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RESEARCHES ON SELENIUM ORGANIC COMPOUNDS. VI BROMINE, SULFO AND MERCURY DERIVATIVES OF 2,4-DIPHENYL-SELENOPHENE AND EXPERIMENTS WITH SOME RELATED COMPOUNDS[1]

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Introductory

Following up the work of Bogert and Herrera,[3] the chemistry of 2,4-diphenyl-selenophene has been investigated further by the preparation and study of various bromine, sulfo and mercury derivatives.

Bromine Derivatives

By the direct action of bromine upon the selenophene, di-, tri- and tetrabromo derivatives resulted, the product formed being determined by the amount of bromine used per mole of the selenophene, the nature of the solvent, the presence or absence of catalysts, and other factors. Inasmuch as the tribromo derivative obtained by the action of bromine upon 5-chloromercuri-2,4-diphenyl-selenophene, which involves the displacement of the -HgCl group, is identical with that formed by the direct action of bromine upon 2,4-diphenyl-selenophene itself, it seems clear that one of the three bromine atoms in the molecules must be in Position 5. The location of the other bromine atoms has not been ascertained.

The action of chlorine, phosphorus tri- or pentachloride, upon 2,4-diphenyl-selenophene under various conditions, yielded only tars.

Sulfo Derivatives

Dil. sulfuric acid was without action upon 2,4-diphenyl-selenophene. The concentrated acid dissolved it, forming an orange or brownish solution which later changed to a tar. By the action of chlorosulfuric acid upon a solution of the selenophene in a large excess of petroleum ether, a tetrasulfonic acid was prepared.

Mercury Derivatives

The 5-halogeno- and 5-cyanomercuri derivatives were prepared by methods which have been shown to give satisfactory results in the thiophene field. These were the following.

1. When an alcoholic solution of the 2,4-diphenyl-selenophene was

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[3] Bogert and Herrera, THIS JOURNAL, **45**, 238 (1923).

treated with the mercuric halide, in the presence of sodium acetate, the mercuri derivative gradually separated in crystalline form.

2. An acetone solution of mercuri-*bis*(2,4-diphenyl-selenophene) was heated for ten minutes with the mercuric halide or cyanide, the insoluble material removed and the mercuri derivative precipitated from the filtrate by the addition of water.

In applying the first of these methods, it was found that the yield of chloromercuri derivative was 90% in 24 hours, and of bromomercuri derivative only 50% in 48 hours, while no iodomercuri derivative at all could be obtained.

We have not attempted any direct proof of the structure of these mercury derivatives, in view of the well-established fact that in the thiophene group the alpha is far more reactive than the beta position.[4]

No dihalogenomercuri derivatives were isolated in any of these reactions, an observation which is in agreement with the unreactivity of the beta position in such compounds.

From equal molecular proportions of the 5-chloromercuri derivative and potassium bromide, in acetone solution, there were obtained both the corresponding 5-bromomercuri derivative and the mercuri-*bis*(2,4-diphenylselenophene-5); with sodium iodide, the product was the *bis* compound, with only traces of the 5-iodomercuri derivative; and with sodium cyanide, there resulted both the 5-cyanomercuri derivative and the *bis* compound, except that when two moles of cyanide were used to one of the chloromercuri compound the sole product was the *bis* compound. The 5-bromomercuri derivative (one mole) with two moles of sodium bromide gave the *bis* compound.

Both the 5-bromo- and the 5-cyano-mercuri derivatives, when boiled in benzene, toluene or xylene solution, decomposed into 2,4-diphenylselenophene and the mercurous salt.

The reactivity and instability of these 5-halogenomercuri derivatives increased in the order $Cl < Br < I$.

Volhard[5] has shown that 2-chloromercuri-thiophene reacts with acid chlorides as follows: $C_4H_3SHgCl + RCOCl \longrightarrow C_4H_3SCOR + HgCl_2$, and Steinkopf and Bauermeister[4e] discovered that such ketones were easily prepared from thiophene and the acid chloride, in the presence of a small amount of 2-chloromercuri-thiophene as catalyst. Steinkopf and Jaff[4g] have secured similar ketones by the use of phosphorus pentoxide as condensing agent. When applied to 2,4-diphenyl-selenophene, neither the Steinkopf-Bauermeister method nor that of Steinkopf and Jaff yielded any of the desired ketones.

