isomer of the 2,2,9,9-tetramethyl-5,6-diphenyl-decandione-3,8, melting at 208°.

MIDDLETOWN, CONNECTICUT

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, STANFORD UNIVERSITY]

SALTS OF THE TOLYL AND MIXED PHENYL-TOLYL SELENONIUM HYDROXIDES[1]

BY H. M. LEICESTER AND F. W. BERGSTROM

RECEIVED AUGUST 19, 1931 PUBLISHED DECEMBER 10, 1931

Introduction

In a previous investigation,[2] which had for its original purpose a study of trialkyl and triaryl selenonium radicals and their approximate placement in an electropotential series, a number of salts of triphenylselenonium hydroxide were prepared. The primary material from which all of these salts were obtained was triphenylselenonium chloride, the product of the action of diphenyl selenium dichloride upon benzene in the presence of aluminum chloride. The following equations indicate the steps in this synthesis:

$$2C_6H_5N_2Cl + K_2Se_x = (C_6H_5)_2Se + 2KCl + 2N_2 + (x - 1)Se \tag{1}$$

$$(C_6H_5)_2Se + O \xrightarrow{HNO_3} (C_6H_5)_2SeO \tag{2}$$

$$(C_6H_5)_2SeO + 2HCl = (C_6H_5)_2SeCl_2 + H_2O \tag{3}$$

$$(C_6H_5)_2SeCl_2 + C_6H_6 \xrightarrow{AlCl_3} (C_6H_5)_3SeCl + HCl \tag{4}$$

In continuation of this work, we have prepared salts of *m*- and *p*-tolyl and of mixed phenyl-*p*-tolyl selenonium hydroxides and have developed a method of synthesis that may throw some light upon the relative electronegativities of the aryl groups attached to the selenium.

Preparation of Triarylselenonium Salts.—Since the synthesis of triphenyl selenonium chloride described in our earlier paper was so readily effected by condensing diphenyl selenium dichloride with benzene in the presence of aluminum chloride, in accordance with equations 1–4 above, it was correctly surmised that the tri-*p*-tolyl and many of the mixed phenyl-tolyl selenonium salts could be prepared in the same manner. Thus, symmetrical diarylselenium dichlorides were made from potassium polyselenide and the appropriate diazotized amine (aniline, *m*- or *p*-toluidine) as represented by equation 1.[3] Di-*m*- and di-*p*-tolyl selenides were prepared in this manner and converted by the action of concentrated nitric

---

[1] From the Ph.D. dissertation of Dr. Leicester. A paper presented at the Eugene, Oregon, meeting of the A. A. A. S., June, 1930 and at the Cincinnati meeting of the American Chemical Society, September, 1930.

[2] Leicester and Bergstrom, THIS JOURNAL, 51, 3587 (1929).

[3] This method was first described by Schoeller, *Ber.*, 52, 1517 (1919), and somewhat extended in our earlier paper.

and hydrochloric acids to the selenoxides (equation 2) and then to the dichlorides (equation 3). The latter were coupled with benzene or toluene in the presence of anhydrous aluminum chloride to give the salts listed in Table I.

TABLE I

SYNTHESIS OF SELENONIUM SALTS BY THE FRIEDEL-CRAFTS REACTION

	Starting materials		Product
1	Ph_2SeCl_2[a]	$CH_3C_6H_5$	Ph_2(*p*-Tol)SeCl
2	Ph(*p*-Tol)$SeCl_2$	C_6H_6	Ph_2(*p*-Tol)SeCl
3	(*p*-Tol)$_2SeCl_2$	C_6H_6	Ph(*p*-Tol)$_2$SeCl
4	(*p*-Tol)$_2SeCl_2$	$CH_3C_6H_5$	(*p*-Tol)$_3$SeCl

[a] Ph, Phenyl; *p*-Tol, *p*-tolyl.

