[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

SOME ARYLTIN-LITHIUM COMPLEXES

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In an earlier report from this laboratory the formation of the complex, triphenyltin-lithium (from stannous chloride), and some of its reactions were described (1). A more extensive investigation into the nature of this and similar aryltin-lithium complexes has been made, and the findings are herein reported.

The preparation of triphenyltin-lithium is a two-step process, the first step being displacement of the chlorine atoms bonded to the tin atom as chloride ions by the phenyl anion of phenyllithium to form diphenyltin. The second step involves addition of a phenyl anion to the open octet of the tin atom in diphenyltin to form the complex, triphenyltin-lithium. The attraction of the

$$\ddot{Sn}Cl_2 + 2\,\overset{-}{C_6H_5}\overset{+}{Li} \rightarrow (C_6H_5)_2\ddot{Sn} + 2\,\overset{+}{Li}\overset{-}{Cl}$$

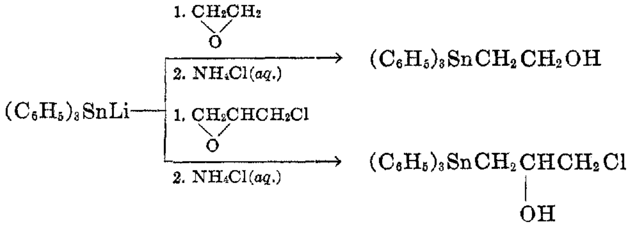
$$(C_6H_5)_2\ddot{Sn} + \overset{-}{C_6H_5}\overset{+}{Li} \rightarrow [(C_6H_5)_2\ddot{Sn}\leftarrow\overset{-}{C_6H_5}]\overset{+}{Li}$$

phenyl anion for the diphenyltin must be strong as the complex does not appear to be involved in an equilibrium system with its component parts as evidenced by reactions with gaseous carbon dioxide, benzophenone, and benzalacetophenone. If the complex did dissociate into its component parts, it would be expected that the phenyllithium would react with these compounds to form benzoic acid, triphenylcarbinol, and diphenyl-β-styrylcarbinol, respectively. In each reaction the only compound formed was tetraphenyltin, and in the last two reactions, good recoveries of the ketones were made.

In continuing the study of this complex toward unsaturated linkages, triphenyltin-lithium was treated with *trans*-stilbene. Once again there was no apparent reaction and a 96% recovery of the hydrocarbon was made. This result is in sharp contrast with that obtained in the treatment of triphenylsilyl-potassium with *trans*-stilbene. These compounds form β-triphenylsilyl-α,β-diphenyl ethylpotassium which on hydrolysis yields triphenyl-α,β-diphenylethylsilane (2).

$$(C_6H_5)_3SiK + C_6H_5CH{=}CHC_6H_5 \rightarrow (C_6H_5)_3SiCH(C_6H_5)CH(C_6H_5)K \xrightarrow{H_2O} (C_6H_5)_3SiCH(C_6H_5)CH_2(C_6H_5)$$

Triphenyltin-lithium does possess sufficient reactivity to successfully attack the oxirane ring as evidenced by the preparation of triphenyl-2-hydroxyethyltin



$$(C_6H_5)_3SnLi \xrightarrow[\text{2. }NH_4Cl(aq.)]{\text{1. }CH_2CH_2O} (C_6H_5)_3SnCH_2CH_2OH$$

$$(C_6H_5)_3SnLi \xrightarrow[\text{2. }NH_4Cl(aq.)]{\text{1. }CH_2CHCH_2Cl\text{ (O)}} (C_6H_5)_3SnCH_2\underset{OH}{\underset{|}{C}}HCH_2Cl$$

(45 %) and triphenyl-2-hydroxy-3-chloropropyltin (27 %) by reaction of ethylene oxide and epichlorohydrin, respectively, with the complex. Triphenyl-2-hydroxyethyltin (59 %) had been previously prepared by the reaction of triphenyltin-sodium with ethylene oxide in liquid ammonia (3).

