[Contribution from the Chemical Laboratory of Iowa State College]

REDUCED REACTIVITY ASSOCIATED WITH A TRIPHENYLTIN LINKAGE

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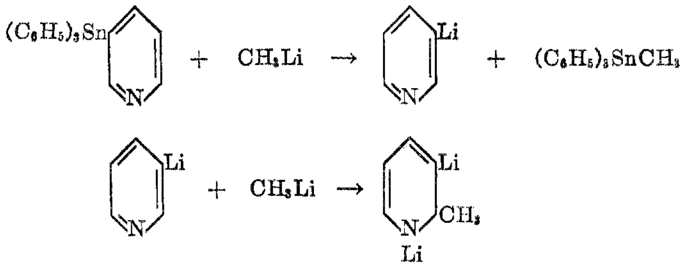
In the course of an investigation into the preparation of organotin compounds containing functional groups, some interesting effects have been observed in molecules which have one of the carbon atoms of a cyclic system attached to a tin atom. This union of tin to carbon in a cyclic system seems to decrease the tendency of the ring to undergo reactions which are characteristic of the system when it is not bonded to tin.

An example of this phenomenon is the failure of triphenyl-2-furyltin to undergo the Diels-Alder reaction with maleic anhydride. Several attempts to prepare the adduct were unsuccessful, as evidenced by an almost quantitative recovery of starting material. Attempts to condense crotonaldehyde with triphenyl-2-furyltin also resulted in an almost quantitative recovery of the starting tin compound.[2] The ring-opening conditions used for the preparation of acetonylacetone from 2,5-dimethylfuran (1), when applied to triphenyl-2-furyltin, resulted in the cleavage of the carbon-tin bond and probable scission of a carbon-oxygen bond.

A similarly lowered activity of the pyridine ring in triphenyl-3-pyridyltin was observed. Methyllithium appeared not to add across the azomethine linkage during a four-hour reaction period at −35°. When the same reaction was run at room temperature, 50% of the tin compound was recovered unchanged. The 50% recovery of triphenyl-3-pyridyltin can be explained by the following sequence of reactions (equation 1). First, one molecule of methyllithium attacks the 3-pyridyl carbon-tin bond to cleave the pyridine nucleus from the triphenyltin group. Immediately upon rupture of the carbon-tin bond, the pyridine ring is attacked by a second molecule of methyllithium which adds across the azo-



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[2] A study of compounds having the trimethylstannyl group in place of the triphenylstannyl group might throw light on the contribution of steric and electronic factors.

methine linkage. This mechanism is supported to some extent by the fact that methyllithium is used up in a 2:1 ratio.[3]

It has been suggested previously that a carbon-lithium bond at the 3-position of pyridine may contribute to the partial deactivation of the azomethine linkage, thus permitting the existance of halogen-metal interconversion products between bromopyridines and *n*-butyllithium (2). The findings reported herein would tend to support a postulation that metals, in general, have a tendency toward deactivation of some ring systems containing functional groups, but the difference in the kind of bonding in the two types of compounds does not allow a fair comparison. The carbon-tin bonds of organotin compounds have a definite tendency toward covalency, while the organolithium compounds are believed to exist in solution as ion pairs (3). On the basis of the latter viewpoint it is probably the carbanion in close proximity to the azomethine linkage that is the deactivation factor mentioned previously in this discussion (2).

Another interesting example of reduced activity is the apparent abnormal behavior of the bromine atom in triphenyl-*p*-bromophenyltin. It has not as yet been found possible to form a Grignard reagent from this material, even when a modified "entrainment" method was used (4). Although it is known that a metal-metal interconversion reaction is usually faster than a halogen-metal interconversion (5) it was thought that the reaction of *n*-butyllithium with triphenyl-*p*-bromophenyltin might produce some of the desired halogen-metal interconversion product if the metal-metal interconversion could be slowed down sufficiently. The desired interconversion, however, did not take place. A reaction between *tert*-butyllithium and triphenyl-*p*-bromophenyltin was carried out in an attempt to take advantage of some of the steric effects of the *tert*-butyl compound. It has been reported (6) that a 90% recovery of starting material was obtained from the reaction between *tert*-butyllithium and triphenyl-*p*-bromophenyllead in "unsaturate-free" petroleum ether. When this reaction was run with the corresponding tin compound decomposition and metal-metal interconversion took place. The reaction of this bromo compound with lithium metal apparently did not produce any of the desired triphenyl-*p*-lithiophenyltin. These results, demonstrating apparent reduced reactivity, are summarized in Table I.

