

[CONTRIBUTION FROM THE JESSE METCALF CHEMICAL LABORATORY OF BROWN UNIVERSITY]

## PHENYL TIN COMPOUNDS

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**Introduction.**—The description of the properties of the known phenyltin compounds as given in the literature shows that they resemble the corresponding alkyl derivatives in many respects. The investigations of Kraus with Sessions<sup>2</sup> and Greer<sup>3</sup> on compounds of trimethyltin and of dimethyltin, indicate that these groups exhibit marked amphoteric properties. It has been shown that the sodium derivatives of these groups are very reactive toward electronegative elements or compounds containing such elements. The reactions of triphenyltin and diphenyltin should resemble, to a certain extent, those of the analogous methyl compounds and this investigation is intended to supply data concerning the reactions of the former groups.

The procedure adopted in this investigation is similar to that employed by Kraus and Sessions.<sup>2</sup> The apparatus employed for using liquid ammonia as a solvent is that described by White.<sup>4</sup>

### Preparation of Materials

**Tetraphenyltin** was used as the starting material in this investigation and was prepared chiefly by the method of Polis<sup>5</sup> with slight modifications. During the latter part of the research a process was developed for the preparation of the material by means of zinc diphenyl. A yield above 90% of a very pure product was obtained by the latter procedure.

**A. Sodium-tin Alloy Method.**—Bromobenzene was refluxed with about four times the calculated quantity of a 14% sodium-tin alloy on an oil-bath for 12 hours. The resulting gray solid mass was treated with cold carbon tetrachloride to remove unchanged bromobenzene, and then repeatedly extracted with boiling carbon tetrachloride or benzene. The tetraphenyltin so obtained melted at 225–226° after one recrystallization; yield, about 50%.

**B. Zinc Diphenyl Method.**—A quantity of phenylmagnesium bromide was prepared in the usual way in a 3-necked boiling flask, provided with a reflux condenser fitted with a calcium chloride tube, a dropping funnel and a tube through which a current of nitrogen could be introduced. On completion of the reaction a suspension of dry zinc chloride in absolute ether was added through the dropping funnel. Reaction took place immediately. Toluene was then added and the ether distilled on a water-bath. To the cooled solution was added a solution of an equivalent amount of stannic chloride in toluene and the mixture boiled for one hour. All of these manipulations were carried out in an atmosphere of nitrogen. After cooling, dil. hydrochloric acid

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<sup>2</sup> Kraus with Sessions, *THIS JOURNAL*, **47**, 2361 (1925).

<sup>3</sup> Kraus and Greer, *ibid.*, **47**, 2568 (1925).

<sup>4</sup> White, *ibid.*, **45**, 780 (1923).

<sup>5</sup> Polis, *Ber.*, **22**, 2915 (1889).

was added and the solution filtered. The residue was extracted with boiling benzene. The toluene layer of the filtrate was united with the benzene extracts and the mixture concentrated and cooled; yield, 91.2%; m. p., 224–225°.

**Triphenyltin Bromide.**—When a solution of tetraphenyltin in chloroform is treated with bromine, two phenyl groups are replaced by bromine. Polis<sup>5</sup> states that iodine has no effect upon tetraphenyltin, but results in this Laboratory show that iodine may be successfully employed when it is desired to replace but one phenyl group.

To 150 g. of tetraphenyltin, in a 1500cc. distilling flask provided with a reflux condenser and having the side arm closed with a stopper, was added 975 g. of chloroform and the mixture boiled while 90 g. of iodine was added in small portions. After each addition of iodine the solution immediately became decolorized, until near the end, when a brown color appeared which was not discharged after boiling for one hour. The chloroform was distilled on a water-bath. The iodobenzene which was formed in the reaction was removed by distilling under a pressure of 13 mm. The residue, consisting of crude triphenyltin iodide, was dissolved in ether and filtered to remove unchanged tetraphenyltin. The ether solution was shaken in a separatory funnel with three portions of 30% sodium hydroxide solution and the layers were separated. The ether layer, containing triphenyltin hydroxide, was shaken with concd. hydrobromic acid, the layers were separated and the ether layer was dried over sodium sulfate. On concentration of the ether solution, 86 g. of triphenyltin bromide was obtained which, after recrystallization from ether, melted sharply at 120–121°; yield, about 50%.