Triphenyltin-lithium reacts promptly with iodine to form triphenyltin iodide but the reaction is complicated by a rapid attack on the iodide, as formed, by excess triphenyltin-lithium, resulting in the formation of hexaphenylditin (4).

$$(C_6H_5)_3SnLi + I_2 \rightarrow (C_6H_5)_3SnI + LiI$$
$$(C_6H_5)_3SnLi + (C_6H_5)_3SnI \rightarrow (C_6H_5)_6Sn_2 + LiI$$

Triphenyltin iodide (57 %) is successfully prepared by refluxing a reaction mixture in which an ether-xylene solution is used as solvent for 4 hours. It is thought that the organotin halide is formed by cleavage of the hexaphenylditin, formed in the early stages of the reaction, by unreacted iodine.

$$(C_6H_5)_6Sn_2 + I_2 \rightarrow 2\ (C_6H_5)_3SnI$$

Tetraphenyltin (82 %) has been prepared by reaction of triphenyltin-lithium and bromobenzene (4) and the success of this reaction suggested that other symmetrical organotin compounds could be prepared through the use of similar complexes. The preparation of symmetrical organotin compounds using these complexes as intermediates may have an advantage in some cases over the usual laboratory method, which employs stannic chloride and an organolithium compound or a Grignard reagent, in that the stannous chloride is more easily handled than is stannic chloride. Three other complexes, tri-*p*-tolyltin-lithium, tri-*m*-tolyltin-lithium, and tri-*o*-tolyltin-lithium, were prepared. The reaction of the first two complexes with appropriate tolyl halides led to the preparation of tetra-*p*-tolyltin (74 %) and tetra-*m*-tolyltin (80 %), but the treatment of tri-*o*-tolyltin-lithium with *o*-iodotoluene yielded hexa-*o*-tolylditin (45 %) instead of the desired tetra-*o*-tolyltin. Reaction of this latter complex with benzyl chloride gave tri-*o*-tolylbenzyltin (2 %), hexa-*o*-tolylditin (38 %), and tetra-*o*-tolyltin (7 %). From the results of these reactions it is thought that the steric hindrance presented by the three *o*-tolyl groups probably prevents a successful attack on the halide from taking place.

The hexa-*o*-tolylditin isolated in these latter reactions melted at 298–300°. It has been reported that hexa-*o*-tolylditin was prepared by reduction of tri-*o*-tolyltin bromide in benzene with sodium metal and ethanol (5). This product melted at 208–210°. In order to clear up this apparent discrepancy another sample of hexa-*o*-tolylditin was prepared by reacting tri-*o*-tolyltin chloride with sodium shot in refluxing xylene. The compound thereby obtained melted at 298–300°, showed no depression in a mixture melting point with a sample of the solid isolated from the tri-*o*-tolyltin-lithium reactions, and had the same infrared spectrum as this latter sample.

The structure of hexa-*o*-tolylditin suggested that the compound might possibly dissociate to some extent in benzene to form tri-*o*-tolyltin. Therefore, a benzene solution of this ditin compound was treated with oxygen but apparently no reaction took place as evidenced by a 93 % recovery of starting material.

EXPERIMENTAL

Hydrolysis of triphenyltin-lithium. Triphenyltin-lithium (1) was prepared by the addition of 0.135 mole (3 equivalents) of phenyllithium in 123 ml. of ether to 8.54 g. (0.045 mole) of anhydrous stannous chloride suspended in 100 ml. of ether at −10°. The reaction mixture was then hydrolyzed by pouring it into 400 ml. of a saturated ammonium chloride solution with vigorous stirring. The suspended solid was filtered off and air-dried, the layers were separated, and the ether layer was dried over sodium sulfate.

The solid recovered on hydrolysis was crystallized from petroleum ether (b.p. 77–120°) to yield 2.1 g. (14.6%) of tetraphenyltin[1, 2] melting at 222–225°. The ether layer was filtered from the sodium sulfate and distilled from a water-bath to yield a yellow solid. This solid was crystallized from petroleum ether (b.p. 77–120°) to yield 2.1 g. (10.9%) of hexaphenylditin melting at 226–228°. In a similar reaction the isolation of hexaphenylditin in a 61% yield was reported (1).

This procedure outlines the general method used in the work-up of the following reaction mixtures.

Carbonation with gaseous carbon dioxide. Dry carbon dioxide gas was passed over the surface of a suspension containing 0.045 mole of triphenyltin-lithium in 262 ml. of ether at −10°. After 4 hours the reaction mixture was hydrolyzed as above.

The solid recovered on hydrolysis was extracted with benzene and filtered hot. On cooling, 3.4 g. (23.6%) of tetraphenyltin melting at 222–225° was obtained. The ether layer was extracted with three 15-ml. portions of 15% potassium hydroxide solution, and then dried over sodium sulfate. All aqueous layers were combined but acidification yielded no benzoic acid. The solid obtained on distillation of the ether was crystallized from petroleum ether (b.p. 77–120°) to yield 2.5 g. (15.9%) of hexaphenylditin melting at 227–230°.