In order to prepare selenonium salts containing *o*- and *m*-tolyl groups, another method of synthesis was sought and found in the fusion of the diaryl selenium dichlorides with the mercury diaryls. It was expected that the reactions would involve only the replacement of one chlorine atom of the dichloride by an aryl group in accordance with the equation

$$R''_2SeCl_2 + HgR'_2 = R'HgCl + R'R''_2SeCl \qquad (5)$$

It shortly became evident that at least two other reactions were taking place. These are represented by the equations

$$3R'_2Hg + 2R''_2SeCl_2 = 2R'_3SeCl + 2R''HgCl + R''_2Hg \qquad (6)$$
$$R_2Hg + 2R_2SeCl_2 = R_3SeCl\cdot HgCl_2 + R_3SeCl \qquad (7)$$

Occasionally, as in the reaction between mercury diphenyl and di-*p*-tolylselenium dichloride, (5) and (6) occur simultaneously. Conversely, when mercury di-*p*-tolyl and diphenylselenium dichloride are fused together, diphenyl *p*-tolyl selenium dichloride is formed in accordance with equation (5). Reaction (7) occurs when the aryl groups attached to both the mercury and the selenium are the same. The peculiar replacement of *p*-tolyl in a selenium compound by phenyl (*cf.* equation 6) appears to be connected with the relative electronegativities of the two groups and will be referred to later.

The selenonium salts prepared by the fusion method (equations 5, 6, 7) are shown in Table II.

TABLE II

SYNTHESIS OF SELENONIUM SALTS WITH THE USE OF MERCURY DIARYLS

Reaction type	Starting materials	Product
5	(*p*-Tol)$_2$Hg and (Ph)$_2SeCl_2$	Ph_2(*p*-Tol)SeCl
5	(Ph)$_2$Hg and (*p*-Tol)$_2SeCl_2$	Ph(*p*-Tol)$_2$SeCl
6	(Ph)$_2$Hg and (*p*-Tol)$_2SeCl_2$	(Ph)$_3$SeCl
7	(*p*-Tol)$_2$Hg and (*p*-Tol)$_2SeCl_2$	(*p*-Tol)$_3$SeCl
7	(*m*-Tol)$_2$Hg and (*m*-Tol)$_2SeCl_2$	(*m*-Tol)$_3$SeCl

Di-*o*- and di-*m*-tolyl mercury react in the sense of equation (5) with diphenyl selenium dichloride. These reactions have not yet been carried out on a sufficiently large scale to identify with certainty all of the reaction products. Selenonium salts were formed, as shown by the precipitation of the sparingly soluble iodides with potassium iodide solution. *o*-Tolyl mercuric chloride, formed in accordance with reaction (5), was the only aryl mercuric chloride identified among the reaction products.

The properties of the selenonium salts are, in general, very similar. They form double salts with ease and frequently separate from aqueous solution with water of crystallization. All are very soluble in chloroform and insoluble in ether. The chlorides are very soluble in cold water while the iodides are only sparingly soluble, although they dissolve readily in hot water. Nevertheless, salts of the individual bases possess certain distinctive properties.

Diphenyl-*p*-tolylselenonium chloride is a thick viscous oil when precipitated by ether from chloroform solution. After heating to drive off all of the solvent, it cools to a brittle highly hygroscopic glass which will not crystallize. Other salts of this base while often forming glasses can usually be obtained in crystalline form.

At first it was thought that this tendency toward the formation of a glass was occasioned by the presence of an isomer, possibly diphenyl-*o*-tolylselenonium chloride, formed as a by-product of the action of diphenyl selenium dichloride on toluene. However, by reference to Tables I and II it will be seen that diphenyl-*p*-tolylselenonium chloride was also prepared from phenyl *p*-tolyl selenium dichloride and benzene, and from mercury di-*p*-tolyl and diphenyl selenium dichloride. Since only one selenonium salt could be formed in the latter two reactions, and since the salts prepared by the three methods were identical in behavior, it is apparent that the difficulty experienced in crystallization is a characteristic property of the compound.

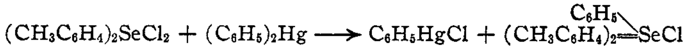
Of the remaining salts, di-*p*-tolylphenylselenonium chloride shows a marked tendency to separate from solution as a viscous liquid or glass which crystallizes slowly. Tri-*m*-tolylselenonium salts, although showing some tendency to form glasses, can be obtained in crystalline form with little difficulty. Tri-*p*-tolylselenonium salts are very readily crystallized and do not form glasses. It would seem that the tendency to crystallize is stronger the more symmetrical the molecule.