**Diphenyltin Dibromide.**—The diphenyltin dihalides used in this investigation were prepared by the direct bromination of tetraphenyltin by the method of Smith and Kipping.<sup>6</sup>

A solution of the required amount of bromine in carbon tetrachloride was slowly added to a suspension of tetraphenyltin in the same solvent. After boiling for two hours, the solvent, together with the bromobenzene formed in the reaction, was removed by steam distillation. The residue was treated with a 15% solution of sodium hydroxide and the diphenyltin oxide so formed was washed with water, alcohol and ether. It was suspended in absolute alcohol and treated with dry hydrogen bromide gas until solution occurred. Excess of hydrogen bromide was removed by passing a stream of carbon dioxide through the solution. The alcohol was distilled and the diphenyltin dibromide fractionally distilled under a pressure of 2 to 3 mm. The fraction boiling at 184–185° on crystallizing melted at 36–38°; yield, 35%.

### Compounds of Triphenyltin

**Sodium Triphenyltin.**—When sodium is allowed to react upon a solution of triphenyltin bromide in liquid ammonia, immediate reaction occurs with the formation of a solution of sodium triphenyltin according to the following equation:  $(C_6H_5)_3SnBr + 2Na = (C_6H_5)_3SnNa + NaBr$ .

**PROPERTIES.**—It is a pale yellow, amorphous powder, soluble in liquid ammonia with formation of a pale yellow solution, and somewhat soluble in anhydrous ether. Its chemical reactions are described below.

**Reaction with Oxygen.**—When a current of dry oxygen gas was passed through a solution of sodium triphenyltin in liquid ammonia, a white

<sup>6</sup> Smith and Kipping, *J. Chem. Soc.*, 103, 2034 (1913).

precipitate was formed. On evaporating the ammonia and extracting the residue with hot benzene, triphenyltin hydroxide, tetraphenyltin and diphenyltin oxide were found.

These products were identified in the following manner. On fractional crystallization of the benzene extract there was first obtained a white powder which melted at 221–223°. Equal portions of this product and tetraphenyltin melted at the same point. The last portions of the benzene extract deposited colorless, rhombic tablets that melted at 117–118°. Equal portions of this product and triphenyltin hydroxide melted at the same point. A tin analysis gave 32.37% of tin; calcd. for  $(C_6H_5)_3SnOH$ , 32.42%. The product from the original reaction, which was insoluble in benzene, was washed with hot water to remove inorganic salts. It was found to be insoluble in the usual organic solvents and did not melt. It was suspended in absolute ether and treated with dry hydrogen chloride until a clear solution was obtained. On evaporating the ether and treating the residual oil with water, a white powder was obtained which melted at 188–189°. This was diphenyltin hydroxychloride and was obtained according to the following reactions:  $(C_6H_5)_2SnO + 2HCl = (C_6H_5)_2SnCl_2 + H_2O$ ;  $(C_6H_5)_2SnCl_2 + H_2O = (C_6H_5)_2Sn(OH)Cl + HCl$ .

