[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

SALTS OF TRIPHENYLSELENONIUM HYDROXIDE[1]

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In salts of the type of tetramethylammonium chloride, $(CH_3)_4NCl$, and trimethylsulfonium chloride, $(CH_3)_2SCl$, the radicals $(CH_3)_4N$ and $(CH_3)_3S$ play the part of metals, and like the metals can be arranged in an electropotential series or series of relative electro-affinities.[2] Tetramethylammonium and trimethylsulfonium thus occupy positions near the head of this series, comparable with the positions occupied by the alkali metals, which they resemble in character. Now it has customarily been assumed that replacement of one or more indifferent methyl groups by groups of a distinct negative character, such as phenyl, diminishes the electropositiveness of the radical as a whole. While this appears to be true in a qualitative sense[3] there are several apparent exceptions, notably the recently synthesized tri-, tetra- and pentaphenylchromium hydroxides,[4] which are bases of moderate strength in spite of the large number of negative phenyl groups in their molecules.

A determination of the effect of different alkyl or aryl groups upon the position of these substituted -onium radicals in the electropotential series would thus appear to be a problem worthy of further study. The present investigation was undertaken for the purpose of supplying such information for the little known trialkyl and triaryl selenonium groups. As a prelude to this work it was found necessary to devise an adequate method for the preparation of the selenonium salts. In this paper is reported the synthesis of some salts of triphenylselenonium hydroxide.

Jackson[5] prepared the first selenonium compound, trimethylselenonium iodide, $(CH_3)_3SeI$, as well as the corresponding dimethylbenzyl and the tribenzyl salts, the last named not being recognized until Fromm and Martin[6] proved its structure. Pieverling[7] made an extensive study of the triethylselenonium salts, and Pieroni and Coli[8] isolated the selenohydrate, $(C_2H_5)_3SeSeH$. Scott[9] prepared trimethyl- and triethylselenonium per-

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[1] Presented at the Regional Meeting of the Pacific Division of the American Association for the Advancement of Science, at Berkeley, California, June, 1929.

[2] Kraus, THIS JOURNAL, **46**, 2196 (1924); Kraus, "Radicals as Chemical Individuals," Columbia University Press, **1927**.

[3] Hein and Meininger, *Z. anorg. allgem. Chem.*, **145**, 95 (1925).

[4] Hein, *Ber.*, **54**, 1905 (1921); Hein and Schwartzkopff, *ibid.*, **57**, 8 (1924). The corresponding alkyl chromium hydroxides have not been prepared, and so are not available for comparison.

[5] Jackson, *Ann.*, **179**, 1 (1875).

[6] Fromm and Martin, *ibid.*, **401**, 187 (1913).

[7] Pieverling, *ibid.*, **185**, 331 (1877); *cf.* also Rathke, *ibid.*, **152**, 210 (1869).

[8] Pieroni and Coli, *Gazz. chim. ital.*, II, **44**, 349 (1914).

[9] Scott, *Proc. Chem. Soc.*, **20**, 156 (1904).

iodides. This completes the work on the aliphatic salts. Hilditch and Smiles[10] prepared certain aromatic selenonium salts by the action of aluminum chloride upon anisole or phenetole and selenium dioxide. The yields were very low and the products impure. The structure of these compounds has recently been proved by Morgan and Burstall,[11] who have also prepared several hydroxyarylselenonium salts from phenols and selenium oxychloride. In addition, Carrara,[12] Pope and Neville,[13] and Edwards, Gaythwaite, Kenyon and Philips[14] have prepared compounds in which one of the three organic groups attached to the selenium atom is $-CH_2COOH$.

The selenium halides of the type $SeCl_4$ seem to offer an excellent starting point for the synthesis of compounds of the desired kind, due to the reactivity of the halogen atoms. However, it was found that too many side reactions occurred, and the Grignard, the Wurtz–Fittig, and the Friedel–Crafts reactions all yielded complex mixtures. It therefore seemed best to simplify the preparation by the use of a compound in which some of the halogen atoms of the selenium tetrahalide were already replaced by organic groups. Such a compound, diphenylselenium dichloride, $(C_6H_5)_2SeCl_2$, was successfully employed in a Friedel–Crafts reaction. The following equations represent the essential steps in the complete synthesis of triphenylselenonium chloride

$$2C_6H_5N_2Cl + K_2Se = (C_6H_5)_2Se + N_2 + 2KCl$$

$$(C_6H_5)_2Se + O \overset{HNO_3}{=} (C_6H_5)_2SeO$$

$$(C_6H_5)_2SeO + 2HCl = (C_6H_5)_2SeCl_2 + H_2O$$

$$(C_6H_5)_2SeCl_2 + C_6H_6 \overset{AlCl_3}{=} (C_6H_5)_3SeCl + HCl$$

The chloride thus prepared forms a white, crystalline hydrate, $(C_6H_5)_3SeCl\cdot 2H_2O$, with great ease on exposure to moist air. From the chloride it is easy to prepare other salts by double decomposition. Thus the water solution of the chloride yields a precipitate of the iodide or dichromate on treatment with a soluble salt of hydriodic or dichromic acid, an alcoholic solution of the chloride gives the picrate with picric acid, and the nitrate may be prepared by mixing aqueous solutions of the chloride with silver nitrate. In crystallizing the chloride from ethylene bromide, it was found that a quantitative conversion into triphenylselenonium bromide took place. This rather unusual reaction forms the best method for the preparation of the water-soluble bromide.

