[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF IOWA STATE COLLEGE]

REACTION OF TRIPHENYLTIN-LITHIUM WITH ORGANIC HALIDES

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Received November 24, 1952

The preparation of triphenyltin-lithium from stannous chloride and phenyllithium has been described (1), and this article reports the findings of more extensive investigation into the chemical nature of the organometallic complex. Triphenyltin-lithium is thought to be a complex formed by the addition of phenyllithium to diphenyltin (2). The central tin atom in diphenyltin has an open octet which is readily filled by the phenyl anion of phenyllithium.

$$(C_6H_5)_2\overset{\bullet\bullet}{Sn} + \overset{\ominus}{C_6H_5}\!:\ \overset{\oplus}{Li} \rightarrow [(C_6H_5)_2\overset{\bullet\bullet}{Sn} \leftarrow C_6H_5]^{\ominus}\ \overset{\oplus}{Li}$$

In order to investigate the stability of the complex, triphenyltin-lithium has been treated with gaseous carbon dioxide, Dry Ice, benzophenone, and benzalacetophenone. In each case the only compound formed was tetraphenyltin (*ca.* 10%). From many preparations it is known that some tetraphenyltin is obtained in all reactions in which triphenyltin-lithium takes part. In the last two reactions high recoveries of the ketones were made. These results coupled with the fact that triphenyltin-lithium does not give a positive Color Test I (1, 4) has led to the conclusion that triphenyltin-lithium is a stable complex which does not dissociate into its component parts, diphenyltin and phenyllithium, under the conditions used in carrying out the reactions reported here.

Triphenyltin-lithium has been reacted with a series of organic halides to form unsymmetrical compounds of the type $(C_6H_5)_3SnR$. Aryl chlorides, such as chlorobenzene, apparently do not react readily with the complex but under corresponding conditions aryl bromides and iodides react promptly. More active organic chlorides, such as benzyl chloride, do react with triphenyltin-lithium to form the desired unsymmetrical organotin compounds (1).

$$(C_6H_5)_3SnLi + RX \rightarrow (C_6H_5)_3SnR + LiX$$

Hexaphenylditin (52.8%) and triphenylsilyltriphenyltin (71.3%) have been prepared by reacting triphenyltin chloride and triphenylchlorosilane, respectively, with the complex (1).

When *o*-substituted aryl iodides were reacted with triphenyltin-lithium a secondary reaction, along with that of formation of the unsymmetrical compound (R_3SnR') took place. It was thought that a halogen-metal interconversion reaction (3) occurred between the substituted iodobenzene and the complex. This reaction was explored further, and the results and conclusions are reported below.

$$(C_6H_5)_3SnLi + o\text{-}IC_6H_4R \rightarrow (C_6H_5)_3SnI + o\text{-}LiC_6H_4R$$

In order to obtain authentic specimens of the unsymmetrical organotin compounds prepared for the first time, triphenyltin chloride was reacted with appropriate organolithium compounds or Grignard reagents. The preparation of these compounds by this latter method results in higher yields as the by-product, tetraphenyltin, which accompanies all preparations involving triphenyltin-lithium, is not formed, thereby allowing more direct and efficient purification of the desired compounds.

$$(C_6H_5)_3SnCl + RLi \text{ or } RMgX \rightarrow (C_6H_5)_3SnR + LiCl \text{ or } MgXCl$$

EXPERIMENTAL

Preparation of triphenyl-2,6-dimethylphenyltin. Triphenyltin-lithium (1) was prepared by dropwise addition of 0.135 mole of phenyllithium in 157 ml. of ether to 8.54 g. (0.045 mole) of finely ground anhydrous stannous chloride suspended in 100 ml. of ether at −10° by vigorous stirring. Color Test I (4) was negative after the addition of the phenyllithium solution was completed. Then 10.5 g. (0.045 mole) of 2,6-dimethyliodobenzene in 40 ml. of ether was added. No apparent change took place, but a Color Test I made one minute after the addition of the halide solution was very strongly positive. The ice-bath was removed and the mixture brought to reflux. Color Test I remained positive for 90 minutes after refluxing started. The reaction mixture was refluxed for a total of 18 hours, and hydrolyzed by pouring it into 400 ml. of saturated ammonium chloride solution, with good stirring. The solid which came out of solution on hydrolysis was filtered off and air-dried, the layers were separated, and the ether layer was dried over sodium sulfate.

