[Contribution from the Chemical Laboratory of Iowa State College]

STUDIES CONCERNING WATER-SOLUBLE ORGANOTIN COMPOUNDS

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Although organotin compounds have shown little promise in the field of chemotherapy, the possibility that certain types may exhibit marked therapeutic properties is not precluded since so few of these compounds have been investigated. By sufficiently "masking" the tin and providing water-solubility, it is possible that the toxicity of these compounds might be reduced and their absorption in the body enhanced so that a more accurate estimate of their effectiveness in chemotherapy would be possible. This study was undertaken in an attempt to introduce water-solubilizing groups into organotin compounds, or to provide these compounds with reactive groups that might be utilized in subsequent reactions leading to water-soluble tin compounds.

Halogen-metal interconversion reactions (1) have opened up a new field in which organolithium compounds containing certain functional groups may be prepared in satisfactory yields (2, 3). These organolithium compounds may be used to introduce organic radicals containing functional groups into organotin compounds of the R_4Sn type. However, when compounds of the $R_3R'Sn$, $R_2R'_2Sn$, etc. types are to be prepared, it is desirable to convert these organolithium compounds into the corresponding organomagnesium compounds by means of anhydrous magnesium bromide to avoid formation of side products, probably by a redistribution reaction. The following new compounds were prepared by the use of the halogen-metal interconversion reaction: triphenyl-*o*-hydroxyphenyltin, triphenyl-*p*-hydroxyphenyltin, di-*o*-hydroxyphenyldiphenyltin, triphenyl-*o*-hydroxymethylphenyltin, and triphenyl-*p*-hydroxymethylphenyltin.

The halogen-metal interconversion reactions with the halogen-substituted phenols and benzyl alcohols give the lithium salts of the hydroxyphenyllithiums and hydroxymethylphenyllithiums. These can then be reacted directly, or, after conversion to the corresponding organomagnesium compounds, with the organotin halide to form the hydroxyl-containing organotin compound (I).

$$o\text{-BrC}_6\text{H}_4\text{OH} + 2\ n\text{-C}_4\text{H}_9\text{Li} \rightarrow o\text{-LiC}_6\text{H}_4\text{OLi} + 2\ n\text{-C}_4\text{H}_{10}$$

$$o\text{-LiC}_6\text{H}_4\text{OLi} + \text{MgBr}_2 \rightarrow o\text{-BrMgC}_6\text{H}_4\text{OLi} + \text{LiBr}$$

$$o\text{-BrMgC}_6\text{H}_4\text{OLi} + (\text{C}_6\text{H}_5)_3\text{SnCl} \rightarrow (\text{C}_6\text{H}_5)_3\text{Sn}(o\text{-LiOC}_6\text{H}_4) + \text{MgBrCl}$$

$$(\text{C}_6\text{H}_5)_3\text{Sn}(o\text{-LiOC}_6\text{H}_4) \xrightarrow{\text{NH}_4\text{Cl (aqueous)}} \underset{\text{I}}{(\text{C}_6\text{H}_5)_3\text{Sn}(o\text{-HOC}_6\text{H}_4)}$$

Attempts to prepare triphenyl-*p*-aminophenyltin by this method were unsuccessful. The reaction led to the formation of a red tar from which no definite compounds could be isolated. In one case, however, a small amount of material

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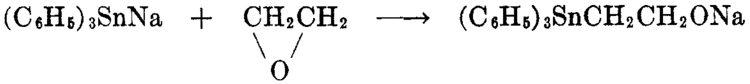
melting at 167–169° was obtained by resorting to purification through the hydrochloride. The tin content of this material approximated that of triphenyl-*p*-aminophenyltin but was not close enough to be conclusive.