The aromatic selenonium salts when distilled are all decomposed into an aryl halide and a diaryl selenide. Thus it was found that diphenyl-*p*-tolylselenonium iodide decomposes almost entirely into iodobenzene and phenyl *p*-tolyl selenide; di-*p*-tolylphenylselenonium iodide is decomposed almost entirely into iodobenzene and di-*p*-tolyl selenide; and tri-*p*-tolylselenonium iodide is broken down into *p*-iodotoluene and di-*p*-tolyl selenide.

Preliminary conductivity measurements indicate that the triarylselenonium iodides are weak electrolytes and approach the maximum conductivity only at very high dilutions. The corresponding hydroxides are much better conductors.

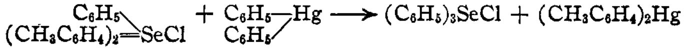
Since a solution of triphenylselenonium hydroxide may readily be prepared by the action of triphenylselenonium iodide upon silver oxide in water, it would appear a simple matter to obtain the solid base by concentration of this solution either at 100° or at room temperatures in a vacuum desiccator over sulfuric acid. Unfortunately in either case the hydroxide is decomposed to give diphenyl selenium oxide and a liquid that appears to be benzene. This behavior parallels the decomposition of the phosphonium hydroxides of Fenton and Ingold[4] into a trialkyl phosphine oxide and a hydrocarbon.

The replacement of chlorine and *p*-tolyl by the phenyl group in the reactions

 (8)

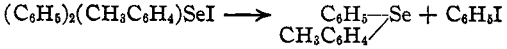
$$(CH_3C_6H_4)_2SeCl_2 + (C_6H_5)_2Hg \longrightarrow C_6H_5HgCl + \begin{matrix}C_6H_5\diagdown\\ (CH_3C_6H_4)_2{=}\end{matrix}SeCl \tag{8}$$

and

 (9)

$$\begin{matrix}C_6H_5\diagdown\\ (CH_3C_6H_4)_2{=}SeCl\end{matrix} + \begin{matrix}C_6H_5\diagdown\\ C_6H_5\diagup\end{matrix}Hg \longrightarrow (C_6H_5)_3SeCl + (CH_3C_6H_4)_2Hg \tag{9}$$

the elimination of iodobenzene in the thermal decomposition of diphenyl-*p*-tolylselenonium iodide in accordance with the equation

 (10)

$$(C_6H_5)_2(CH_3C_6H_4)SeI \longrightarrow \begin{matrix}C_6H_5\diagdown\\ CH_3C_6H_4\diagup\end{matrix}Se + C_6H_5I \tag{10}$$

and other reactions of a similar nature throw some light on the relative electronegativities of the aryl groups attached to the selenium and the mercury. Since these reactions obviously proceed with a diminution of free energy, we may assume—although proof is lacking—that the elements or groups of most widely divergent character will tend to unite with each other. Thus, in equation 6, chlorine is the most electronegative element present and mercury the least (*i. e.*, the most electropositive), the selenium, the phenyl and *p*-tolyl groups occupying a position somewhere between the other two. The selenium is undoubtedly more negative than either of the organic groups.

The formation of phenyl mercuric chloride in reaction (8) is to be expected, since mercury and chlorine differ more in electroaffinity than selenium and chlorine. As a result of this, a phenyl group replaces one chlorine attached to the selenium. The remaining chlorine, held now by a polar bond, is unreactive, and can therefore be disregarded in the reaction of equation (9). Bearing in mind that this reaction is not deep-seated enough to disrupt the selenonium salt and cause the formation of mercuric selenide, one should expect the mercury to unite with the most negative of the two aryl groups, rather than with the selenium. Therefore, since mercury di-*p*-tolyl is formed, it would seem that the *p*-tolyl group is more negative than the phenyl. This appears also to be the case in reaction (10), where the most negative atom, iodine, unites with the least negative group, phenyl.

---

[4] Fenton and Ingold, *J. Chem. Soc.*, 2342 (1929).

If, on the other hand, diphenyl selenium dichloride is fused with mercury di-*p*-tolyl, the two most divergent elements, mercury and chlorine, unite as would be predicted, and diphenyl-*p*-tolylselenonium chloride is formed. Further reaction of the selenonium salt with mercury di-*p*-tolyl cannot occur since the mercury is already attached to the more negative of the organic groups.