Reaction with benzophenone. To 0.11 mole of triphenyltin-lithium 20.0 g. (0.11 mole) of benzophenone was added in one portion. The reaction mixture was stirred for 2 hours at −10° and hydrolyzed. The solid recovered on hydrolysis was extracted with petroleum ether (b.p. 77–120°) and filtered hot. On cooling, 3.5 g. (9.5%) of tetraphenyltin melting at 223–225° was obtained. Work-up of the ether layer led to the isolation of 12.6 g. (60.0% recovery) of benzophenone (b.p. 124%/0.8 mm., m.p. 46°) and 5.7 g. (14.8%) of hexaphenylditin melting at 226–229°.

During the course of the work-up of the reaction mixture, particular attention was paid to the possible isolation of triphenylcarbinol but no trace of this compound was found.

Reaction with benzalacetophenone. To 0.045 mole of triphenyltin-lithium 9.5 g. (0.045 mole) of benzalacetophenone was added in one portion. The reaction mixture was stirred at reflux for 24 hours and hydrolyzed.

The solid recovered on hydrolysis was extracted with petroleum ether (b.p. 77–120°) and filtered hot. On cooling, 1.5 g. (7.8%) of tetraphenyltin melting at 224–225° was obtained. Work-up of the ether layer led to the isolation of a brown gum weighing 10.0 g. Various attempts to crystallize this gum were unsuccessful. In order to determine the nature of the gum a sample of it was reacted with phenylhydrazine to form a phenylhydrazone melting at 116–119° (the phenylhydrazone of benzalacetophenone melts at 120°). A second sample was reacted with 2,4-dinitrophenylhydrazine to form a 2,4-dinitrophenylhydrazone melting at 243–245° (the 2,4-dinitrophenylhydrazone of benzalacetophenone melts at 245°). Although these results did not conclusively eliminate the presence of a small amount of diphenyl-β-styrylcarbinol, it was concluded that the gum was principally unreacted benzalacetophenone.

Preparation of triphenyl-2-hydroxyethyltin. To 0.045 mole of triphenyltin-lithium 15.0 g.

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[1] Unless stated otherwise, the compounds reported herein were identified by the method of mixture melting points. All melting points are uncorrected.

[2] Each of the organotin compounds mentioned herein gave a positive qualitative test for tin as reported recently in this Journal (6).

of ethylene oxide in 20 ml. of ether was added. The color of the reaction mixture changed from tan to light yellow almost immediately. The reaction mixture was stirred for 1 hour, with the cooling bath in place, and hydrolyzed.

The solid recovered on hydrolysis was extracted with petroleum ether (b.p. 77–120°), treated with Norit-A, and filtered hot. On cooling, 1.0 g. (5.2%) of tetraphenyltin melting at 223–225° was obtained. The ether layer yielded an oil which was extracted with 100 ml. of methanol, and filtered hot. On cooling, a trace of solid came out of solution. The methanol solution was decanted and the residue set aside. The methanol was removed by distillation from a water-bath, and the residue was dissolved in the minimum amount of refluxing petroleum ether (b.p. 77–120°). On cooling, 8.3 g. (44.8%) of triphenyl-2-hydroxyethyltin (3) melting at 66–67° was obtained.

Preparation of triphenyl-2-hydroxy-3-chloropropyltin. To 0.045 mole of triphenyltin-lithium, 12.3 g. of epichlorohydrin was added in one portion. The color of the reaction mixture changed from tan to gray almost immediately. The mixture was then stirred for 1 hour, with the cooling bath in place, and hydrolyzed.

The solid recovered on hydrolysis was extracted with petroleum ether (b.p. 77–120°), treated with Norit-A, and filtered hot. On cooling, 1.9 g. (9.9%) of tetraphenyltin melting at 224–226° was obtained. The ether layer yielded an oil which was extracted with 100 ml. of methanol, and filtered hot. On cooling, a trace of solid came out of solution. The methanol solution was decanted and the residue was set aside. The methanol was removed by distillation from a water-bath, and crystals were obtained from the residual oil by vigorous mixing with 25 ml. of petroleum ether (b.p. 60–70°). The yield of crude product melting at 94–97° was 8.7 g. (43.5%). This material was extracted with 50 ml. of petroleum ether (b.p. 77–120°), and filtered hot. On cooling, 5.4 g. (27.0%) of triphenyl-2-hydroxy-3-chloropropyltin melting at 97–99° was obtained.