The presence of triphenyltin hydroxide may be accounted for by assuming the following series of reactions in which the sodium oxytriphenyltin formed by oxidation is hydrolyzed by moisture present in the air and in the solvent used:  $(C_6H_5)_3SnNa + O = (C_6H_5)_3SnONa$ ;  $(C_6H_5)_3SnONa + H_2O = (C_6H_5)_3SnOH + NaOH$ . These reactions fail to account for the presence of tetraphenyltin and diphenyltin oxide. It was noted that tetraphenyltin was formed in drying some triphenyltin hydroxide and experiments indicated that tetraphenyltin and diphenyltin oxide may be formed from triphenyltin hydroxide by thermal decomposition according to the following equation:  $2(C_6H_5)_3SnOH \cdot 1\frac{1}{2}H_2O = (C_6H_5)_4Sn + (C_6H_5)_2SnO + 4H_2O$ . This reaction illustrates the tendency of phenyl groups to wander from one tin atom to another with the formation of a higher phenylated derivative. Aronheim<sup>7</sup> made use of this tendency in the preparation of triphenyltin halides from diphenyltin dihalides by the action of sodium amalgam or ammonia gas under suitable conditions.

**Thermal Decomposition of Triphenyltin Hydroxide.**—One and a half g. of freshly precipitated triphenyltin hydroxide was placed in a weighed Pyrex glass tube and subjected to a temperature of 230–240° for two hours under a pressure of 3 mm. The tube was cooled and weighed. The loss in weight (0.1 g.) represented that of any readily volatile product. A sublimate (0.75 g.) consisting of long needles melted at 222–223°. A mixture of equal portions of this and tetraphenyltin melted at the same point. A white residue (0.6 g.) which was insoluble in water, alcohol and ether and did not melt under 300°, was analyzed for tin by the method of Krause.<sup>8</sup>

<sup>7</sup> Aronheim, *Ann.*, 194, 145 (1878).

<sup>8</sup> Krause, *Ber.*, 53, 173 (1920).

*Anal.* Subs., 0.1105, 0.1157: SnO<sub>2</sub>, 0.0579, 0.0608. Calcd. for (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>SnO: Sn, 41.17. Found: 41.27, 41.39; av., 41.33.

The amounts of the different substances formed according to the above equations were as follows: water, (C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>Sn, (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>SnO: calcd., 0.15, 0.81, 0.55; found, 0.10, 0.75, 0.60.

The action of oxygen on sodium triphenyltin was repeated as described above except that cold benzene was used as the extracting agent. In this case only triphenyltin hydroxide was obtained. It is evident that even at the boiling point of benzene, triphenyltin hydroxide underwent the same decompositions as at the higher temperature. A similar reaction at higher temperature has been noted with trimethyltin hydroxide.<sup>9</sup>

**Reaction with Aryl Halides.**—When a sodium salt of the alkyl or aryl tin group is treated with an organic halide in liquid ammonia, reaction in general occurs with the formation of a sodium halide. If the residual hydrocarbon group has a marked affinity for tin, combination between the two groups will occur. On treating sodium triphenyltin with a series of aryl halides which contained another group in the nucleus beside the halogen, reaction between the two, in general, did not occur. The aryl halides employed were *p*-chloro-aniline, *m*-chloro-aniline, sodium *o*-chlorophenolate, sodium *p*-bromobenzoate and *o*-chloronitrobenzene. It was found that reaction occurred with sodium triphenyltin when the reacting compound contained carboxyl or nitro groups. With *p*- and *m*-chloro-aniline only triphenyltin and aniline could be found as products of the reaction, and with *o*-chlorophenol the products were triphenyltin and phenol. Sodium *p*-bromobenzoate appeared to react with sodium triphenyltin to form triphenyltin benzoic acid, but the product was unstable, being hydrolyzed to triphenyltin hydroxide and benzoic acid. *o*-Chloronitrobenzene reacted vigorously with sodium triphenyltin to form colored products which could not be definitely identified. It is possible that the nitro group was involved in this reaction.