Triphenyl-β-hydroxyethyltin (II) was prepared by the reaction of triphenyltinsodium and ethylene oxide in liquid ammonia. This reaction proceeded smoothly, giving a 59% yield of (II).

$$(C_6H_5)_3SnCl + Na \xrightarrow{NH_3(l)} (C_6H_5)_3SnNa$$



$$(C_6H_5)_3SnNa + \underset{\diagdown\;\diagup \atop O}{CH_2CH_2} \longrightarrow (C_6H_5)_3SnCH_2CH_2ONa$$

$$(C_6H_5)_3SnCH_2CH_2ONa \xrightarrow{NH_4Cl\ (aqueous)} \underset{II}{(C_6H_5)_3SnCH_2CH_2OH}$$

The Grignard reagent or the organolithium compound can be prepared directly from the dimethylaminophenyl bromides. Therefore, triphenyl-*o*-dimethylaminophenyltin and triphenyl-*p*-dimethylaminophenyltin were prepared for subsequent studies in this manner without resorting to the halogen-metal interconversion reaction.

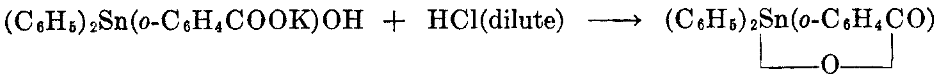
Potassium permanganate oxidation of triphenyl-*p*-hydroxymethylphenyltin (III) gave the expected triphenyl-*p*-carboxyphenyltin (IV), whereas oxidation of triphenyl-*o*-hydroxymethylphenyltin (V) in an analogous manner gave entirely unexpected results. The product after acidification from the oxidation of V was probably the inner salt of diphenyl-*o*-carboxyphenyltin hydroxide (VI), although its exact structure was not definitely established. This product (VI) after conversion to what was supposedly diphenyl-*o*-carboxyphenyltin chloride (VII) was esterified with diazomethane to give a product which was probably diphenyl-*o*-carbomethoxyphenyltin chloride (VIII). The tin contents of VI and VIII corresponded closely to those calculated for their assumed compositions. One possible set of reactions for the oxidation of V and subsequent reactions is given below.

$$\underset{III}{(C_6H_5)_3Sn(p\text{-}C_6H_4CH_2OH)} + KMnO_4 \rightarrow (C_6H_5)_3Sn(p\text{-}C_6H_4COOK) \xrightarrow{H^+}$$

$$\underset{IV}{(C_6H_5)_3Sn(p\text{-}C_6H_4COOH)}$$

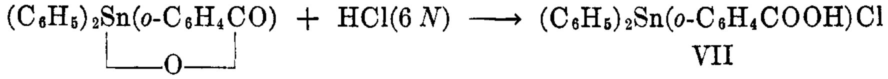
$$3\,\underset{V}{(C_6H_5)_3Sn(o\text{-}C_6H_4CH_2OH)} + 4\,KMnO_4 \longrightarrow$$

$$3\,(C_6H_5)_2Sn(o\text{-}C_6H_4COOK)OH + 3\,C_6H_6 + 4\,MnO_2 + KOH + H_2O$$



$$(C_6H_5)_2Sn(o\text{-}C_6H_4COOK)OH + HCl(dilute) \longrightarrow (C_6H_5)_2\underbrace{Sn(o\text{-}C_6H_4CO)}_{O}$$

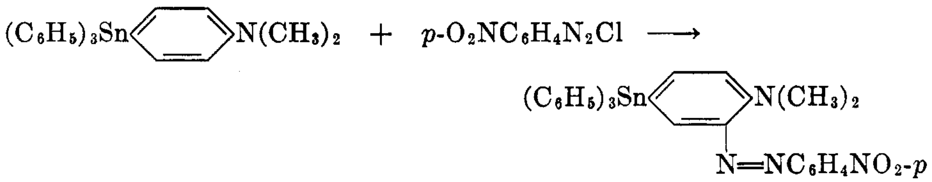
VI



$$(C_6H_5)_2\underset{\llcorner\_\_O\_\_\lrcorner}{Sn(o\text{-}C_6H_4CO)} + HCl(6\,N) \longrightarrow \underset{\text{VII}}{(C_6H_5)_2Sn(o\text{-}C_6H_4COOH)Cl}$$

$$(C_6H_5)_2Sn(o\text{-}C_6H_4COOH)Cl + CH_2N_2 \longrightarrow \underset{\text{VIII}}{(C_6H_5)_2Sn(o\text{-}C_6H_4COOCH_3)Cl} + N_2$$