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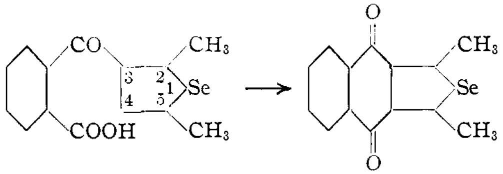
[4] Steinkopf and others, *Ann.*, (a) **403**, 27, 45, (b) 50, (c) 61, (d) 66, (e) 69 (1914); (f) **407**, 94 (1914); (g) **413**, 333 (1916); (h) **424**, 23 (1921); etc.

[5] Volhard, *Ann.*, **267**, 178 (1892).

Related Compounds

When selenoxene[6,7] was condensed with phthalic anhydride, in the presence of aluminum chloride, the phthaloylselenoxene (I) was obtained; this is analogous structurally to benzoylbenzoic acid and to phthaloylthioxene.[8,4f] The action of concd. sulfuric acid upon this caused it to change to an intense red, presumably due to the formation of the selenium compound (II) corresponding to anthraquinone and thiophanthrene,[4f,9] but the amount of pure material available was insufficient to prove this.

I



II

Experiments to obtain the 3,5-dialkyl-2,4-diphenyl-selenophenes by fusion of the anils of propio- or butyrophenone with selenium yielded only tar. From propiophenone-anil and sulfur, however, the corresponding 3,5-dimethyl-2,4-diphenyl-thiophene was prepared, and its formation supports the hypothesis of the mechanism of these reactions advanced by Bogert and Herrera.[3]

Experimental Part

Selenophene.—Foa[10] obtained what she believed to be selenophene itself by heating sodium succinate with phosphorus triselenide, and described it as a yellow oil, b. p. 147–149° (250 mm.). We obtained a similar product by heating succinic acid with phosphorus pentaselenide in a sealed tube; but the yield was very low, and further study of this substance has been deferred.

Attempted Preparation of 2-Methyl-selenophene and of 2,4-Dimethyl-selenophene.—Mixtures of levulinic acid and phosphorus triselenide were heated at different temperatures and for different lengths of time, both at ordinary pressure and in sealed tubes, but no 2-methyl-selenophene was obtained. At lower temperatures, but little reaction occurred and much of the levulinic acid was recovered; at higher temperatures, there was extensive decomposition and tar formation.[6,11]

When a mixture of equivalent proportions of acetone-anil and metallic selenium was heated for eight hours at 240°, some unchanged acetone-anil was recovered, but no 2,4-dimethyl-selenophene could be isolated from the melt.

[6] Paal, *Ber.*, **18**, 2255 (1885).

[7] Zoppellari, *Gazz. chim. ital.*, **24**, II, 399 (1894).

[8] Ernst, *Ber.*, **19**, 3278 (1886).

[9] Scholl and Seer, *Ann.*, **394**, 131 (1912).

[10] Foa, *Gazz., chim. ital.*, **39**, II, 527 (1909).

[11] Compare also Kues and Paal, *Ber.*, **19**, 555 (1886).

2,5-Dimethyl-selenophene (**2,5-Selenoxene**) was prepared by the method of Paal,[6,7] from acetonyl-acetone and phosphorus pentaselenide at 180°. For our purposes the fraction boiling at 140–160° (758 mm.) (yield, 26%) was found to answer satisfactorily, the boiling point of the pure product being given by Paal as 155–157° (corr.).

Phthaloylselenoxene (I).—To a suspension of 27 g. of phthalic anhydride in 200 cc. of carbon disulfide there were added 9 g. of selenoxene and then very gradually (1.5 hours) 25 g. of finely divided aluminum chloride. The mixture was boiled gently for two hours during constant stirring, allowed to settle for a few minutes, the supernatant liquid decanted hot, and the cooled dark residue treated with 100 cc. of ice water and 20 cc. of concd. hydrochloric acid. The yellow crystalline solid obtained was washed with water, extracted twice with 400 cc. of dil. sodium hydroxide solution, the filtered alkaline extracts were acidified with hydrochloric acid, and the precipitated phthaloylselenoxene was crystallized from toluene. Nodules of pale yellow crystals resulted; m. p., 155.5° (corr.), soluble in alcohol or ether; yield, 1.1 g., or 7%.