The solid (3.4 g.) recovered on hydrolysis was extracted with 300 ml. of petroleum ether (b.p. 77–120°), and filtered hot. On cooling, 2.4 g. (12.5%) of tetraphenyltin melting at 227–228° was obtained. The ether solution was filtered from the sodium sulfate, and concentrated to dryness by distillation on a water-bath. The solid residue was recrystallized three times from the minimum amount of ethanol to yield 7.0 g. (34.1%) of triphenyl-2,6-dimethylphenyltin melting at 116–119°. Both products were identified by mixture melting points with authentic specimens.

This procedure was used to prepare the compounds listed in Table I with modifications as noted.

Carbonation of triphenyltin-lithium with Dry Ice. Triphenyltin-lithium was prepared by the addition of 0.135 mole of phenyllithium in 152 ml. of ether to 8.54 g. (0.045 mole) of stannous chloride in ether at −10°. The reaction mixture was then carbonated by pouring it on a Dry Ice-ether slurry. On warming to room temperature the ethereal solution was filtered from the solid suspended in it. This solid was extracted with 100 ml. of petroleum ether (b.p. 77–120°), and filtered hot. On cooling, 0.9 g. (4.7%) of tetraphenyltin melting at 222–225° was obtained. A mixture melting point with an authentic specimen showed no depression. The insoluble solid was extracted with 50 ml. of water and filtered hot. Acidification of the aqueous solution with concentrated hydrochloric acid yielded a clear solution from which no benzoic acid was obtained.

The ethereal solution was evaporated to dryness, and the residue was extracted with 50 ml. of refluxing petroleum ether (b.p. 77–120°) for 0.5 hour, and the filtrate decanted. The insoluble solid was treated as above, and no benzoic acid was obtained. Nothing was recovered from the petroleum ether solution.

Reaction of triphenyltin-lithium with 2,6-dimethyliodobenzene followed by carbonation with Dry Ice. Triphenyltin-lithium was prepared from 18.97 g. (0.10 mole) of stannous chloride and 0.30 mole of phenyllithium in 310 ml. of ether. Color Test I was negative after the addition of the phenyllithium solution was completed. Then 23.2 g. (0.10 mole) of 2,6-dimethyliodobenzene was added. Color Test I made one and ten minutes after addition of the halide was strongly positive. The reaction mixture was carbonated by pouring it on a Dry Ice-ether slurry ten minutes after addition of the halide. On warming to room temperature the ethereal solution was filtered from the solid suspended in it. This solid was extracted with 100 ml. of benzene for two hours, and filtered hot. On cooling, 11.0 g. of solid melting over the range 195–215° was obtained. The benzene mother liquor was evaporated to dryness, and the solid residue was crystallized from petroleum ether (b.p. 77–120°) to yield 1.3 g. of solid melting over the range 193–218°. The solid which was insoluble in the original benzene extraction was refluxed with 50 ml. of water and filtered hot. Acidification of this aqueous layer yielded a clear solution.

The ethereal solution was evaporated to dryness, the residue was extracted with 100 ml. of refluxing benzene for 0.5 hour, and the filtrate decanted. The insoluble solid was extracted with 100 ml. of water, and filtered hot. Acidification of this aqueous solution with concentrated hydrochloric acid precipitated 2.8 g. (18.7%) of 2,6-dimethylbenzoic acid melting at 115–116° (mixture melting point). The benzene solution was evaporated to dryness, and the solid residue was crystallized from petroleum ether (b.p. 97–120°) to yield 1.9 g. of solid melting over the range 196–214°.

The three high melting solids (14.2 g.) were combined. Infrared spectra[1] showed the material to be a mixture of tetraphenyltin and hexaphenylditin. The solid was extracted with successive 50-ml. portions of carbon disulfide. Hexaphenylditin is very much more soluble in this solvent than tetraphenyltin, and the two compounds were separated from each other by this extraction method. Each 50-ml. portion of solution was allowed to evaporate to dryness, and each solid fraction was crystallized from a minimum amount of petroleum ether (b.p. 77–120°). A total of 8.7 g. (66.6% based on the amount of acid recovered) of hexaphenylditin melting at 231–232° and 4.3 g. (10.8%) of tetraphenyltin melting at 228–229° were recovered. Both compounds were identified by mixture melting points with authentic specimens.