The coupling reaction between organotin compounds containing functional groups which facilitate azo compound formation and diazonium chlorides was studied. Apparently the diazonium chloride solution causes cleavage of the organotin compound. Of the numerous different coupling reactions attempted, only in the case of triphenyl-*p*-dimethylaminophenyltin could a pure tin-containing azo compound be isolated and then only after repeated recrystallization. The azo compound which was isolated was triphenyl-4-dimethylamino-3-(4′-nitrophenylazo)phenyltin (IX) from the reaction of triphenyl-*p*-dimethylaminophenyltin and *p*-nitrobenzenediazonium chloride.



IX

Several additional reactions were investigated as possible means for introducing functional groups into organotin compounds. Attempts to introduce the sulfonyl chloride group directly into tetraphenyltin gave only cleavage products even at −75°. No apparent reaction between phenylboric acid and stannic chloride was observed; therefore, substituted phenylboric acids containing functional groups were not investigated. Tetraphenyltin was not affected by prolonged heating with an alkaline solution, but triphenyl-*o*-hydroxyphenyltin was cleaved, thereby excluding the Reimer-Tiemann reaction as a possible method for the introduction of an aldehyde group in organotin compounds.

EXPERIMENTAL

Triphenyltin chloride from tetraphenyltin and stannic chloride. Triphenyltin chloride was prepared from tetraphenyltin and stannic chloride by a method similar to that described by Kocheshkov and co-workers (4).

Triphenyltin iodide. Triphenyltin iodide was prepared according to the method described by Chambers and Scherer (5) for the preparation of triphenyltin bromide with triphenyltin iodide as an intermediate which was not isolated.

After the iodine was added, the chloroform and iodobenzene were removed by distillation, the latter under reduced pressure. A Soxhlet extractor was then employed to extract the crude triphenyltin iodide from the unreacted tetraphenyltin with ether. After crystallization from petroleum ether (b.p. 77–117°), there was obtained a 70% yield of pure triphenyltin iodide melting at 119–121°.

Tetraethyltin. Tetraethyltin was prepared by the reaction of ethyl bromide and an alloy of tin, sodium, and zinc according to the method described by Harada (6). The "large excess" of ethyl bromide to which Harada refers is greater than 60% since a smaller excess results in a violent reaction which takes place several hours after the reactants are mixed and gives very poor yields of tetraethyltin.

Triethyltin bromide. Triethyltin bromide was prepared by slowly adding 11.2 g. (0.070 mole) of bromine to 16.4 g. (0.070 mole) of tetraethyltin which was stirred and cooled in an ice-salt bath. By fractional distillation of the resulting liquid there was collected 17.6 g. (88%) of triethyltin bromide boiling at 105–107° (15 mm.), n_D^{20} 1.5240.

Diphenyltin dichloride. Diphenyltin dichloride was prepared in a manner similar to that described by Kocheshkov (7).

Anhydrous magnesium bromide. Bromine was added slowly to a large excess of magnesium turnings in ether. The large excess of magnesium was used to prevent the formation of small fragments of magnesium which are difficult to remove when the solution is filtered through glass wool. Both layers which form during the preparation were used since the ether layer contains some magnesium bromide in solution.

Triphenyl-o-hydroxyphenyltin. To a cold solution of 0.246 mole of *n*-butyllithium in 490 cc. of ether was added rapidly 21.3 g. (0.123 mole) of *o*-bromophenol in 25 cc. of ether. After 40 minutes 0.25 mole of anhydrous magnesium bromide in approximately 100 cc. of ether was added. Then 47.4 g. (0.123 mole) of triphenyltin chloride was added and after the mixture had stirred for two hours, it was hydrolyzed with a cold solution of ammonium chloride and the ether layer was dried over sodium sulfate. The ether was removed by distillation and the residue boiled for ten minutes with 100 cc. of ethanol to remove unreacted materials. After the mixture was cooled, it was filtered and the residue, which consisted of crude triphenyl-*o*-hydroxyphenyltin, was crystallized from chloroform. Yield, 31 g. (57%) of pure triphenyl-*o*-hydroxyphenyltin which melted with decomposition between 176–182°, depending on the rate of heating. When the temperature was raised from 170° to 176° over a period of nine minutes the compound melted with decomposition at 176–177°.