Anal. Calcd. for $C_{14}H_{12}O_3Se$: C, 54.72; H, 3.90. Found: C, 54.79; H, 3.87.

Treated with concd. sulfuric acid, this product developed an intense red coloration.

2,4-Diphenyl-selenophene was prepared as described by Bogert and Herrera,[3] except that the temperature of the bath was kept at 235–240° for 20 hours, this lower temperature and longer heating increasing the yield to 90%. The product formed colorless glistening scales, m. p. 112.3° (corr.), as described by them.

An attempt to nitrate this by the action of fuming (d., 1.5) nitric acid upon its acetic anhydride solution, following the method of Steinkopf and Lützkendorf[4a,12] in the thiophene field, gave only tar.

A warm alcoholic iodine solution was without action upon the diphenylselenophene, in the presence of mercuric oxide.

A mixture of 5 g. of the diphenyl-selenophene, a few milligrams of its 5-chloromercuri derivative and 5 g. of acetyl chloride, was heated in a flask according to the process of Steinkopf and Bauermeister,[4e] but no ketone could be isolated from the resulting tar.

3,5-Dimethyl-2,4-diphenyl-thiophene.—Propiophenone-anil was prepared as described by Reddelien,[13] who reported its m. p. as 50°. Our product formed pale yellow crystals; m. p., 53° (corr.); yield, 80%.

A mixture of 25 g. of propiophenone-anil with 8 g. of powdered roll sulfur was heated for six hours at 240°. A vigorous evolution of hydrogen sulfide occurred and aniline separated. The melt was distilled under a pressure of 20 mm. and the fraction boiling at 250–280° was decolorized

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[12] Compare also Bogert and Herrera, Ref. 3.

[13] Reddelien, *Ber.*, **43**, 2478 (1910).

and crystallized from alcohol to a constant melting point of 163.8° (corr.). The colorless, glistening scales dissolved freely in chloroform, or ether acetone, less readily in alcohol, benzene or glacial acetic acid, and were practically insoluble in water, sodium hydroxide solution or hydrochloric acid.

Anal. Calcd. for $C_{18}H_{16}S$: C, 81.76; H, 6.10. Found: C, 81.37; H, 6.21.

With concd. nitric acid it gave a yellow color, and with concd. sulfuric a yellowish-brown. When it was dissolved in alcohol, the solution treated with mercuric chloride and sodium acetate and the mixture allowed to stand, with occasional agitation, no chloromercuri derivative was formed.

Fusion of Propiophenone-anil with Selenium.—Mixtures of propiophenone-anil and powdered selenium, in equimolar proportions, were heated at temperatures between 220° and 300°, for from 2 to 72 hours. Aniline and hydrogen selenide were liberated freely during the heating, and the melt was finally distilled under a pressure of 30 mm.; the portion boiling at 270–330° was collected, at 10° intervals but from these fractions no crystalline products could be recovered directly, or by treatment with benzaldehyde or with mercuric chloride and sodium acetate.

Fusion of *n*-Butyrophenone-anil with Sulfur and with Selenium.—Butyrophenone-anil does not appear to have been described hitherto. Our product was prepared by the Reddelien[13] method and formed a pale yellow oil; b. p., 198–202° (25 mm.); yield, 60%.

An equimolar mixture of this product and powdered roll sulfur was heated for eight hours at 200–220°. Hydrogen sulfide and aniline separated. The residual melt was distilled under a pressure of 29 mm. and the fraction boiling at 300–310° formed a reddish-yellow oil which solidified to a pale yellow, crystalline mass. After crystallization from *n*-butyl alcohol, in the presence of decolorizing carbon, colorless lustrous flakes were obtained, m. p. 286° (corr.), that were rather difficultly soluble in *n*-butyl alcohol or glacial acetic acid, still more difficultly soluble in acetone, ethyl alcohol or benzene, and practically insoluble in water or ether. The amount of pure product isolated was insufficient for satisfactory analysis and identification as 3,5-diethyl-2,4-diphenyl-thiophene.