Anal. (7) Calc'd for $C_{21}H_{21}ClOSn$: Sn, 26.76. Found: Sn, 26.77.

Reaction with trans-stilbene. To 0.045 mole of triphenyltin-lithium, 8.1 g. (0.045 mole) of *trans*-stilbene in 200 ml. of ether was added. No apparent change took place and Color Test I (8) remained negative throughout the course of the reaction. The mixture was stirred for 72 hours, and carbonated by pouring it on to a Dry Ice-ether slurry.

On warming to room temperature the ether mixture was extracted with 100 ml. of water. The layers were separated, and the ether layer was dried over sodium sulfate. Acidification of the aqueous layer yielded a clear solution. No acid was recovered. The ether layer yielded a white solid which was extracted with 200 ml. of methanol, and filtered hot. On cooling, 7.8 g. (96.4% recovery) of *trans*-stilbene melting at 121–124° was obtained.

Reaction with iodine. To 0.045 mole of triphenyltin-lithium, 11.4 g. (0.045 mole) of iodine in 100 ml. of ether was added dropwise. At first the iodine color was discharged as the solution was added but near the end of the addition the iodine color became permanent and was not completely discharged. Ten minutes after the iodine addition was completed, the reaction mixture was hydrolyzed by pouring it into an aqueous solution of sodium thiosulfate. The iodine color was thereby discharged.

The solid recovered on hydrolysis was extracted with petroleum ether (b.p. 77–120°), and filtered hot. On cooling, 9.0 g. of solid melting over the range 190–195° was obtained. The ether layer yielded a solid which was extracted with 150 ml. of petroleum ether (b.p. 77–120°). On cooling, 1.0 g. of solid melting over the range 190–200° was obtained. The two solids were combined but further attempts to purify the mixture by recrystallization were unsuccessful. Infrared analysis showed the solid to be a mixture of tetraphenyltin and hexaphenylditin. No trace of triphenyltin iodide was found.

Run 2. In this run 11.4 g. (0.045 mole) of iodine in 150 ml. of xylene was added to 0.045 mole of triphenyltin-lithium in 200 ml. of ether, and the reaction mixture was refluxed for 4 hours. The iodine color was not completely discharged. The reaction mixture was hydrolyzed as in Run 1.

The ether-xylene solution was concentrated to about 75 ml. by distillation and cooled to 60°. Then 20 ml. of methanol was added to the concentrated solution which was then placed in a refrigerator for 3 hours. On cooling, some solid came out of solution. This was filtered off and was recrystallized from petroleum ether (b.p. 77–120°) to yield 1.4 g. (7.3%) of tetraphenyltin melting at 223–225°. The mother liquor was evaporated to dryness by pulling a stream of air over the surface of the solution, and the solid residue was recrystallized from 200 ml. of petroleum ether (b.p. 77–120°) to yield 10.0 g. of triphenyltin iodide melting at 118–119°. Concentration of the petroleum ether mother liquor led to the recovery of an additional 2.0 g. of product melting at 117–119°. The total yield of triphenyltin iodide was 12.0 g. (56.7%).

Preparation of tri-p-tolyltin-lithium. Over a period of 1.5 hours, 0.135 mole of *p*-tolyllithium in 141 ml. of ether was added dropwise to 8.54 g. (0.045 mole) of finely ground anhydrous stannous chloride suspended in 100 ml. of ether. During the addition the mixture was cooled in an ice-salt bath whose temperature was maintained near −10°, and all operations were carried out under nitrogen.

The phenomena which occurred during the addition of the *p*-tolyllithium solution were as follows: the first few drops produced a yellow color. The color gradually increased in intensity and was bright yellow at 0.5 equivalent of *p*-tolyllithium, deep yellow at 1.0 equivalent, very deep red at 2.0 equivalents, and olive drab at 3.0 equivalents. Color Test I remained negative until the 3.0 equivalents' point had been reached.

Preparation of tetra-p-tolyltin. To 0.045 mole of tri-*p*-tolyltin-lithium 10.8 g. (0.045 mole plus 10%) of *p*-iodotoluene in 50 ml. of ether was added. The mixture was refluxed for 1.5 hours and was hydrolyzed.