**Reaction with Phenylmercuric Iodide. Phenylmercuric Amine.**—The reaction between sodium triphenyltin and phenylmercuric iodide was carried out in liquid ammonia solution with the expectation that a compound of tin and mercury might be formed according to the following equation: (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SnNa + C<sub>6</sub>H<sub>5</sub>HgI = (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SnHgC<sub>6</sub>H<sub>5</sub> + NaI. It was found, however, that the reaction did not take place in the expected manner but gave rise to triphenyltin, sodium iodide, mercury and phenylmercuric amine. The mechanism of the reaction was not investigated. The phenylmercuric amine (C<sub>6</sub>H<sub>5</sub>HgNH<sub>2</sub>) was obtained by fractional crystallization of the absolute alcoholic extract of the reaction products. Triphenyltin and sodium iodide were obtained, respectively, in the first two crops, the phenylmercuric amine being obtained on concentration of the

<sup>9</sup> R. H. Bullard, *Dissertation*, Brown University, 1925.

mother liquor. After several recrystallizations from absolute alcohol it melted sharply at 123.5–124°. Fusion with metallic sodium showed absence of halogen. On heating with sodium carbonate in a test-tube a mirror of mercury was deposited on the upper part of the tube. This gave red mercuric iodide on addition of a crystal of iodine to the tube while still warm. On heating the original compound with soda lime, a strong odor of ammonia was noticed and a heavy coloration was obtained with mercurous nitrate paper.

*Anal.* (Grignard and Abelmann's method).<sup>10</sup> Subs., 0.1008: Hg, 0.0678. Calcd. for  $C_6H_5HgNH_2$ : Hg, 68.37. Found: 67.26.

*Mol. wt.* (cryoscopic method; solvent, benzene). Subs., 0.0674: solvent, 17.25;  $\Delta t$ , 0.067. Calcd. for  $C_6H_5HgNH_2$ : mol. wt., 293.6. Found: 298.

**Phenylmercuric Amine.**—The same compound that was described above should be obtained by allowing phenylmercuric iodide to react with potassium amide in liquid ammonia. Accordingly, a solution of potassium amide was prepared by the method of Franklin<sup>11</sup> using iron oxide as a catalyst and some phenylmercuric iodide added and allowed to react for 12 hours. On extracting the reaction products with benzene a substance was obtained which gave all the tests described in connection with phenylmercuric amine and melted at 122–123°. An equal mixture of this compound and the compound obtained by the action of sodium triphenyltin on phenylmercuric iodide melted at 122–123°.

**Triphenyltin Acetic Acid.**—In the course of the study of the compounds of triphenyltin, attempts were made to cause sodium triphenyltin to react with monochloro-acetic ester in ether solution. The sodium salt was formed in the usual manner, the ammonia completely removed and an ether solution of the ester added. There appeared to be no reaction and no definite compounds could be separated from the resulting mixture. The evidence obtained from these results suggests that reactions of this type do not easily take place in ether.

As a reaction between sodium triphenyltin and the chloro-acetic ester could not be carried out in ammonia, owing to the reactivity of the latter reagent towards the solvent, the sodium salt of monochloro-acetic acid was used, reaction taking place according to the following equation:  $(C_6H_5)_3SnNa + CH_2ClCOONa = (C_6H_5)_3SnCH_2COONa + NaCl$ .

On addition of sodium monochloro-acetate to an ammonia solution of sodium triphenyltin, reaction took place with the formation of a glittering white precipitate. On evaporation of the ammonia, extraction with water and acidification with acetic acid, a white precipitate was obtained which, after recrystallization from 80% acetic acid, melted at 122–122.5°. No halogen could be detected by the Beilstein test.

<sup>10</sup> Grignard and Abelmann, *Bull. soc. chim.*, [4] 19, 25 (1916).

<sup>11</sup> Franklin, *Am. Chem. J.*, 47, 300 (1912).

**PROPERTIES.**—It formed white plate-like crystals; m. p., 122–122.5°. It is soluble in most organic solvents except petroleum ether in which its solubility is slight, and it is practically insoluble in water. It is best recrystallized from 80% acetic acid. The sodium salt is very soluble in water, undergoing hydrolysis and forming a very fine precipitate which is very difficult to separate by filtration.

*Anal.* (Krause's method).<sup>8</sup> Subs., 0.1417, 0.1018: SnO<sub>2</sub>, 0.0525, 0.0374. Calcd. for (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SnCH<sub>2</sub>CO<sub>2</sub>H: Sn, 29.09. Found: 29.18, 28.93; av., 29.05.