Another observation of some interest is that the melting points of the

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[10] Hilditch and Smiles, *J. Chem. Soc.*, **93**, 1384 (1908).

[11] Morgan and Burstall, *ibid.*, 3260 (1928).

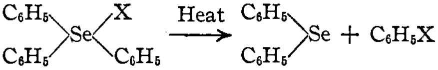
[12] Carrara, *Gazz. chim. ital.*, II, **24**, 173 (1894).

[13] Pope and Neville, *J. Chem. Soc.*, **81**, 1552 (1902).

[14] Edwards, Gaythwaite, Kenyon and Philips, *ibid.*, 2293 (1928).

chloride, bromide and iodide are very close to one another, 230, 236 and 237.5°, respectively. In a similar way the tri-(4-hydroxyphenyl)-selenonium chloride of Morgan and Burstall[11] melts at 232° and the bromide at 237°, while their tri-(3-methyl-4-hydroxyphenyl)-selenonium chloride melts at 231°. Since all these melting points are accompanied by decomposition, it appears that the breakdown at this temperature is rather a property of the selenonium type of molecule and is little affected by the substituent parts, as long as these are aryl in character.

In the case of the triphenylselenonium halides the decomposition occurs as follows



$$(C_6H_5)_2Se(X)(C_6H_5) \xrightarrow{\text{Heat}} (C_6H_5)_2Se + C_6H_5X$$

where X is a halogen atom. Presumably the other compounds mentioned decompose in an analogous fashion. This reaction is exactly similar to that of the trialkylselenonium halides, save that the latter is reversible. It was, in fact, this method which Pieverling[7] used in his synthesis, the reaction being

$$(C_2H_5)_2Se + C_2H_5I \longrightarrow (C_2H_5)_2SeI$$

At 80° the reverse reaction occurs and the two liquids on the left-hand side of the equation distil over, to reunite in the cold. The reaction in the aromatic series appears to be irreversible, however, and even ethyl iodide does not react with diphenyl selenide over a period of several months.

Experimental Part

Diphenyl Selenide.—This compound was at first prepared from diphenyl sulfone and selenium, according to the method of Krafft and Lyons.[15] However, an extension of the method of Schoeller[16] was found to be more rapid and economical. Three hundred and sixty grams of powdered potassium hydroxide and 240 g. of black, powdered selenium were thoroughly mixed and heated on an oil-bath to 140°, at which temperature they fused together. To a solution of the fused mass in 400 cc. of ice water was added slowly and in small portions at a time an ice cold solution of diazotized aniline hydrochloride from 138 g. aniline. To complete the reaction, the solution was separated from the viscous selenium-containing black mass in the bottom of the reaction vessel and heated to boiling. While still hot this was poured back upon the viscous black mass, which was then stirred up with the liquid.[17] The precipitate of selenium was filtered off and the lower liquid layer of the filtrate, consisting of diphenyl selenide, separated. The selenium was washed with ether or chloroform and the washings combined with the selenide. The combined liquids were distilled and the fraction boiling at 300–315° was the desired diphenyl selenide; yield, 125 g., or 72%, based upon the aniline used.

Diphenyl Selenium Dichloride.[18]—The diphenyl selenide (125 g.) was dissolved in an excess of commercial concentrated nitric acid and commercial concentrated hydrochloric acid was added. The dense yellow precipitate resulting was filtered, washed with

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[15] Krafft and Lyons, *Ber.*, **27**, 1761 (1894).

[16] Schoeller, *ibid.*, **52**, 1517 (1919).

[17] In this manner all danger of breaking the container was avoided.

[18] *Cf.* Zeise, *Ber.*, **28**, 1670 (1895); Foster and Brown, THIS JOURNAL, **50**, 1185 (1928).

water and crystallized once from benzene. The compound thus treated is still yellow, but is sufficiently pure to be used in the preparation of triphenylselenonium chloride; yield, 141 g., or 87%, calculated on the basis of the diphenyl selenide.

Triphenylselenonium Chloride, $(C_6H_5)_3SeCl$.—Eighty grams of anhydrous aluminum chloride was suspended in 100 cc. of dry benzene. The reaction flask was cooled with ice and 40 g. of diphenylselenium dichloride was added in portions over a period of twenty minutes. The flask was cooled and shaken throughout the addition. If these precautions were not observed, the mixture became warm and the product was largely a tar. During the reaction the liquid became dark red-brown, the aluminum chloride dissolved and hydrochloric acid was given off. After all of the dichloride had been added the mixture was allowed to stand for three hours at room temperature; 200 cc. of water was then cautiously added. The benzene layer was separated and discarded and the water solution extracted with chloroform. The extract was evaporated to small bulk and treated with three times its volume of ether. A yellow oil at once separated and quickly solidified to a pale yellow powder. This was filtered and crystallized from methyl ethyl ketone.[19] In this manner 30 g. of white crystals was obtained, a yield of 66%. They were very soluble in water, alcohol and chloroform, slightly soluble in acetone, but insoluble in ether. If the compound was allowed to stand in moist air or was recrystallized from wet solvents, it took up water to form a dihydrate. A sample crystallized from a little water gave the same compound. This became completely anhydrous after heating for half an hour at 100° in air.