The solid recovered on hydrolysis was extracted with benzene. On cooling, 11.1 g. of tetra-*p*-tolyltin melting at 233–235° was obtained. Concentration of the benzene mother liquor led to the recovery of 4.3 g. of product melting at 232–234°. An additional 1.0 g. of product melting at 232–234° was obtained from the ether layer. The total yield of tetra-*p*-tolyltin was 16.4 g. (74.2%).

Preparation of tri-m-tolyltin-lithium. As outlined above tri-*m*-tolyltin-lithium was prepared by the dropwise addition of 0.135 mole of *m*-tolyllithium in 141 ml. of ether to 8.54 g. (0.045 mole) of stannous chloride in 100 ml. of ether.

The following color changes occurred during the addition of the *m*-tolyllithium solution: the first few drops produced a yellow color. The color gradually increased in intensity and was bright yellow at 1.5 equivalents, deep red at 2.0 equivalents, red at 2.5 equivalents, and red-brown at 3.0 equivalents. Color Test I remained negative until the 3.0 equivalents' point had been reached.

Preparation of tetra-m-tolyltin. To 0.045 mole of tri-*m*-tolyltin-lithium 7.8 g. (0.045 mole) of *m*-bromotoluene in 20 ml. of ether was added. The mixture was refluxed for 24 hours and was hydrolyzed. The solid recovered on hydrolysis was crystallized from 100 ml. of methanol plus 40 ml. of benzene to yield 15.5 g. of tetra-*m*-tolyltin melting at 122–123°. Concentration of the methanol-benzene mother liquor led to the recovery of 1.9 g. of product melting at 122–123°. The total yield of tetra-*m*-tolyltin was 17.4 g. (80.2%).

Preparation of tri-o-tolyltin-lithium. As above tri-*o*-tolyltin-lithium was prepared by the dropwise addition of 0.135 mole of *o*-tolyllithium in 150 ml. of ether to 8.54 g. (0.045 mole) of stannous chloride in 100 ml. of ether.

Addition of the *o*-tolyllithium solution produced the following color changes: the first few drops gave a yellow color. The color gradually increased in intensity and was bright yellow at 0.5 equivalent, orange at 1.0 equivalent, deep red-brown at 2.0 equivalents, deep red-brown at 2.5 equivalents, and deep brown at 3.0 equivalents. Color Test I remained negative until the 3.0 equivalents' point had been reached.

Preparation of tetra-o-tolyltin. To 0.045 mole of tri-*o*-tolyltin-lithium, 10.8 g. (0.045 mole plus 10%) of *o*-iodotoluene was added. The color of the reaction mixture changed from deep brown to light tan in about 5 minutes after addition of the halide. The mixture was refluxed for 6 hours, stirred overnight, and hydrolyzed.

The solid recovered on hydrolysis was extracted with 40 ml. of benzene, and filtered hot. The solid which did not go into solution weighed 7.4 g. and melted at 297–300°. On cooling, an additional 0.4 g. of solid melting at 298–300° was obtained from the benzene solution.

It was suspected that this high-melting solid was hexa-*o*-tolylditin (4) and a sample was analyzed.

Anal. (7). Calc'd for $C_{42}H_{42}Sn_2$: Sn, 30.27. Found: Sn, 30.01.

The ether layer yielded a viscous yellow oil which partially solidified on standing in a refrigerator for 24 hours. The supernatant oil was decanted, and the solid was crystallized from 80 ml. of 50% benzene-methanol solution. On cooling, 0.9 g. (4.2%) of tetra-*o*-tolyltin melting at 211–213° was obtained. The total yield of hexa-*o*-tolylditin was 7.8 g. (44.6%).

Preparation of hexa-o-tolylditin. In a 125-ml. flask were placed 4.0 g. (0.0094 mole) of tri-*o*-tolyltin chloride, 3.0 g. of sodium shot, 10 ml. of benzene, and 30 ml. of xylene. The reaction mixture was refluxed for 1 hour, and filtered hot. The solvent was removed by passing a stream of air over the surface of the solution. The solid residue was crystallized twice from the minimum amount of benzene to yield 2.3 g. (62.1%) of hexa-*o*-tolylditin melting at 298–300°. A mixture melting point between a sample of this material and that isolated in the previous reaction showed no depression.

Reaction of hexa-o-tolylditin with oxygen. In a 250-ml. flask was placed 3.0 g. (0.0038 mole) of hexa-*o*-tolylditin in 200 ml. of benzene and oxygen was bubbled through the solution for 24 hours. During the last 2 hours the solution was refluxed. The benzene was then removed by distillation, and the solid residue was crystallized from the minimum amount of benzene to yield 2.8 g. (93.4% recovery) of hexa-*o*-tolylditin melting at 298–300°.

