated bromide (*v. infra.*); the mother-liquor on evaporation and addition of ether yielded the tribrominated bromide as a white, microcrystalline powder. After repeated crystallisation this *bromide* melted at 251° to a red liquid (Found: Br, 47·4; Se, 11·4. $C_{18}H_{12}O_3Br_4Se$ requires Br, 47·4; Se, 11·7%). The tribrominated bromide was insoluble in water and organic media except alcohol, but dissolved readily in aqueous caustic soda; dilute acetic acid precipitated the complex oxide (m. p. 198°), which was decomposed readily by chlorine water, yielding 2 : 4-dichloro-6-bromophenol, m. p. 67—68°.

Tri-3 : 5-*dibromotri*-4-*hydroxytriphenylselenonium bromide* (VI) was precipitated in the more sparingly soluble fraction from the foregoing experiment in combination with the tribrominated bromide. Repeated evaporation with bromine and crystallisation from alcohol led to the pure hexabrominated *bromide*, obtained in sparingly soluble, lustrous, white prisms, decomp. 261° (Found : Br, 61·6. $C_{18}H_9O_3Br_7Se$ requires Br, 61·35%). Chlorine water eliminated selenium from this hexabrominated salt and furnished 4-chloro-2 : 6-dibromophenol, m. p. 92°.

Isomeric trihydroxytriphenylselenonium chloride,

$(HO{\cdot}C_6H_4)_3SeCl,2H_2O$.

The acetone filtrates from tri-4-hydroxytriphenylselenonium chloride yielded on evaporation an isomeric *selenonium chloride*, crystallising with two molecular proportions of water and decomposing at 125° (Found : C, 50·6; H, 4·5; Se, 18·6; Cl, 8·0; loss on heating at 110°, 9·5. $C_{18}H_{15}O_3ClSe,2H_2O$ requires C, 50·3; H, 4·45; Se, 18·4; Cl, 8·4; loss, 8·4%). This salt dissolved in hot water, but separated on evaporation as a colourless, viscous gum setting to a glass over sulphuric acid. It possessed the chemical properties of the tri-*p*-isomeride, but the small yield (1—2 g.) rendered orientation experiments impracticable. From a solution in aqueous caustic soda, carbon dioxide or dilute acetic acid precipitated the amorphous oxide (decomp. 180°), and methylation yielded successively a viscid trimethoxytriphenylselenonium chloride and a mercurichloride (m. p. 54—55°).

2. o-*Cresol and Selenium Oxychloride*.—Selenium oxychloride (16·6 g.; 1 mol.) in 50 c.c. of chloroform was stirred into a solution of *o*-cresol (33·6 g.; 3 mols.) in 400 c.c. of the same solvent. After an hour the mixture was refluxed until the heavy, red oil which first separated became converted into solid selenonium salt. The chloroform solution was decanted; the residue, after being washed with acetone, crystallised from alcohol–ether as a white powder, decomp. 231° (yield, 10 g.) (Found : C, 57·7; H, 5·1; Cl, 7·9; Se, 17·8. $C_{21}H_{21}O_3ClSe$ requires C, 57·8; H, 4·9; Cl, 8·1; Se, 18·2%).

Tri-4-*hydroxytri*-3-*methyltriphenylselenonium chloride* (VII) was insoluble in water and most organic solvents but dissolved in alcohol. Alcoholic ferric chloride gave no coloration, but warm concentrated sulphuric acid produced a green tint. When an alkaline solution of this chloride was treated with carbon dioxide or dilute acetic acid the corresponding *selenonium oxide* (VIII) was precipitated as an amorphous powder, decomp. 236° (Found : Se, 19·6. $C_{42}H_{42}O_7Se_2$ requires Se, 19·4%).

The addition of nitric acid to an alkaline solution of this oxide gave the *nitrate*, decomp. 224°, which was crystallised from alcohol (Found: N, 3·3. $C_{21}H_{21}O_6NSe$ requires N, 3·0%).

Tri-5-bromotri-4-hydroxytri-3-methyltriphenylselenonium bromide (IX) was produced on stirring small quantities of the foregoing oxide into excess of bromine. Hydrogen bromide was evolved and after the violent reaction had subsided the mixture was taken to dryness; after being triturated with ether, the white residue was crystallised from boiling alcohol, the brominated *bromide* separating in silvery prisms darkening and decomposing at 253° (Found: Br, 44·8. $C_{21}H_{18}O_3Br_4Se$ requires Br, 44·6%). When added to an alkaline solution of this brominated selenonium bromide, dilute acetic acid precipitated the amorphous oxide, which was decomposed by chlorine water, giving 5-chloro-3-bromo-*o*-cresol (m. p. 48°).