Anal. Calc'd for $C_{24}H_{20}OSn$: Sn, 26.81. Found: Sn, 26.70.

Triphenyl-p-hydroxyphenyltin, di-o-hydroxyphenyldiphenyltin, triethyl-o-hydroxyphenyltin, triphenyl-o-hydroxymethylphenyltin, and triphenyl-p-hydroxymethylphenyltin. These compounds were all prepared in essentially the same manner as described for triphenyl-*o*-hydroxyphenyltin. Tables I and II contain the details of their preparation and their physical properties.

Reaction of triphenyltin iodide and p-aminophenyllithium. A solution of 0.190 mole of *n*-butyllithium in 240 cc. of ether was added to 10.9 g. (0.063 mole) of *p*-bromoaniline in 50 cc. of ether. After the mixture had been stirred for one hour, during which time a yellow precipitate formed, a slight excess of anhydrous magnesium bromide in ether was added. Then 21.2 g. (0.0444 mole) of triphenyltin iodide was added, and the mixture was stirred for 15 minutes before it was hydrolyzed with ice-water. After the ether layer was dried over sodium sulfate the solvent was removed. The red residue which resulted was boiled with ethanol and then recrystallized from chloroform-methanol yielding a red solid melting between 185° and 200°.

Attempts to purify this material invariably led to the formation of a considerable amount of red tar. A portion of this impure red solid was dissolved in ether and precipitated as the hydrochloride with dry hydrogen chloride gas. The hydrochloride was quickly filtered and the free amine was regenerated with dilute ammonium hydroxide. The dark yellow material thus obtained melted at 167–169°. Purification of this material thru the hydrochloride was not very successful since less than 20% was recovered. Cleavage of the tin-carbon linkage by hydrogen chloride undoubtedly occurred to a large extent during the time required to precipitate the hydrochloride. The values for the tin content of the material melting at 167–169° were too high for triphenyl-*p*-aminophenyltin to be conclusive.

Anal. Calc'd for $C_{24}H_{21}NSn$: Sn, 26.85. Found: Sn, 27.7 and 27.7.

Triphenyl-β-hydroxyethyltin. Triphenyltin-sodium was prepared by adding slowly 2.76 g. (0.12 gram-atom) of sodium to a stirred solution of 23.1 g. (0.06 mole) of triphenyltin

TABLE I

ORGANOTIN COMPOUNDS CONTAINING HYDROXYL GROUPS

NO.	ORGANOTIN COMPOUND	FORMULA	YIELD, %	M.P., °C.	ANALYSIS, Sn, %	
					Calc'd	Found
1	Triphenyl-*p*-hydroxyphenyltin	$(C_6H_5)_3Sn(p\text{-}C_6H_4OH)$	10	201–203[a]	26.81	27.2, 27.4
2	Di-*o*-hydroxyphenyldiphenyltin	$(C_6H_5)_2Sn(o\text{-}C_6H_4OH)_2$	68	136–138[a]	25.88	26.2, 26.35
3	Triethyl-*o*-hydroxyphenyltin[b]	$(C_2H_5)_3Sn(o\text{-}C_6H_4OH)$	54	155–156/15 mm.	39.74	39.85
4	Triphenyl-*o*-hydroxymethylphenyltin	$(C_6H_5)_3Sn(o\text{-}C_6H_4CH_2\text{-}OH)$	64	158–159	25.99	26.4, 26.4
5	Triphenyl-*p*-hydroxymethylphenyltin	$(C_6H_5)_3Sn(p\text{-}C_6H_4CH_2\text{-}OH)$	66	98–100	25.99	26.0, 26.2

[a] Melting points depend on rate of heating. Rates used: (1) 190–201°/10 min., (m.p. 210–211° by heating 190–210°/5 min.); (2) 120–136°/5 min. [b] Density, d_4^{25} 1.3150, refractive index n_D^{25} 1.5379.