Similar fusions carried out with the anil and selenium yielded hydrogen selenide, aniline, dark oils and tar, but none of the crystalline selenophene sought.

Dibromo-2,4-diphenyl-selenophene.—A solution of 5 g. of 2,4-diphenylselenophene in 50 cc. of glacial acetic acid was mixed with a solution of 10 g. of bromine in 10 cc. of the same solvent and the mixture allowed to stand for several days at laboratory temperature. A crystalline solid separated. This was removed, washed with alcohol, dried thoroughly in an oven and crystallized twice from alcohol, giving colorless, glassy needles, m. p. 86.7° (corr.), that were very slightly soluble in water, ether or glacial acetic acid; yield, 5 g., or 80%.

Anal. Calcd. for $C_{16}H_{10}Br_2Se$: C, 43.53; H, 2.26. Found: C, 43.20; H, 2.30.

Tribromo-2,4-diphenyl-selenophene.—To a solution of 1.5 g. of 2,4-diphenylselenophene in 20 cc. of glacial acetic acid and containing a very small amount of iodine, there was added very slowly a solution of 10 g. of bromine in 10 cc. of the same solvent. The mixture was kept in the dark for 48 hours at laboratory temperature. The crystalline solid which separated was collected, dried, and crystallized from glacial acetic acid until it appeared in transparent, pale, straw-colored needles and its melting point remained constant at 126.7° (corr.); yield, 1 g., or 36%. It was soluble in ethyl or *n*-butyl alcohol, acetone or ether, and practically insoluble in water.

Anal. Calcd. for $C_{16}H_9Br_3Se$: C, 37.01; H, 1.74; Br, 46.15. Found: C, 37.20; H, 1.77; Br, 46.58.

In another experiment, 1.5 g. of the selenophene was added to 20 cc. of hot glacial acetic acid, a solution of 10 g. of bromine in 10 cc. of the same solvent poured in and the mixture allowed to stand for several days at laboratory temperature. When the crude crystalline product was treated with hot glacial acetic acid, the tribromo derivative was dissolved, while the dibromo remained as an insoluble, heavy oil which congealed as it cooled. The dibromo derivative was purified by repeated crystallization from acetone, and the tribromo from alcohol. The former melted at 86.7° (corr.) and the latter at 126.7° (corr.), neither of which melting-points was changed by admixture with pure di- or tribromo derivatives of different origin. The yield of dibromo derivative was 0.07 g., and of tribromo 0.4 g.

As noted beyond, this same tribromo derivative was obtained by the action of bromine, in the presence of water, upon the 5-chloromercuri-2,4-diphenyl-selenophene.

A futile effort was made to nitrate this tribromo derivative by the method of Steinkopf and Lützkendorf.[4a]

Tribromo-2,4-diphenyl-selenophene and Methyl Iodide.—To 0.5 g. of sodium shavings covered by 100 cc. of absolute ether were added 1 g. (0.002 mole) of tribromo-2,4-diphenyl-selenophene and 3 g. (0.02 mole) of methyl iodide. After 24 hours at ordinary temperature, the mixture was boiled gently for several hours and the hot solution decanted from the separated sodium halide and excess of sodium. As it cooled, this hot solution deposited colorless, minute, felted hairs. Recrystallized from alcohol, the product melted at 139.8° (corr.); yield, 0.46 g., or 74%.

Anal. Calcd. for $C_{17}H_{11}Br_3Se$: C, 38.20; H, 2.06. Found: C, 37.80; H, 2.12.

Although these analytical values agree fairly well with those calculated for a methyl-tribromo derivative, the formation of such a product would seem to involve so abnormal a reaction that further work is necessary to establish the identity of the compound.