TABLE I

TRIPHENYL SELENONIUM SALTS. $(C_6H_5)_3Se— = R$

Salt	Formula	Decomp. temp.,[a] °C.	Selenium,[b] % Calcd.	Selenium,[b] % Found	Acidic element, % Calcd.	Acidic element, % Found	Solvent for crystallization
Chloride	RCl	230	22.87	22.44	10.26	10.32	MeCOEt
Chloride dihydrate	$RCl\cdot2H_2O$	...[c]	...	...	9.28	9.23[d]	Water
Bromide[e]	RBr	236	20.29	20.09	20.45	20.51	MeCOEt
Iodide[f]	RI	237.5	18.11	18.05	29.06	29.31	Water
Dichromate	$R_2Cr_2O_7$	238	...	...	12.44	12.50	Dilute HAc
Picrate	$RC_6H_2N_3O_2$	...[g]	14.71	14.84	...	...	Alcohol
Nitrate[h]	RNO_3	...[i]	21.26	21.06	...	...	MeCOEt

[a] All temperatures are corrected. [b] Determined by the method of Shaw and Reid, THIS JOURNAL, **49**, 2330 (1927). [c] Begins to lose water at about 82° in air. [d] Percentage loss of two molecules of water at 100°: calcd., 9.43; found, 9.32. [e] Prepared by dissolving the chloride in boiling ethylene bromide. On cooling, the bromide separates out. [f] On exposure to light, the white iodide slowly turns yellow. [g] M. p., 141–142°. [h] Separates from concd. water solution on addition of concd. nitric acid. [i] M. p. 107–108°.

Thermal Decomposition of the Triphenylselenonium Halides.—On heating the iodide to its melting point, a rather violent boiling took place and on cooling the substance remained liquid. This liquid was separated by fractionation into a substance boiling at 180–190° and another boiling at 295–302°. The first fraction was proved to be iodobenzene (b. p. 185°) by conversion into phenyl iodoso chloride. This was further checked by a mixed melting point with a known sample of phenyl iodoso chloride. The second fraction was identified as diphenyl selenide (b. p. 302°) by conversion into

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[19] The ketone was dried over anhydrous copper sulfate, as suggested by Locke, *Ind. Eng. Chem.*, **16**, 956 (1924).

diphenylselenium dibromide, the identity of which was confirmed by a mixed melting point with some known diphenylselenium dibromide.[20]

In an entirely similar manner, triphenylselenonium bromide yielded two liquids boiling at 153–156 and 300–304°. The last was obviously diphenyl selenide, the first, bromobenzene (b. p. 156°). The chloride gave the selenide and a liquid boiling at 130–140°, which appeared to be chlorobenzene (b. p. 132°).

Summary

1. A method has been described for the synthesis of triphenylselenonium chloride, $(C_6H_5)_3SeCl$, by the action of benzene upon diphenylselenium dichloride in the presence of aluminum chloride.

2. From triphenylselenonium chloride the following salts have been prepared by metathesis: the bromide, iodide, dichromate, picrate and nitrate. Triphenylselenonium hydroxide appears to be a base of moderate strength.

3. The chloride, bromide and iodide have been shown to decompose with heat to give diphenyl selenide and chloro-, bromo- or iodobenzene, respectively.

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THE BROMINATION OF DESYLACETOPHENONE

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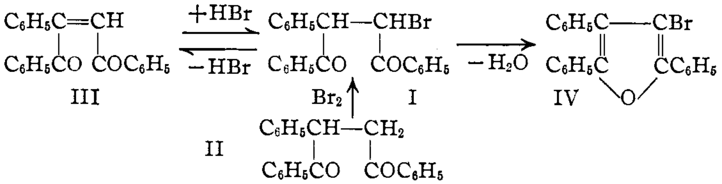
In an earlier paper[1] in which it was shown that bromofurans are produced when diacylstyrenes are treated with hydrogen bromide, the assumption was made that an open-chain addition product containing bromine was an intermediate product. Such a substance could form the ring compound by a loss of water from its enolic modification. Although the reaction undoubtedly took this course, unfortunately we were unable to isolate this bromo ketone (I)



In an attempt to prepare the latter substance, desylacetophenone (II), the saturated diketone corresponding to phenyldibenzoylethylene (III), was treated with bromine. In both chloroform and acetic acid solutions a quantitative yield of the bromofuran (IV) was obtained. Since the pri-

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[20] Krafft and Vorster, *Ber.*, **26**, 2818 (1893).

[1] Allen and Rosener, THIS JOURNAL, **49**, 2110 (1927).