*Mol. wt.* (cryoscopic method; solvent, benzene). Subs., 0.5237, 0.8550: solvent, 35.5, 35.5;  $\Delta t$ , 0.208, 0.337. Calcd. for (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SnCH<sub>2</sub>CO<sub>2</sub>H: mol. wt., 409. Found: 363, 366.

**Triphenyltin Hydride.**—Foster<sup>12</sup> first obtained triphenyltin hydride by the action of ammonium bromide on sodium triphenyltin, but did not have this compound in sufficient quantity and purity to establish its composition and to study its properties. The hydride is formed according to the following equation: (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SnNa + NH<sub>4</sub>Br = (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SnH + NaBr + NH<sub>3</sub>.

Five g. of triphenyltin bromide was placed in a reaction tube and 50 cc. of ammonia condensed upon it. Sodium was added in small portions until a permanent blue color was obtained; 0.63 g. of sodium was required. On addition of 1.25 g. of ammonium bromide this solution became colorless with the formation of a pasty, white precipitate. The ammonia was allowed to evaporate and the residue extracted with ether and filtered. On evaporating the ether in an atmosphere of ammonia, there was obtained a cloudy yellow oil containing a white crystalline solid melting at 229–232°, which could be removed by filtration. Later information showed that this solid was triphenyltin formed by the oxidation of triphenyltin hydride. The clear oily liquid obtained by filtration immediately became cloudy again upon exposure to air. On subjecting this liquid to vacuum distillation in a flask from which the air had been displaced by ammonia, it was found to boil at 173–174° (6 mm.) with the formation of a clear, water-white, oily liquid. This was sealed in glass tubes in an atmosphere of nitrogen.

*Anal.* (Carius method). Subs., 0.1728, 0.1700: SnO<sub>2</sub>, 0.0740, 0.0730. Calcd. for (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SnH: Sn, 33.90. Found: 33.75, 33.82; av., 33.78.

*Mol. wt.* (cryoscopic method; solvent, benzene). Subs., 0.4010, 0.7926: solvent, 26.1, 26.1;  $\Delta t$ , 0.234, 0.460. Calcd. for (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SnH: mol. wt., 351. Found: 336, 338.

**REACTION WITH OXYGEN.**—A small portion of triphenyltin hydride was dissolved in absolute alcohol and dry oxygen passed through the solution for fifteen minutes. A white, crystalline powder was formed which, upon recrystallization from ether, melted at 232–233°. Triphenyltin melts at 232.5°. As the reaction takes place according to the following equation, 2(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SnH + O = 2(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Sn + H<sub>2</sub>O, all manipulations of triphenyltin hydride must be carried out in an inert atmosphere.

**REACTION WITH SODIUM.**—Sodium reacted with triphenyltin hydride in liquid ammonia with the formation of sodium triphenyltin. When the latter solution was treated with triphenyltin chloride a white precipitate was formed, which when recrystallized from benzene melted at 231–232°. It was triphenyltin and was formed according to the following equations: (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SnH + Na = (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SnNa + 1/2H<sub>2</sub>; (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SnNa + (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SnCl = 2(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Sn + NaCl.

<sup>12</sup> Foster, *Master's Thesis*, Clark University, 1923.

### Diphenyltin

Free diphenyltin has been prepared by E. Krause<sup>8</sup> by the action of phenylmagnesium bromide on tin tetrachloride in an atmosphere of nitrogen. He found that it was a yellow powder melting from 126° to 130° and decomposed at 205°. It was soluble in the usual organic solvents and was easily oxidized in air to white diphenyltin oxide. When freshly prepared and dissolved in benzene it was found to be monomolecular. On standing, the compound polymerized until, in the pentamolecular(?) form, it was no longer soluble and precipitated from the benzene solution.