Kharasch and Marker,[5] as a result of the examination of a number of reactions of the type, R–Hg–R′ + HCl = R′H + RHgCl, have also concluded that the *p*-tolyl group is more negative than the phenyl.

Experimental Part

Diphenyl-*p*-tolylselenonium Chloride.—This was prepared from 50 cc. of toluene, 15 g. of anhydrous aluminum chloride, and 20 g. of diphenylselenonium chloride, in the manner represented by equations (1) to (4), inclusive.[6] The experimental procedure was the same as in the preparation of triphenylselenonium chloride. The chloroform extract of the water solution of the hydrolyzed reaction product was evaporated to small bulk and treated with ether. The viscous brown oil which separated did not become solid when heated for fifteen minutes at 100°. The molten mass cooled to a very hygroscopic glass. The chlorine analysis reported below is somewhat high because it was impossible to purify the salt by crystallization.

Anal. Calcd. for $C_{19}H_{17}SeCl$: Cl, 9.86. Found: Cl, 10.19.

Following the same procedure, a diphenyl-*p*-tolylselenonium chloride of identical properties was prepared from benzene, aluminum chloride and phenyl *p*-tolyl selenium dichloride. The latter was synthesized from the corresponding selenide of Gaythwaite, Kenyon and Phillips.[7]

An additional preparation of this salt was effected by fusing equimolecular quantities of diphenyl selenium dichloride with mercury di-*p*-tolyl,[8] in accordance with equation 5. The mixture was heated until fusion began, after which the reaction proceeded without external heat. The cooled reaction mixture was extracted with water to remove the soluble selenonium salt. The aqueous solution was filtered and extracted with chloroform, the chloroform solution concentrated and then treated with one-third its volume of ether. The same brown oil was obtained as in the first two preparations.

Diphenyl-*p*-tolylselenonium Iodide.—When a water solution of diphenyl-*p*-tolylselenonium chloride was treated with a solution of sodium iodide a yellowish viscous oil was precipitated. This slowly solidified when stirred. After repeated crystallizations from water, the salt was obtained in the form of clusters of white needles which turned yellow on exposure to light; decomposition point, 199–200°, corr.

Anal. Calcd. for $C_{19}H_{17}SeI$: Se, 17.55. Found: Se, 17.35.

Diphenyl-*p*-tolylselenonium iodide, when dry distilled, decomposes into compounds boiling at 180–200° and at 307–308°. The first fraction, since it yielded on nitration a compound melting at 170–171°, was evidently iodobenzene (b. p. 188°)

---

[5] Kharasch and Marker, THIS JOURNAL, **48**, 3130 (1926); Kharasch and Reinmuth, *J. Chem. Ed.*, 5, 404 (1928).

[6] In Reference 2, p. 3590, 30 g. of anhydrous aluminum chloride should have been used in the preparation of triphenylselenonium chloride instead of 80 g.

[7] Gaythwaite, Kenyon and Phillips, *J. Chem. Soc.*, 2283 (1928).

[8] All mercury diaryls were made by the method of Nesmejanow and Kahn, *Ber.*, **62**, 1018 (1929).

whose nitration product, *p*-nitroiodobenzene, melts at 171.5°. The second fraction was converted to a dibromide, which melts at 128–129° (dec.) and therefore would appear to differ from the phenyl-*p*-tolylselenonium dibromide of Gaythwaite, Kenyon and Phillips (m. p. 149–150°).[7] Accordingly, phenyl-*p*-tolyl selenide was synthesized by heating phenyl-*p*-tolyl sulfone with selenium, a synthesis already successfully used in the preparation of diphenyl selenide from diphenyl sulfone.[7,9] The reaction product was distilled and converted to the dibromide (*cf.* equations 2 and 3), which was found to melt at 128–129°. The identity of this dibromide with the dibromide prepared from the 307–308° fraction obtained in the pyrolysis of diphenyl-*p*-tolylselenonium iodide was confirmed by the determination of a mixed melting point of the two (127.5–128.5°). The reason for the low melting point of the phenyl-*p*-tolyl selenide dibromide of the present work as compared with the product of Gaythwaite, Kenyon and Phillips has not been determined.