TABLE I

PREPARATION OF $(C_6H_5)_3SnR$ FROM $(C_6H_5)_3SnLi$ AND RX

HALIDE	YIELD OF $(C_6H_5)_3SnR$, %	YIELD OF $(C_6H_5)_4Sn$, %	REACTION CONDITIONS
Benzyl chloride	21.7	60.0	1.5 hrs. at −35°
Ethyl iodide	36.4	26.9	1.5 hrs. at reflux
Iodobenzene		80.8	6 hrs. at reflux
Bromobenzene		82.2	6 hrs. at reflux
Chlorobenzene		22.9	6 hrs. at reflux
p-Iodotoluene[b]	—	—	1.5 hrs. at reflux
o-Iodotoluene[a]	25.3	24.5	18 hrs. at reflux
2,4-Dimethyliodobenzene[a]	42.7	13.0	17 min. at −10°
2,5-Dimethyliodobenzene[a]	43.0	8.3	17 min. at −10°
2,6-Dimethyliodobenzene[a]	34.1	12.5	18 hrs. at reflux
Bromomesitylene	38.8	12.4	24 hrs. at reflux
Iodomesitylene[a]	13.7	7.8	24 hrs. at reflux
p-Bromoanisole	30.1	17.7	6 days at 25°
o-Iodoanisole[a]	24.3	—[d]	17 min. at −10°
p-Iodochlorobenzene[c]	19.7	6.8	24 hrs. at reflux

[a] Entered into the halogen-metal interconversion reaction as explained below. [b] No pure compounds were isolated. [c] A 14.0% recovery of halide was made. [d] No attempt was made to isolate the tetraphenyltin.

This procedure was used to identify the organolithium compounds formed upon halide addition to triphenyltin-lithium, and the results are summarized in Table II.

Preparation of triphenyl-2,4-dimethylphenyltin. In a 500-ml. three-necked flask was placed 19.25 g. (0.05 mole) of triphenyltin chloride in 100 ml. of ether. To this was added,

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[1] The infrared investigations were carried out by Dr. V. A. Fassel and M. Margoshes of the Ames Laboratory, Iowa State College.

dropwise and with good stirring, 0.05 mole of 2,4-dimethylphenyllithium in 102 ml. of ether. After the addition was completed the reaction mixture was refluxed for one hour, and hydrolyzed by pouring it into 400 ml. of saturated ammonium chloride solution, with good stirring. Color Test I was negative at the end of the reflux period. The layers were separated, and the ether layer was dried over sodium sulfate.

The ether was removed by distillation leaving an oil. On refluxing the oil with 50 ml. of methanol for 15 minutes it solidified. The methanol was then decanted, and the solid was recrystallized twice from a methanol-benzene (4:1) solution to yield 16.2 g. (71.2%) of triphenyl-2,4-dimethylphenyltin melting at 113–115°.

TABLE II

REACTION OF $(C_6H_5)_3SnLi$ WITH RX, FOLLOWED BY CARBONATION WITH DRY ICE

HALIDE	REACTION TIME BEFORE CARBONATION	YIELD OF ACID, %	YIELD OF $(C_6H_5)_3SnR$, %
	min.		
o-Iodotoluene	2	11.5	19.2
2,4-Dimethyliodobenzene	2	9.3	13.3
2,5-Dimethyliodobenzene	2	3.7	19.5
2,6-Dimethyliodobenzene	10	16.2, 18.7	—[a]
Iodomesitylene	10	20.3	—[a]
o-Iodoanisole	2	4.4	12.1

[a] No $(C_6H_5)_3SnR$ compound was isolated.

TABLE III

PREPARATION OF $(C_6H_5)_3SnR$ FROM $(C_6H_5)_3SnCl$ AND RM

$(C_6H_5)_3SnR$	M.P., °C.	YIELD, %	ANALYSIS[a,b] FOR TIN	
			Calc'd	Found
Triphenyl-2,4-dimethylphenyltin	113–115	71.2	26.08	25.97
Triphenyl-2,5-dimethylphenyltin	97–99	49.7	—[c]	—
Triphenyl-2,6-dimethylphenyltin	118–119	44.5	26.08	26.13
Triphenylmesityltin	157–158	74.2	25.30	25.24
Triphenyl-*o*-methoxyphenyltin	129–130	36.0	25.97	26.10
Triphenyl-*p*-methoxyphenyltin	151–152	37.1	25.97	26.21

[a] Each of these organotin compounds gave a positive qualitative test for tin as recently reported by Gilman and Goreau, *J. Org. Chem.*, **17**, 1470 (1952). [b] The quantitative analyses for tin were carried out as outlined by Gilman and Rosenberg, *J. Am. Chem. Soc.*, **75**, in press (1953). [c] Krause and Schmitz, *Ber.*, **52**, 2150 (1919).