TABLE II

PREPARATION DETAILS OF ORGANOTIN COMPOUNDS CONTAINING HYDROXYL GROUPS

NO.	ORGANIC HALIDE SOLN.			n-C_4H_9Li SOLN.		STIR. TIME (min.)	$MgBr_2$[a] (moles)	$(C_6H_5)_3SnCl$ (moles)	STIR. TIME (min.)	RECRYSTALLIZATION MEDIUM
	RX	(moles)	ETHER (cc.)	n-C_4H_9Li (moles)[b]	ETHER (cc.)					
1	p-BrC_6H_4OH	0.098	50	0.196	245	75	0.225[c]	0.054	120	Methanol; $CHCl_3$-pet. ether (77–117°)
2	o-BrC_6H_4OH[d]	.105	25	.21	250	50	.27[c]	.042[e]	90	Ether-pet. ether (28–380°)
3	o-BrC_6H_4OH	.0565	50	.113	290	45	.12	.0565[f]	[g]	Fractionally distilled
4	o-$BrC_6H_4CH_2OH$[d,h]	.0965	50	.193	240	60	.22	.0835[i]	60	Ethanol; $CHCl_3$-pet. ether (77–117°)
5	p-$BrC_6H_4CH_2OH$[d,j]	.107	50	.214	240	60	.225	.0856	60	Ethanol-H_2O; benzene-pet. ether (60–68°)

[a] Approximate concentration 1 mole $MgBr_2$/500 cc. ether. Stirred with n-C_4H_9Li approximately 15 min. [b] Determined by the analytical procedure of Gilman and Haubein (8). [c] The organotin compound could not be prepared when the $MgBr_2$ was omitted. [d] n-Butyllithium added to RX. [e] $(C_6H_5)_2SnCl_2$ used instead of $(C_6H_5)_3SnCl$. [f] $(C_2H_5)_3SnBr$ in 25 cc. of ether. [g] Permitted to stand overnight. [h] Prepared in a manner similar to that described for the preparation of *p*-bromobenzyl alcohol by Gilman and Melstrom (3). [i] Enough added to give a negative color test. [j] Prepared as described by Gilman and Melstrom (3).

chloride in 300 cc. of liquid ammonia. The ammonia was then permitted to evaporate until approximately 50 cc. remained. Ether (200 cc.) was added and the remaining ammonia was removed in a vacuum (100 mm.). After this treatment, a yellow amorphous precipitate of triphenyltin-sodium had formed. Then an excess of ethylene oxide (approximately 15 g.) in ether was added to the triphenyltin-sodium which was cooled in an ice-bath. After one hour of stirring, the mixture was hydrolyzed with ice-water and then the ether layer was dried over sodium sulfate. Removal of the ether followed by crystallization of the product from petroleum ether (b.p. 77–117°) gave 19.4 g. of crude β-hydroxyethyltriphenyltin melting at 67–69° (with turbidity). A second crystallization from the same solvent did not change the melting point. From methanol, however, after removal of a small amount of insoluble material from the hot solution by filtration, there was obtained 13.8 g. or a 59% yield of β-hydroxyethyltriphenyltin melting at 65–68° without turbidity. A second recrystallization of a small portion of this material from methanol decreased the melting point range to 67–68°. The chief impurity was probably hexaphenylditin (m.p. 237°).

The analysis was made on the material melting at 67–68°.

Anal. Calc'd for $C_{20}H_{20}OSn$: Sn, 30.05. Found: Sn, 30.35, 30.8.

Triphenyl-o-dimethylaminophenyltin. To a solution of *o*-dimethylaminophenylmagnesium bromide, prepared from 14.0 g. (0.07 mole) of *o*-bromodimethylaniline and 1.8 g. (0.074 gram-atom) of magnesium in 200 cc. of ether, was added 19.9 g. (0.042 mole) of triphenyltin iodide. After the solution had been stirred for 45 minutes, it was hydrolyzed with a cold ammonium chloride solution and the ether layer was dried over sodium sulfate. The ether was removed and to the resulting viscous liquid was added 50 cc. of boiling methanol. The crystals obtained by cooling the methanol solution were recrystallized twice from methanol, by first effecting solution with the minimum amount of chloroform. There was obtained 12.6 g. or a 64% yield, based on the triphenyltin iodide, of triphenyl-*o*-dimethylaminophenyltin melting at 110–112°.