It is quite possible that small amounts of *p*-iodotoluene and diphenyl selenide were formed in this pyrolysis, but, if so, they were not present in sufficiently large amounts for positive identification.

Di-*p*-tolyl Selenide.—This compound, first prepared by Zeiser[10] by heating mercury di-*p*-tolyl with selenium, may better be synthesized from *p*-toluidine according to the method of equation (1). The procedure was the same as for the preparation of diphenyl selenide.[3]

However, since the selenide is a solid at ordinary temperatures, the mixture of selenide and selenium obtained after the reaction of the diazotized *p*-toluidine with the sodium polyselenide solution was filtered off and extracted with chloroform in a Soxhlet extractor. The chloroform extract was distilled and the fraction boiling at 320–335° (760 mm.) was collected and crystallized from alcohol as white needles, m. p. 69°; yield, 70%. This was converted by nitric and hydrochloric acids into the dichloride in accordance with the method of equations (2) and (3); decomposition point, 188–189°, corr.

Anal. Calcd. for $C_{14}H_{14}SeCl_2$: Se, 23.84. Found: Se, 23.65.

Di-*p*-tolylphenylselenonium chloride was prepared from 50 cc. of benzene, 15 g. of aluminum chloride and 20 g. of di-*p*-tolyl selenium dichloride. The addition of ether to the concentrated chloroform solution of the salt first threw down a viscous oil which soon became solid. This crystallized from moist methyl ethyl ketone as colorless needles of the dihydrate.

Anal. Calcd. for $C_{20}H_{19}SeCl \cdot 2H_2O$ (preparation not heated): Cl, 8.65. Found: Cl, 8.85.

The latter melted at about 130° and on continued heating at this temperature lost a molecule of water to form the crystalline monohydrate; decomposition point, 189–190° corr. The anhydrous salt could not be obtained.

Anal. Calcd. for $C_{20}H_{19}SeCl \cdot H_2O$: Cl, 9.05. Found: Cl, 9.09, 9.18 (two preparations).

Di-*p*-tolylphenylselenonium Iodide and Picrate.—The iodide, prepared by adding an aqueous solution of sodium iodide to a solution of the chloride, was crystallized from water in white glistening plates decomposing at 189–191°, corr. On dry distillation it gave a liquid boiling at 188–198°, whose nitro derivative melted at 170–171° (iodobenzene boils at 189° and *p*-nitroiodobenzene melts at 171.5°) and a solid melting at 69° and boiling at 320–330° (760 mm.); di-*p*-tolyl selenide melts at 69–69.5°.

Anal. Calcd. for $C_{20}H_{19}SeI$: I, 27.28. Found: I, 27.14.

---

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

[10] Zeiser, *ibid.*, **28**, 1672 (1895).

The iodine was weighed as silver iodide, obtained by adding silver nitrate to a dilute aqueous solution of the salt.

The picrate, prepared from alcoholic picric acid and a solution of the chloride in alcohol, formed yellow needles, m. p. 158–159°, corr.

Anal. Calcd. for $C_{26}H_{21}SeN_3O_7$: Se, 13.98. Found: Se, 13.90.

The Reaction between Di-*p*-tolylselenium Dichloride and Mercury Diphenyl.—These substances, in the proportion of 1.5 moles of mercury diphenyl to 1 mole of the dichloride gave, after fusion and the usual extractions with water and chloroform, a white solid which was at first thought to be di-*p*-tolylphenylselenonium chloride. The chlorine analysis, however, was higher than the expected value and the decomposition points of the iodide and picrate formed from it were, respectively, 182–183° and 134–135°. Both of these values were lower than the decomposition points of the corresponding derivatives of di-*p*-tolylphenyl- and triphenylselenonium hydroxide. The unknown salt was then dry distilled. It yielded, besides the aryl halide, which would be chlorobenzene in any case, two substances boiling, respectively, at 300–312° and above 320° (760 mm.). The former remained liquid and appeared to be diphenyl selenide, b. p. 302°. The latter solidified and was di-*p*-tolyl selenide, as shown by its melting point (69–69.5°). For further proof, each selenide was converted by concd. nitric and hydrochloric acids into the dichloride. The decomposition points were taken simultaneously in the same bath. The dichloride from the lower boiling selenide decomposed at 183°, that from the higher boiling fraction decomposed at 188°. Since the decomposition point of diphenyl selenium dichloride is 183°,[11] diphenyl selenide must have been present in the decomposition mixture from the selenonium salt. This could only have arisen from triphenylselenonium chloride, and hence it is evident that a mixture of triphenyl- and di-*p*-tolylphenylselenonium chlorides must have been formed. From the larger amount of di-*p*-tolyl selenide present, it was apparent that di-*p*-tolylphenylselenonium chloride was the main product of the reaction.