This procedure was used to prepare the compounds listed in Table III with minor modifications as noted. The last two compounds listed were prepared using a Grignard reagent in place of the organolithium compound.

DISCUSSION

The change in Color Test I from negative before addition of 2,6-dimethyliodobenzene to positive after its addition is most directly explained by assuming a halogen-metal interconversion reaction between the halide and triphenyltinlithium. The products formed by this reaction would be triphenyltin iodide and

2,6-dimethylphenyllithium. The latter compound was indirectly identified by conversion to 2,6-dimethylbenzoic acid (18.7%) by means of the carbonation reaction, and the hexaphenylditin obtained in the same reaction is believed to arise by reaction of triphenyltin-lithium with the triphenyltin iodide, as formed.

$$(C_6H_5)_3SnLi + 2,6\text{-}(CH_3)_2C_6H_3I \rightarrow (C_6H_5)_3SnI + 2,6\text{-}(CH_3)_2C_6H_3Li$$

$$2,6\text{-}(CH_3)_2C_6H_3Li + CO_2 \xrightarrow{H^+} 2,6\text{-}(CH_3)_2C_6H_3CO_2H$$

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

Of those halides tested only iodo-compounds with one or both *o*-positions substituted with methyl or methoxy groups entered into the halogen-metal interconversion reaction.

o-Substitution appears to be necessary as indicated by the fact that *o*-iodotoluene and *o*-idoanisole undergo the interconversion reaction while *p*-iodotoluene and *p*-bromoanisole do not interconvert.

The interconversion reaction is accompanied by the usual nucleophilic displacement of the iodine atom bonded to the substituted benzene ring by triphenyltin-lithium to form an unsymmetrical organotin compound. Both reactions occur simultaneously and it is difficult to say which is more important. The presence of this competing reaction is confirmed by the isolation of triphenyl-*o*-tolyltin (19.2%) from the reaction of *o*-iodotoluene with triphenyltin-lithium followed by carbonation just two minutes after halide addition.

$$(C_6H_5)_3SnLi + o\text{-}CH_3C_6H_4I \rightarrow (C_6H_5)_3SnC_6H_4CH_3\text{-}o$$

In the reactions with 2,6-dimethyliodobenzene and iodomesitylene, where carbonation was carried out ten minutes after halide addition, no unsymmetrical organotin compounds were isolated. Apparently the presence of methyl groups in the *o*-positions markedly decreases the velocity of the substitution reaction. This decrease is probably due to the steric hindrance presented by the two methyl groups. At the same time there is an apparent increase in the interconversion reaction as indicated by the increased yields of 2,6-dimethylbenzoic and mesitoic acids. Whether this increase is due to the lack of competition from the substitution reaction or from some electronic effect due to the presence of the second *o*-substituent can not be ascertained from the available data.

If, as proposed, the triphenyltin iodide reacts immediately with triphenyltin-lithium a question arises about the ultimate fate of the organolithium compound formed by the halogen-metal interconversion reaction. There are four possible reactions which the organolithium compound may undergo; first, it may couple with unreacted arylhalide to form a substituted diphenyl compound; second, it may cleave the solvent, diethyl ether; third, it may enter into a metal-metal interconversion reaction (5, 6) with the unsymmetrical organotin compound as formed; fourth, it may cleave the tin-tin bond of hexaphenylditin to form triphenyltin-lithium and an unsymmetrical organotin compound. From the known behavior of organolithium compounds the first two reactions are of minor importance under the experimental conditions used. In a reaction of hexaphenylditin with phenyllithium, tetraphenyltin was obtained in an 88.6% yield, thereby supporting the fourth alternative listed above.

$$(C_6H_5)_3SnSn(C_6H_5)_3 + C_6H_5Li \rightarrow (C_6H_5)_4Sn + (C_6H_5)_3SnLi$$

SUMMARY

It has been found that triphenyltin-lithium is a stable complex which apparently does not dissociate into its component parts, diphenyltin and phenyllithium, under the experimental conditions described. The complex was reacted with a series of organic halides to form unsymmetrical organotin compounds of the type $(C_6H_5)_3SnR$. In reactions between triphenyltin-lithium and *o*-substituted iodobenzene compounds a halogen-metal interconversion accompanied the normal nucleophilic coupling reaction. Several reference unsymmetrical organotin compounds were prepared by reaction of triphenyltin chloride with appropriate organolithium compounds and Grignard reagents.

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