Tetrabromo-2,4-diphenyl-selenophene.—When 4 g. of bromine was dropped slowly into a boiling solution of 1 g. of the selenophene in 20 cc. of alcohol in direct sunlight and the solution was subsequently concentrated, a colorless crystalline mass separated as the mixture cooled. By repeated crystallization from *n*-butyl alcohol, colorless minute felted hairs were obtained which melted constantly at 176.5° (corr.), and were soluble in alcohol, ether or carbon tetrachloride, but practically insoluble in water; yield, 0.6 g., or 30%.

Anal. Calcd. for $C_{16}H_8Br_4Se$: C, 32.05; H, 1.34. Found: C, 31.76; H, 1.48.

2,4-Diphenyl-selenophene Tetrasulfonic Acid.—To a suspension of 5 g. of the selenophene in 300 cc. of petroleum ether, maintained at a temperature of 0°, 8 cc. of chlorosulfuric acid was added very slowly while the solution was vigorously stirred. The first drop of the acid turned the mixture red. After being stirred for two hours, the mixture was poured upon twice its volume of cracked ice. The bluish-green solution so formed was neutralized with barium carbonate. The barium sulfonate obtained was extracted from the precipitate with hot water, the barium precipitated exactly by sulfuric acid, the filtrate from the barium sulfate evaporated to dryness and the residue crystallized from 50% alcohol. Colorless, long, glassy prisms were thus obtained, freely soluble in water, and melting above 300°; yield, very poor.

Anal. Calcd. for $C_{16}H_{12}O_{12}S_4Se$: S, 21.22. Found: 21.65.

5-Chloromercuri-2,4-diphenyl-selenophene, $ClHgC_{16}H_{11}Se$, has been described by Bogert and Herrera.[3] We found that with efficient mechanical stirring during the first 12 hours, followed by 12 hours' standing at ordinary temperature, the yield was 90% and the melting point of the recrystallized product 224° (corr.), as recorded by them.

When a mixture of this chloromercuri derivative (4 g.), bromine (4 g.) and water (50 cc.) was heated for an hour under a reflux condenser, an 81% yield of the tribromo-diphenyl-selenophene (m. p., 126.7°, corr.) was obtained.

In acetone solution, equal molecular proportions of this chloromercuri compound and potassium bromide reacted with formation of both the 5-bromomercuri derivative (m. p., 215°, corr.) and the mercuri-*bis*(2,4-diphenyl-selenophene-5) (m. p., 236.7°, corr.). The behavior with sodium iodide and cyanide is recorded beyond.

Attempted nitration of this 5-chloromercuri derivative by the Steinkopf and Lützkendorf[1a] process gave only tar. Similar lack of success attended our efforts to sulfonate it in petroleum ether solution with chlorosulfuric acid.

5-Bromomercuri-2,4-diphenyl-selenophene, $BrHgC_{16}H_{11}Se$.—A solution of 5 g. of the selenophene in 1 liter of 95% alcohol was treated with a 33% aqueous solution of sodium acetate (50 g.) and 250 cc. of a cold saturated solution of mercuric bromide. The mixture was well stirred and left at room temperature for two days. The separated solid when crystallized from alcohol formed microscopic, colorless, felted hairs, m. p. 215° (corr.), soluble also in benzene, toluene or glacial acetic acid; yield, 50%.

This same compound was obtained when mercuri-*bis*(2,4-diphenyl-selenophene-5) (0.6 g.) was heated for ten minutes with mercuric bromide (0.4 g.) in acetone solution. A mixture of the two products likewise melted at 215° (corr.). Its formation from the 5-chloromercuri derivative is noted above.

Anal. Calcd. for $C_{16}H_{11}BrHgSe$: Hg, 35.88. Found: 35.35.

When a toluene solution of this compound was boiled, it decomposed with formation of diphenyl-selenophene and mercurous bromide. By the action of two moles of sodium bromide upon one of this bromomercuri derivative, in acetone solution, mercuri-*bis*(2,4-diphenyl-selenophene-5) was obtained in 65% yield; m. p., 236.7° (corr.), which melting point was not altered by admixture with some of the pure *bis* compound of different origin.

5-Iodomercuri-2,4-diphenyl-selenophene, $IHgC_{16}H_{11}Se$, could not be secured by the action of mercuric iodide and sodium acetate upon 2,4-diphenyl-selenophene, or of one mole of sodium iodide upon its 5-chloromercuri derivative in acetone solution.