Preparation of tri-o-tolylbenzyltin. To 0.045 mole of tri-*o*-tolyltin-lithium, 5.9 g. (0.045 mole plus 10%) of benzyl chloride was added. The mixture was brought to reflux and a gradual change in color from deep brown to yellow took place. The mixture was refluxed for 5 hours, stirred overnight, and hydrolyzed.

The solid recovered on hydrolysis was extracted with 500 ml. of benzene. The benzene solution was then concentrated by distillation to about 250 ml. On cooling, 6.5 g. (37.6%) of hexa-*o*-tolylditin melting at 298–300° was obtained. The ether layer yielded a viscous yellow oil. To this oil was added 20 ml. of methanol, and the mixture was placed in a refrigerator overnight. A small amount of solid came out of the mixture. It was filtered off and crystallized from a methanol-benzene solution to yield 0.7 g. of tetra-*o*-tolyltin melting at 214–215°.

The original methanol mother liquor was then concentrated on a steam plate until all solvent was removed, and the oily residue was dissolved in 100 ml. of petroleum ether (b.p. 77–120°). This petroleum ether solution was then chromatographed using Merck and Company adsorption alumina. Petroleum ether (b.p. 60–70°) was used as the elution solvent and the eluate was taken off in fifteen 200-ml. fractions. Fractions 3–8 yielded an additional 0.8 g. of tetra-*o*-tolyltin melting at 213–215°. The total yield of tetra-*o*-tolyltin was 1.5 g. (6.9%). Fractions 11–13 yielded an oil from which crystals were obtained by treatment with a methanol-benzene solution. A total of 0.5 g. (2.3%) of tri-*o*-tolylbenzyltin melting at 105–107° was obtained.

An authentic sample of the desired unsymmetrical organotin compound was prepared as follows: in a 100-ml. flask was placed 5.0 g. (0.012 mole) of tri-*o*-tolyltin chloride in 25 ml. of ether. To this was added, dropwise and with good stirring, 0.015 mole of benzylmagnesium chloride in 25 ml. of ether. The reaction mixture was refluxed for 1 hour and hydrolyzed.

The ether layer yielded an oily solid which was crystallized twice from methanol to yield 3.4 g. (58.6%) of tri-*o*-tolylbenzyltin melting at 108–109°.

Anal. (7) Calc'd for $C_{28}H_{28}Sn$: Sn, 24.73. Found: Sn, 24.96.

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SUMMARY

The complex, triphenyltin-lithium, is not part of an equilibrium system under the conditions used to carry out the reactions herein reported. This complex does not possess sufficient activity to add to the carbon-carbon double bond of *trans*-

stilbene or to the carbon-oxygen double bond of carbon dioxide, benzophenone, or benzalacetophenone, but it does successfully attack the oxirane ring. Complexes other than triphenyltin-lithium may be obtained by substituting other organolithium compounds for phenyllithium, and the preparation of some symmetrical organotin compounds using these complexes as intermediates is described. Treatment of tri-*o*-tolyltin-lithium with *o*-iodotoluene led to the formation of hexa-*o*-tolylditin and only a trace of tetra-*o*-tolyltin. The hexa-*o*-tolylditin made in this manner appears to be unlike the compound previously reported. No reaction took place between this ditin compound and oxygen.

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REFERENCES

(1) GILMAN AND ROSENBERG, *J. Am. Chem. Soc.*, **74**, 531 (1952). See also WITTIG, MEYER, AND LANGE, *Ann.*, **571**, 167 (1951); WITTIG, *Angew. Chem.*, **62**, 231 (1950).
(2) GILMAN AND WU, *J. Am. Chem. Soc.*, **75**, 234 (1953).
(3) GILMAN AND ARNTZEN, *J. Org. Chem.*, **15**, 994 (1950).
(4) GILMAN AND ROSENBERG, *J. Org. Chem.*, **18**, 680 (1953).
(5) MORRIS, BYERLY, AND SELWOOD, *J. Am. Chem. Soc.*, **64**, 1727 (1942).
(6) GILMAN AND GOREAU, *J. Org. Chem.*, **17**, 1470 (1952).
(7) GILMAN AND ROSENBERG, *J. Am. Chem. Soc.*, **75**, 3592 (1953).
(8) GILMAN AND SCHULZE, *J. Am. Chem. Soc.*, **47**, 2002 (1925).