Di-4-hydroxydi-3-methyldiphenyl selenide (X). After tri-4-hydroxytri-3-methyltriphenylselenonium chloride had been separated in the selenium oxychloride condensation, the chloroform filtrate was evaporated to a viscid oil and distilled in steam. A little unchanged *o*-cresol appeared first, but the main distillate consisted of 5-chloro-*o*-cresol (m. p. 48°). The brown, gummy residue was extracted repeatedly with petroleum (b. p. 80—100°) and on cooling the solution an oil separated which after repeated extractions solidified in small, pale yellow needles, m. p. 98—99° (Found: C, 56·9; H, 4·9; Se, 26·7. $C_{14}H_{14}O_2Se$ requires C, 57·3; H, 4·8; Se, 27·0%).

When boiled with concentrated hydriodic acid, the dihydroxyditolyl selenide readily decomposed with elimination of black selenium and production of 5-iodo-*o*-cresol (m. p. 72°).

Although insoluble in water, this complex selenide dissolved readily in either aqueous caustic soda or the common organic solvents. Concentrated sulphuric acid gave a deep green tint even in the cold.

3. p-*Cresol and Selenium Oxychloride.*—*p*-Cresol (67·2 g.; 3 mols.), dissolved in 500 c.c. of chloroform, was treated with selenium oxychloride (33·2 g.; 1 mol.) diluted with 50 c.c. of the same solvent. The well-stirred mixture slowly assumed a deep red colour, hydrogen chloride was evolved and selenonium chloride separated. The mixture was refluxed, and the precipitate washed with acetone and ether (yield, 17·5 g.). After crystallisation from hot alcohol and drying in a vacuum desiccator, the selenonium chloride retained alcohol of crystallisation which was removed at 110° (Found: C, 57·85; H, 6·0; Cl, 7·1; Se, 15·45; loss on heating at 110°, 14·4. $C_{21}H_{21}O_3ClSe,1\frac{1}{2}C_2H_6O$ requires C, 57·0; H, 6·0; Cl, 7·0; Se, 15·7;

loss, 13·7%). This preparation gave the iodoform reaction with iodine in aqueous caustic soda.

Tri-2-hydroxytri-5-methyltriphenylselenonium chloride (XI), which decomposed at 260—265°, was insoluble in water but dissolved in hot alcohol or in aqueous caustic soda. Concentrated sulphuric acid developed no coloration in the cold but, on warming, an olive-green tint changing to deep red. Alcoholic ferric chloride gave a faint olive-green tint. The corresponding complex *oxide* (XII), a white, amorphous powder, decomp. 160°, was precipitated by carbon dioxide or dilute acetic acid from an alkaline solution of the foregoing chloride (Found: Se, 19·1. $C_{42}H_{42}O_7Se_2$ requires Se, 19·4%). With bromine water this complex oxide was readily decomposed, yielding 3 : 5-dibromo-*p*-cresol (m. p. 48°).

Tri-3-bromotri-2-hydroxytri-5-methyltriphenylselenonium bromide (XIII), obtained by the action of anhydrous bromine on the oxide in the manner employed for the analogue from *o*-cresol, separated from hot alcohol in pinkish-white prisms, decomp. 195° (Found: Br, 45·0. $C_{21}H_{18}O_3Br_4Se$ requires Br, 44·6%).

Di-2-hydroxydi-5-methyldiphenyl selenide (XIV). The chloroform filtrate from the selenium oxychloride condensation after separation of the selenonium chloride was evaporated nearly to dryness and distilled in steam. The distillate contained 3-chloro-*p*-cresol (b. p. 196°/760 mm.; yield, 12·0 g.). The dried residue was extracted repeatedly with petroleum (b. p. 40—60°). Repeated crystallisation of the extracted material yielded the white *selenide*, m. p. 111° (Found: C, 57·0; H, 4·8; Se, 26·9. $C_{14}H_{14}O_2Se$ requires C, 57·3; H, 4·8; Se, 27·0%).

This complex aromatic selenide, although insoluble in water, dissolved readily in the common organic solvents. Cold concentrated sulphuric acid gave a deep green tint, becoming red on warming; alcoholic ferric chloride developed a deep green coloration. Concentrated hydriodic acid eliminated selenium from the selenide and yielded 3-iodo-*p*-cresol (m. p. 37—38°).

5-*Chloro*-4 : 4′-*dihydroxy*-3 : 3′-*ditolyl* (XVI). This singular by-product separated from the last fractions of the foregoing diaryl selenide in yellow clumps and after crystallisation from petroleum was obtained as a white, crystalline powder, m. p. 129—130° (yield, about 1 g.) [Found: C, 67·9; H, 4·85; Cl, 13·9; *M* (in camphor), 254·7. $C_{14}H_{13}O_2Cl$ requires C, 67·6; H, 5·3; Cl, 14·3%; *M*, 248·5].