Anal. Calc'd for $C_{26}H_{25}NSn$: Sn, 25.28. Found: Sn, 25.7.

Triphenyl-p-dimethylaminophenyltin. The *p*-dimethylaminophenyllithium used was prepared from 13.0 g. (0.065 mole) of *p*-bromodimethylaniline and 0.98 g. (0.14 gram-atom) of lithium in 250 cc. of ether. The solution was permitted to stand for two hours before the clear liquid was decanted carefully through glass wool. The solution of 0.058 mole of *p*-dimethylaminophenyllithium in 235 cc. of ether was added to 22.3 g. (0.058 mole) of triphenyltin chloride in 100 cc. of ether. The mixture was stirred for three hours and then permitted to stand overnight before it was hydrolyzed with a cold solution of ammonium chloride. The ether layer was dried over sodium sulfate and the solvent was removed. The resulting residue was dissolved in the minimum amount of chloroform and 200 cc. of hot ethanol was added. The solution was concentrated to approximately 200 cc., cooled, and the triphenyl-*p*-dimethylaminophenyltin which separated was removed. Yield, 17 g. (62%) of triphenyl-*p*-dimethylaminophenyltin; m.p. 132–134° after two recrystallizations from petroleum ether (b.p. 77–117°).

Anal. Calc'd for $C_{26}H_{25}NSn$: Sn, 25.28. Found: Sn, 25.7.

Oxidation of triphenyl-p-hydroxymethylphenyltin to triphenyl-p-carboxyphenyltin. Over a period of four hours, 7.37 g. (0.0467 mole) of solid potassium permanganate was added, in small amounts, to 16.0 g. (0.035 mole) of triphenyl-*p*-hydroxymethylphenyltin in 150 cc. of alcohol-free acetone. The mixture was allowed to stir one hour longer or until the potassium permanganate color disappeared, and the precipitate was removed and washed with 20 cc. of acetone. The precipitate, consisting of manganese dioxide and the potassium salt of triphenyl-*p*-carboxyphenyltin, was dried in a vacuum desiccator over calcium chloride and finally was extracted with three 75-cc. portions of boiling 95% ethanol. The ethanol extract was cooled and carefully acidified with dilute hydrochloric acid using Methyl Orange as an indicator. Then a few drops of base were added to render the solution just basic to Methyl Orange. The potassium chloride was separated and the ethanol solution was concentrated under reduced pressure to a volume of 100 cc. The warm solution was then carefully acidified to Methyl Orange and diluted slowly with water until a considerable amount of crystals had formed. The solution was cooled and 9.1 g. of crude triphenyl-*p*-carboxyphenyltin melting at 164–166° was removed. After one recrystallization from ethanol-water, there was obtained 7.2 g. or a 44% yield of pure triphenyl-*p*-carboxyphenyltin melting at 166–168°.

Anal. Calc'd for $C_{25}H_{20}O_2Sn$: Sn, 25.22; Neut. equiv., 471.
Found: Sn, 25.0, 25.25; Neut. equiv., 470, 472.