Tri-*p*-tolylselenonium Chloride.—This salt was prepared by the Friedel–Crafts reaction (equations 1–4) from di-*p*-tolyl selenium dichloride and toluene, and also by fusing one mole of mercury di-*p*-tolyl with two moles of di-*p*-tolyl selenium dichloride. The cooled fusion was worked up for the selenonium salt in the customary manner. A portion of the fusion, which was insoluble in water, was found to be the mercuric chloride double salt of tri-*p*-tolylselenonium chloride. The selenonium salt itself was obtained by passing hydrogen sulfide into an alcoholic suspension of the double salt and filtering off the mercuric sulfide, or better by treating an aqueous suspension of the double salt with dilute sodium hydroxide. From the filtered solution the selenonium salt was extracted with chloroform and then precipitated by ether as the monohydrate; decomposition point, 158–160°, corr.

Anal. Calcd. for $C_{21}H_{21}SeCl \cdot H_2O$: Cl, 8.71. Found: Cl, 8.64, 8.76 (two specimens).

Tri-*p*-tolylselenonium Iodide Monohydrate.—Sodium iodide precipitates this salt from an aqueous solution of the chloride as long white needles, decomposing at 202–203°, corr., after recrystallization from water.

Anal. Calcd. for $C_{21}H_{21}SeI \cdot H_2O$: Se, 15.92; I, 25.53. Found: Se, 15.83, 15.93; I, 25.83, 25.89 (two specimens).

When this salt was dry distilled two fractions were obtained, boiling at 208–212° and at 320–325°. The first fraction congealed to a solid, m. p. 32–33°, which was evi-

---

[11] Foster and Brown, THIS JOURNAL, 50, 1185 (1928), state that this substance decomposes at 142°. We have found the higher value, which agrees with the older work.

dently *p*-iodotoluene, m. p. 35° and b. p. 211.5°. The melting point of the solidified second fraction was 69°, indicating it to be di-*p*-tolyl selenide, which melts at 69–69.5°.

Di-*m*-tolyl Selenide.—This was prepared in a yield of 54% from *m*-toluidine (equation 1) as a pale yellow liquid, b. p. 187–188° (corr.), at 16 mm. The dichloride, prepared by the method of equations 2 and 3, formed colorless crystals (from alcohol), which decomposed at 149–150°, corr.

Anal. Calcd. for $C_{14}H_{14}SeCl_2$: Se, 23.84. Found: Se, 23.98.

Tri-*m*-tolylselenonium Salts.—One mole of mercury di-*m*-tolyl and two moles of di-*m*-tolyl selenium dichloride were fused on the water-bath at 75–80°. A small quantity of selenonium salt was extracted from the water-soluble material with chloroform. The water-insoluble residue crystallized from alcohol in colorless plates melting at 145°, corr.

Anal. Calcd. for $C_{21}H_{21}SeCl \cdot HgCl_2$: Hg, 30.43. Found: Hg, 30.73.

The selenonium salt was prepared by precipitating the mercury with hydrogen sulfide or sodium hydroxide. Since the chloride so obtained tended to separate from solution in the glassy form, it was converted into the sparingly soluble iodide by double decomposition; white plates (cryst. from water), decomposing at 156–157°, corr.

Anal. Calcd. for $C_{21}H_{21}SeI$: I, 26.48. Found: I, 26.12.

Solubilities of Triarylselenonium Iodides.—An excess of the iodide was shaken with water at 25° for two hours. Iodine was determined in 25-cc. portions of the equilibrium solutions by the Volhard method.