An acetone solution of mercuri-*bis*(2,4-diphenyl-selenophene-5) (0.6 g.) and mercuric iodide (0.4 g.) was heated for ten minutes, the solution filtered, and the filtrate diluted with water. The crude 5-iodomercuri derivative so precipitated was washed with water, dried and crystallized from alcohol; yield, 30%. All operations were conducted in the dark, as the compound reddened rapidly in the light. The purified product formed colorless crystals; m. p., 176° (corr.).

Anal. Calcd. for $C_{16}H_{11}HgISe$: Hg, 32.84. Found: 32.49.

5-Cyanomercuri-2,4-diphenyl-selenophene, $NCHgC_{16}H_{11}Se$.—Equal molecular proportions of the 5-chloromercuri derivative and sodium cyanide were mixed in acetone solution. Mercuri-*bis*(2,4-diphenyl-selenophene-5) precipitated. Dilution of the filtrate from this caused the separation of the desired 5-cyanomercuri derivative. Recrystallized from alcohol, it formed a colorless pulverulent solid; m. p., 256.4° (corr.); yield, 50%.

Anal. Calcd. for $C_{17}H_{11}NHgSe$: Hg, 39.37. Found: 39.17.

The same product was obtained when mercuri-*bis*(2,4-diphenyl-selenophene-5) (0.6 g.) was heated for ten minutes in acetone solution with mercuric cyanide (0.4 g.); yield, 90%; m. p., 256.4° (corr.); mixed melting point, the same.

When the compound was boiled in benzene, toluene or xylene solution, it decomposed into 2,4-diphenyl-selenophene (m. p., 112.3°, corr.) and mercurous cyanide.

When the 5-chloromercuri derivative was treated with two molecular equivalents of sodium cyanide, the only product isolated was the mercuri-*bis*(2,4-diphenyl-selenophene-5); m. p., 236.7° (corr.); mixed melting point, the same; yield, 75%.

Mercuri-*bis*(2,4-Diphenyl-selenophene-5), $((C_6H_5)_2C_4HSe)_2Hg$.—The formation of this compound from 5-chloromercuri-2,4-diphenyl-selenophene with potassium bromide or sodium cyanide, or from the corresponding 5-bromomercuri derivative and sodium bromide, has been noted in the foregoing. It was obtained also by the interaction of 1.5 g. of the 5-chloromercuri derivative and 1 g. of sodium iodide in acetone solution. The mixture was stirred for six hours, the precipitate removed, washed with water, dried and crystallized from benzene. The *bis* compound thus purified formed pale gray, minute, felted hairs, m. p. 236.7° (corr.), identical with the products obtained by the other methods.

Anal. Calcd. for $C_{32}H_{22}HgSe_2$: Hg, 26.16. Found: 26.53.

The acetone filtrate gave evidence of containing traces of the 5-iodomercuri derivative, but none could be isolated sufficiently pure for identification.[14]

Summary

1. Determination of the optimum temperature for the fusion of acetophenone-anil with selenium, has increased the yield of 2,4-diphenyl-selenophene to 90% from 30%.

2. The following new derivatives of 2,4-diphenyl-selenophene have been prepared and studied: di-, tri-, tetrabromo-, and what appears to be a methyl-tribromo-; tetrasulfo acid; 5-bromomercuri-, 5-iodomercuri- and 5-cyanomercuri-, mercuri-*bis*(2,4-diphenyl-selenophene-5) and phthaloyl-selenoxene.

3. The formation of 3,5-dimethyl-2,4-diphenyl-thiophene by the fusion of propiophenone-anil with sulfur is in agreement with the hypothesis of Bogert and Herrera concerning the mechanism of such reactions.

4. Selenoxene has been condensed with phthalic anhydride to a compound analogous to *o*-benzoylbenzoic acid, and which gives an intensely red color with concd. sulfuric acid, probably due to the formation of a selenium derivative similar structurally to anthraquinone and thiophanthrene.

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[14] Compare Ref. 4c.