4. *Resorcinol and Selenium Oxychloride.*—Resorcinol (33 g.; 3 mols.), suspended in 1000 c.c. of chloroform or dissolved in glacial acetic acid, was treated with selenium oxychloride (16·6 g.; 1 mol.) diluted with 100 c.c. of the same solvent. Each drop of the oxy-

chloride produced a transient green tint and a white precipitate separated. The solid portion of the jelly-like mixture was pressed and dissolved in acetone. On evaporation this solution yielded a selenonium chloride as a white powder. This product was dissolved in alcohol, and a large volume of acetone added; the selenonium chloride then separated slowly with acetone of crystallisation (1 mol.). With ammoniacal iodine the chloride yielded iodoform, thus confirming the presence of acetone. The substance melted at 206° (yield, 30 g.) (Found: C, 49·4; H, 4·5; Cl, 7·0; Se, 16·1; loss on heating at 110°, 12·1. $C_{18}H_{15}O_6ClSe,C_3H_6O$ requires C, 50·4; H, 4·2; Cl, 7·1; Se, 15·8; loss, 11·6%).

*Tri-*2 : 4-*dihydroxytriphenylselenonium chloride* (XVII) dissolved in boiling water to a pale red solution which set to a jelly on cooling. It also dissolved readily in alcohol or aqueous caustic soda but was only sparingly soluble in acetone or glacial acetic acid and insoluble in chloroform or benzene. Aqueous ferric chloride developed a reddish-purple coloration, warm concentrated sulphuric acid gave a green tint, and bromine water decomposed this selenonium chloride completely.

5. β-*Naphthol and Selenium Oxychloride.*—Selenium oxychloride (16·6 g.; 1 mol.), diluted with 100 c.c. of chloroform, was stirred into 43·2 g. of β-naphthol (3 mols.) in 700 c.c. of this solvent. The mixture became warmer and darker and finally almost solid owing to the separation of organic selenide (yield, 35 g.). This product crystallised from acetone in lustrous, colourless prisms, melting at 186° to a red liquid (Found: C, 65·5; H, 3·65; Se, 22·0. $C_{20}H_{14}O_2Se$ requires C, 65·7; H, 3·9; Se, 21·7%).

Although insoluble in chloroform, benzene, ether, or water, *di-*2-*hydroxydi-*1-*naphthyl selenide* (XVIII) dissolved readily in acetone and sparingly in hot alcohol or glacial acetic acid. Cold concentrated sulphuric acid developed a green tint, but alcoholic ferric chloride had no colour effect. This complex selenide dissolved readily in aqueous caustic alkalis and was reprecipitated unchanged by acids. Evaporation of the chloroform filtrate from di-2-hydroxydi-1-naphthyl selenide and distillation in steam of the red residue gave 17 g. of 2-chloro-β-naphthol (m. p. 70°).

6. *Salicylic Acid and Selenium Oxychloride.*—Salicylic acid (41·4 g.; 3 mols.) and selenium oxychloride (16·6 g.; 1 mol.) were heated and stirred in an open basin so long as hydrogen chloride was evolved and until the yellow mixture had assumed a brown tint. After cooling, the hard product was powdered and extracted with hot benzene to remove ill-defined by-products, unchanged salicylic acid and 5-chlorosalicylic acid (m. p. 166—167°). The pale yellow residue (20 g.) was crystallised repeatedly from aqueous

alcohol, *disalicylyl selenide* (*di*-4-*hydroxydiphenyl selenide di*-3-*carboxylic acid,* XIX) being obtained in small, yellowish-white, micaceous plates, sintering at 250° and decomposing at 272° (Found : C, 47·4 ; H, 2·9 ; Se, 23·2. $C_{14}H_{10}O_6Se$ requires C, 47·5 ; H, 2·85 ; Se, 22·4%). Although readily soluble in alcohol, ether, acetone, or glacial acetic acid, the disalicylyl selenide is insoluble in water, chloroform, or benzene. It dissolved readily in aqueous caustic or carbonated alkalis. The very soluble sodium salt was precipitated by ether from alcoholic solution as a hygroscopic precipitate, becoming green on exposure. Cold concentrated sulphuric acid and the selenide developed a green coloration which deepened on warming. Ferric chloride and an alcoholic solution of the selenide gave an intense bluish-violet coloration.

Experiments on the condensation of selenium oxychloride with *m*-cresol, α-naphthol, and 2-hydroxy-3-naphthoic acid failed to furnish well-defined products.

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