Oxidation of triphenyl-o-hydroxymethylphenyltin. To a solution of 16.0 g. (0.035 mole) of triphenyl-*o*-hydroxymethylphenyltin in 150 cc. of alcohol-free acetone was added 7.37 g. (0.0467 mole) of solid potassium permanganate in small portions over a period of five hours. Manganese dioxide was removed and the acetone was evaporated; to the resulting residue was added 30 cc. of 75% ethanol. From this solution, after cooling, there was removed 6.4 g. (40%) of unreacted triphenyl-*o*-hydroxymethylphenyltin. The mother liquor was then acidified (Methyl Orange) with hydrochloric acid and there was obtained 6.6 g. of material which did not melt below 340°. From the manganese dioxide after extraction with alcohol and acidification, there was obtained an additional 0.84 g. of material which did not melt below 340°. The combined portions of material which did not melt were dissolved in a large volume of warm dilute sodium hydroxide and filtered. The filtrate was acidified with acetic acid and the precipitate removed. It was heated with distilled water and then filtered. This material was insoluble in the common organic solvents and did not melt below 340°. No reaction with diazomethane could be detected when this material was suspended in an ether solution of diazomethane. The value for the tin content corresponded closest to that of the inner salt of diphenyl-*o*-carboxyphenyltin hydroxide. The yield of the crude product, assuming it was the inner salt of diphenyl-*o*-carboxyphenyltin hydroxide was 7.44 g. or 54%.

Anal. Calc'd for $C_{19}H_{14}O_2Sn$: Sn, 30.23. Found: Sn, 30.5 and 30.6.

The material which was assumed to be the inner salt of diphenyl-*o*-carboxyphenyltin hydroxide was suspended in ethanol and cold concentrated hydrochloric acid was added until a clear solution resulted after a few minutes. To this clear solution there was added enough 6 *N* hydrochloric acid to precipitate all of the organic material from the alcohol solution. The product, which was assumed to be diphenyl-*o*-carboxyphenyltin chloride, sintered at approximately 200° but did not melt below 340°.

In order to obtain a compound with a melting point this material was dissolved in ether and treated with diazomethane. The product so obtained melted at 168–169° after one crystallization from methanol and was assumed to be diphenyl-*o*-carbomethoxyphenyltin chloride.

Anal. Calc'd for $C_{20}H_{17}ClO_2Sn$: Sn, 26.78. Found: Sn, 27.0 and 27.1.

Triphenyl-4-dimethylamino-3-(4'-nitrophenylazo)phenyltin. A mixture of 7.05 g. (0.05 mole) of triphenyl-*p*-dimethylaminophenyltin in 150 cc. of ethyl acetate and 8.2 g. of sodium acetate in 100 cc. of water was cooled in an ice-bath. To this mixture there was added slowly with vigorous stirring a cold solution of *p*-nitrobenezenediazonium chloride, prepared from 2.07 g. (0.015 mole) of *p*-nitroaniline and 1.04 g. (0.015 mole) of sodium nitrite in 6 cc. of concentrated hydrochloric acid and 15 cc. of water. When the *p*-nitrobenzenediazonium chloride solution was all added the ice-bath was removed and the solution was stirred for two hours, during which a dark red solution was formed. The ethyl acetate was then permitted to evaporate and the amorphous red solid which was left was stirred with 100 cc. of distilled water and then filtered. The red solid was then boiled with 50 cc. of ethanol, cooled, and filtered. The treatment with ethanol was then repeated once more before the red solid was crystallized twice from chloroform-petroleum ether (b.p. 77–117°). After the recrystallizations from chloroform-petroleum ether, there was obtained 1.62 g. (17.5%) of dark yellow material containing tin and nitrogen and melting at 188–190°. The nitrogen content was found to be 10.0% as compared to 9.05% calculated for triphenyl-4-dimethylamino-3-(4'-nitrophenylazo)phenyltin. Since it apparently contained a small amount of azo compound from the cleavage of the organotin compound, another recrystallization was carried out by dissolving in chloroform and adding hot ethanol. From this recrystallization the *triphenyl-4-dimethylamino-3-(4′-nitrophenylazo)phenyltin* separated as a bright yellow solid melting at 190–192°.

Anal. Calc'd for $C_{32}H_{28}N_4O_2Sn$: Sn, 19.20. Found: Sn, 19.80.

Tetraphenyltin and chlorosulfonic acid. To a suspension of 10.65 g. (0.025 mole) of powdered tetraphenyltin in unsaturate-free petroleum ether (b.p. 28–38°) at −75° was added 5.84 g. (0.050 mole) of chlorosulfonic acid. The mixture was stirred for five minutes, and a thick gum was formed. Liquid ammonia, followed by concentrated ammonium hydroxide, was carefully added to the mixture before it was filtered. The filter cake was extracted and crystallized from chloroform; there was obtained 4.0 g. or a 38% recovery of pure tetraphenyltin. From the mother liquor used to crystallize the tetraphenyltin there was obtained 0.7 g. of diphenylsulfone (mixed m.p.) melting at 122–124°. From the neutralized ammonium hydroxide solution was obtained 1.9 g. of material which would not melt when heated. The physical properties of this material indicated that it was metastannic acid.