An attempt was made to prepare this compound by the direct action of sodium on diphenyltin halide in liquid ammonia solution according to the following equation:  $(C_6H_5)_2SnCl_2 + 2Na = (C_6H_5)_2Sn + 2NaCl$ . The product of the reaction was a bright yellow powder which was insoluble in water and in the common organic solvents. It did not melt, but decomposed at 206° and was oxidized to diphenyltin oxide only on standing in the air for several months. On titrating it with a solution of bromine in carbon tetrachloride it was found that 1 g. combined with 0.58 g. of bromine, without the evolution of hydrogen bromide and with the formation of diphenyltin dibromide. The amount of bromine theoretically required for this reaction is 0.586 g.

*Anal.* (Krause's method).<sup>8</sup> Subs., 0.1224, 0.1356, 0.2433:  $SnO_2$ , 0.0663, 0.0741, 0.1316. Calcd. for  $(C_6H_5)_2Sn$ : Sn, 43.58. Found: 42.66, 43.04, 42.60.

From the properties observed and from the analysis, it was apparent that the compound was probably a polymerized form of free diphenyltin. This compound appears to be similar to the corresponding methyl derivative.<sup>8</sup>

Diphenyltin may be prepared in a monomolecular form by means of diphenyltin dihydride. This latter compound decomposes slightly above liquid ammonia temperatures with the evolution of hydrogen. At liquid ammonia temperatures this decomposition is very slow and no noticeable amount of hydrogen is evolved for some time.

DIPHENYLTIN DIHYDRIDE was prepared by forming disodium diphenyltin by the action of sodium on diphenyltin dibromide in liquid ammonia solution according to the following equation:  $(C_6H_5)_2SnBr_2 + 4 Na = (C_6H_5)_2SnNa_2 + 2 NaBr$ . The first addition of sodium produced a yellow precipitate which eventually dissolved forming a deep red solution. When this solution was treated with an excess of ammonium bromide the red color gradually disappeared and a dark brown precipitate was formed.  $(C_6H_5)_2SnNa_2 + 2 NH_4Br = (C_6H_5)_2SnH_2 + 2 NaBr + 2 NH_3$ . The greater portion of the ammonia was allowed to evaporate and absolute ether was added.<sup>13</sup>

The remainder of the ammonia was then allowed to evaporate. During the evaporation of the ammonia a eudiometer was connected to the reaction tube and hydrogen corresponding to one molecular equivalent was obtained. The reaction proceeded

<sup>13</sup> It was found that unless the ether was added before the ammonia had completely evaporated a polymerized product was obtained which was not appreciably soluble in the usual organic solvents.

according to the following equation:  $(C_6H_5)_2SnH_2 = (C_6H_5)_2Sn + H_2$ . The ether solution of diphenyltin, which was bright yellow, was filtered and evaporated in an atmosphere of ammonia. A dark red, viscous oil was obtained which solidified on cooling to a yellow solid. This did not melt, but decomposed at  $205^\circ$  and was readily soluble in the usual organic solvents except ethyl alcohol.

*Anal.* (Krause's method).<sup>8</sup> Subs., 0.2304, 0.2846, 0.1299:  $SnO_2$ , 0.1272, 0.1553, 0.0718. Calcd. for  $(C_6H_5)_2Sn$ : Sn, 43.58. Found: 43.48, 42.98, 43.53.

*Mol. wt.* (cryoscopic method; solvent, benzene). Subs., 0.4960: solvent, 70.5;  $\Delta t$ , 0.127. Calcd. for  $(C_6H_5)_2Sn$ : mol. wt., 273. Found: 284.

The diphenyltin so prepared is not readily oxidized by air while in the solid state, but from its solutions white diphenyltin oxide is rapidly precipitated. The compound differs from that described by E. Krause<sup>8</sup> in its melting point and its reactivity towards oxygen.