Table III

Solubility of Triarylselenonium Iodides, Grams per 100 Cc. of Solution at 25°

Iodide	Solubility
Triphenylselenonium	0.48
Diphenyl-*p*-tolyl	.41
Di-*p*-tolylphenyl	.28
Tri-*p*-tolyl	.15

Triphenylselenonium Hydroxide.—An aqueous solution of triphenylselenonium iodide was boiled with silver oxide to the disappearance of the test for soluble iodides. The filtered solution was strongly basic toward litmus and readily absorbed carbon dioxide from the air. Attempts to isolate the base by evaporating the water at 100° or at room temperatures in a vacuum desiccator resulted in the sudden appearance of milkiness when the solution became fairly concentrated. Upon distillation of this solution a small amount of oil separated and floated on the water in the receiver and while this appeared to be benzene it was present in too small amounts to identify. Treatment of the aqueous solution in the distilling flask with concd. hydrochloric acid gave a precipitate which, after crystallization from alcohol, decomposed at 182–183°, and therefore must have been diphenyl selenium dichloride, m. p. 183°, dec. Hence the decomposition of the triphenylselenonium hydroxide gave benzene (probably) and diphenyl selenium oxide, the aqueous solution of which is converted into the dichloride by hydrochloric acid.

Summary

1. Methods have been described for the preparation of purely aromatic selenonium salts by the Friedel–Crafts reaction and by the fusion of diaryl selenium dichlorides with mercury diaryls.

2. The following new compounds have been described: diphenyl-*p*-tolylselenonium chloride and iodide, di-*p*-tolylphenylselenonium chloride,

iodide and picrate, tri-*p*-tolylselenonium chloride and iodide, di-*m*-tolyl selenide, di-*m*-tolyl selenium dichloride, tri-*m*-tolylselenonium iodide and tri-*m*-tolylselenonium chloride-mercuric chloride.

3. Triphenylselenonium hydroxide has been prepared in dilute solution. The solution when concentrated decomposes into benzene (?) and diphenyl selenium oxide.

4. The formation of triphenylselenonium chloride by fusing di-*p*-tolyl selenide with mercury diphenyl and the thermal decomposition of diphenyl-*p*-tolylselenonium iodide into phenyl iodide and phenyl *p*-tolyl selenide indicate the *p*-tolyl group to be more negative than the phenyl.

STANFORD UNIVERSITY, CALIFORNIA

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

STUDIES IN THE CHLOROPHYLL SERIES.
VIII. THE STRUCTURE OF CHLOROPHYLL *B*

BY J. B. CONANT, EMMA M. DIETZ AND T. H. WERNER

RECEIVED NOVEMBER 6, 1931 PUBLISHED DECEMBER 10, 1931

A study of the transformations of methylphaeophorbide *a* and chlorin *e* has led us to propose structural formulas for these substances and chlorophyll *a*.[1] We have now to report the results of the application of our methods to the *b* series. The analyses of chlorophyll *b* and its transformation products, (phaeophorbide *b*, rhodin *g*) led Willstätter to conclude that the compounds in the *b* series differed from the corresponding *a* compounds by an extra atom of oxygen. More recent analyses by Fischer and coworkers, and in this Laboratory have confirmed this conclusion. Practically no information has been hitherto available about the nature and position of this extra oxygen atom except that the *b* compounds like the *a* compounds can be transformed into phyllo, pyrro and rhodoporphyrins, and therefore this oxygen must be such that it is removed in the drastic autoclave treatment used in preparing the porphyrins.

In all our transformations we have found that the behavior of the *b* compounds is closely analogous to that observed in the *a* series. In every case, however, the reactions are accompanied by more side reactions and the products are more difficult to isolate and purify. Because of the poor yields we have had to be content with evidence which is less satisfactory than in the *a* series. The results are summarized diagrammatically below and are to be compared with those given by the diagrams on pages 361 and 2383 of papers IV and V which deal with the transformations in the *a* series. In this connection it must be recalled that the formulas given in paper IV for

---

[1] Paper V, THIS JOURNAL, **53**, 2382 (1931); see also papers VI and VII, THIS JOURNAL, **53**, 3171, 3522 (1931).