Phenylboric acid and stannic chloride. A solution containing 5.21 g. (0.02 mole) of stannic chloride and 12.8 g. (0.10 mole) of phenylboric acid in 30 cc. of water was refluxed for nine hours. During this time no precipitate nor oil separated, indicating that no organotin compound was formed. After the solution was cooled, the unreacted phenylboric acid was removed and recrystallized from water. There was recovered 8.8 g. or 69% of pure phenylboric acid melting at 218–220°. A strong odor of benzene was detected in the reaction mixture, probably from the decomposition of the phenylboric acid by prolonged heating with water.

Tetraphenyltin and alcoholic sodium hydroxide. A mixture of 10 g. of tetraphenyltin and 40 g. of sodium hydroxide in 200 cc. of 95% ethanol was refluxed for three hours. After the mixture was cooled 300 cc. of distilled water was added and the solution was filtered. After one crystallization from chloroform 9.5 g. or 95% of the tetraphenyltin was recovered.

Triphenyl-o-hydroxyphenyltin and alcoholic sodium hydroxide. This reaction was carried out in exactly the same manner as previously described with tetraphenyltin. A strong odor of benzene was noted in the reaction mixture. Since no precipitate formed when it was poured into water, no unreacted triphenyl-*o*-hydroxyphenyltin (insoluble in base), triphenyltin hydroxide, or diphenyltin oxide could be present. Carbon dioxide was then passed into the solution and some amorphous precipitate, which would not melt, separated. The precipitate contained tin but charred only slightly on ignition indicating that it probably consisted of metastannic acid or phenylstannonic acid or a mixture of both.

SUMMARY

The usefulness of halogen-metal interconversion products for the preparation of organotin compounds containing functional groups has been demonstrated in the preparation of triethyl-*o*-hydroxyphenyltin, triphenyl-*o*-hydroxyphenyltin, triphenyl-*p*-hydroxyphenyltin, di-*o*-hydroxyphenyldiphenyltin, triphenyl-*o*-hydroxymethylphenyltin, and triphenyl-*p*-hydroxymethylphenyltin. The desirability of converting these organolithium halogen-metal interconversion products into the Grignard reagents prior to reaction with the organotin compounds was also demonstrated.

The preparation of triphenyl-*p*-aminophenyltin has been attempted but the identity of the small amount of relatively pure product which was isolated could not be established.

Triphenyl-β-hydroxyethyltin has been prepared.

Triphenyl-*o*-dimethylaminophenyltin and triphenyl-*p*-dimethylaminophenyltin have been prepared.

Triphenyl-*p*-carboxyphenyltin has been prepared by the oxidation of triphenyl-*p*-hydroxymethylphenyltin with potassium permanganate.

Oxidation of triphenyl-*o*-hydroxymethylphenyltin by potassium permanganate gives a product which is probably the inner salt of diphenyl-*o*-carboxyphenyltin hydroxide. From this product, two derivatives have been prepared which are probably diphenyl-*o*-carboxyphenyltin chloride and diphenyl-*o*-carbomethoxyphenyltin chloride.

Triphenyl-4-dimethylamino-3-(4′-nitrophenylazo)phenyltin has been prepared from triphenyl-*p*-dimethylaminophenyltin and *p*-nitrobenzenediazonium chloride.

Attempts to introduce the sulfonyl chloride group directly into tetraphenyltin gave cleavage products even at −75°.

There is no apparent reaction between phenylboric acid and stannic chloride in a hot aqueous solution.

Tetraphenyltin is not affected by prolonged heating with alcoholic sodium hydroxide whereas triphenyl-*o*-hydroxyphenyltin is cleaved under the same conditions.

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