### Action of Sodium on Tetraphenyltin

Sodium reacts with tetraphenyltin in liquid ammonia solution to form sodium triphenyltin and disodium diphenyltin in varying amounts, depending upon the concentration of the sodium and the time of the reaction. High concentrations of sodium and long reaction periods tend to give larger amounts of disodium diphenyltin. Sodium triphenyltin is acted upon by sodium with the formation of a small amount of disodium diphenyltin. Disodium diphenyltin appears to be stable towards further action of sodium.

The amounts of the substances formed were determined by treating the solution containing the products of reaction of sodium on tetraphenyltin with ammonium bromide. This converted the sodium salts into the corresponding hydrides. Triphenyltin hydride is stable and may be determined by extraction with ether. The diphenyltin dihydride, being unstable, immediately begins to decompose with the formation of hydrogen. The hydrogen may be collected and measured, giving an indirect measure of the amount of disodium diphenyltin present. The diphenyltin which is formed by the decomposition of diphenyltin dihydride, being practically insoluble in ether,<sup>13</sup> remains behind after the extraction of the triphenyltin hydride. This may then be weighed and a check obtained on the amount of the disodium diphenyltin compound present.

As stated above, sodium triphenyltin reacts with sodium in liquid ammonia solution to form comparatively small amounts of disodium diphenyltin. The slowness of this reaction probably indicates why a complete conversion to disodium diphenyltin is not obtained. The following series of equations indicate the probable course of the above reactions:  $(C_6H_5)_4Sn + 2Na = (C_6H_5)_3SnNa + C_6H_5Na$ ;  $(C_6H_5)_3SnNa + 2Na = (C_6H_5)_2SnNa_2 + C_6H_5Na$ ;  $C_6H_5Na + NH_3 = C_6H_6 + NaNH_2$ .

The amount of disodium diphenyltin formed from tetraphenyltin was found to range from 9 to 40% depending upon the concentration of the sodium and the time of reaction. The amount of disodium diphenyltin



formed from sodium triphenyltin varied from 2–25% depending upon the concentration and the time. No unchanged tetraphenyltin was observed in any of the experiments. These results are of interest since sodium trimethyltin compounds are not further reduced under corresponding conditions.<sup>2</sup> In the light of the results obtained it appears that with the use of dilute solutions of sodium in equivalent quantity the formation of disodium compounds may be avoided.

### Summary

1. Sodium triphenyltin is readily oxidized in liquid ammonia to sodium oxytriphenyltin which is easily hydrolyzed to triphenyltin hydroxide. Triphenyltin hydroxide undergoes thermal decomposition with the formation of tetraphenyltin, diphenyltin oxide and water.

2. The reaction between sodium triphenyltin and aryl halides was investigated. Direct substitution of the triphenyltin group occurred in practically none of the cases studied.

3. Sodium triphenyltin reacts with phenylmercuric iodide in liquid ammonia to form triphenyltin, sodium iodide, mercury and a new mercurial, phenylmercuric amine. Phenylmercuric amine was also formed by the reaction between phenylmercuric iodide and potassium amide in liquid ammonia.

4. The triphenyltin group may be substituted in acetic acid by the reaction between sodium triphenyltin and sodium monochloro-acetate in liquid ammonia. The properties of triphenyltin acetic acid were studied.

5. Triphenyltin hydride was prepared by the action of ammonium bromide on sodium triphenyltin in liquid ammonia and its properties were studied. Triphenyltin hydride is oxidized to free triphenyltin and water.

6. Diphenyltin was synthesized by the interaction between diphenyltin dibromide and disodium diphenyltin in liquid ammonia. The product of this reaction was a yellow powder whose properties indicated a high state of polymerization. Free diphenyltin was prepared in the monomolecular form by the decomposition of diphenyltin dihydride.

7. Sodium reacts with tetraphenyltin in liquid ammonia to form sodium triphenyltin and disodium diphenyltin in varying amounts depending upon the conditions. Sodium also reacts with sodium triphenyltin with the formation of disodium diphenyltin and thus accounts for the presence of disodium diphenyltin in the reaction of sodium with tetraphenyltin.