A qualitative test for tin in organotin molecules was developed in order to facilitate the work-up of reactions involving organic compounds containing tin. The test is patterned, in so far as testing materials are concerned, after a procedure given by Feigl (7). The test involves cleavage of an organotin compound with bromine and subsequent reduction of tin from the stannic to the stannous state. A drop of the solution containing the stannous ion is placed upon a strip of ammonium phosphomolybdate paper. A blue spot on the test paper indicates a positive test. The test gave positive results with 25 different organic compounds which were known to contain tin.

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[3] An alternative mode of action might involve the cleavage of a phenyl group to give diphenyl-3-pyridylmethyltin, which might then add methyllithium at the azomethine linkage.

EXPERIMENTAL

Triphenyl-2-furyltin. Some attempts to prepare triphenyl-2-furyltin from 2-furylmercuric chloride and triphenyltin chloride did not yield any of the desired product. The compound was prepared in the following manner. Furan (0.1 mole, 7.28 ml.) in 30 ml. of dry ether was added rapidly to a well stirred ethereal solution containing 0.10 mole of *n*-butyllithium (8). The reaction mixture was refluxed for three hours, then allowed to stir at room temperature for ten hours (9). The resulting solution was divided into two equal parts. One portion was treated with 0.05 mole of anhydrous magnesium iodide; then 19.3 g. (0.05 mole) of triphenyltin chloride dissolved in 100 ml. of dry benzene was immediately added. It was necessary to reflux the mixture for three hours before Color Test I (10) was negative. The material was hydrolyzed in cold aqueous ammonium chloride solution; then the organic layer was separated and dried over sodium sulfate. Removal of the solvent, subsequent to filtration, yielded 16.1 g. of crude product. Several recrystallizations from 95% ethanol yielded 13.7 g. (65%) of pure product melting at 158–159°.[4] This compound gave a positive test for furan compounds by the method described by Asahina and co-workers (11). The micro test for tin was positive. The other half of the 2-furyllithium was not converted to the Grignard reagent. It was reacted with 19.3 g. (0.05 mole) of triphenyltin chloride in 100 ml. of dry benzene. Color Test I was negative within 45 minutes. The hydrolysis and work-up were the same as those described for the first half of the material. The yield of pure product, however, was only 44%.

Anal. Calc'd for $C_{22}H_{18}OSn$: Sn, 28.45. Found: Sn, 28.70.

Triphenyl-3-pyridyltin. A solution of 0.07 mole of *n*-butyllithium in 76 ml. of ether was added in a thin stream to 6.78 ml. (0.07 mole) of 3-bromopyridine dissolved in 100 ml. of dry ether at −35° (12). The mixture was stirred for 15 minutes, then 26.98 g. (0.07 mole) of triphenyltin chloride, dissolved in the minimum of dry benzene, was added in a thin stream while the temperature was maintained at −35°. After two hours Color Test I (10) was negative. The reaction mixture was hydrolyzed in cold aqueous ammonium chloride solution and the solid which formed was filtered off. The organic layer was separated, dried over sodium sulfate, and the solvent was distilled at water pump pressure. This gave a solid which was combined with the solid obtained from the hydrolysis mixture. The combined solids were placed in a Soxhlet extractor and extracted with 95% ethanol. The solid obtained from the ethanol was recrystallized twice from absolute ethanol to yield 16.7 g. (58%) of pure material melting sharply at 220°.

Anal. Calc'd for $C_{23}H_{19}NSn$: N, 3.27; Sn, 27.7.
Found: N, 3.27; Sn, 27.9.

Triphenyl-3-pyridyltin methiodide. One gram (0.0024 mole) of triphenyl-3-pyridyltin was suspended in a large excess (7 ml.) of methyl iodide and heated at reflux temperature for 15 minutes. The resulting solution was diluted with 95% ethanol and filtered. The methiodide was obtained in 40% yield by evaporating the solvent from the filtrate and washing the resulting solid with cold ether. The compound melted at 183–184° when the rise in temperature was 2° per minute. This material was also recrystallized from hot water, but there was some decomposition.

Anal. Calc'd for $C_{24}H_{22}INSn$: I, 21.7. Found: I, 21.7.

Triphenyl-2-pyridyltin. Triphenyl-2-pyridyltin was prepared by essentially the same procedure as that described for the preparation of triphenyl-3-pyridyltin except that the halogen-metal interconversion was run at −18° (13) and the compound was purified by recrystallization from petroleum ether (b.p. 77–115°).

The melting point of the pure compound was 178–179° and the yield was 12%.

Anal. Calc'd for $C_{23}H_{19}NSn$: N, 3.27; Sn, 27.7.
Found: N, 3.29; Sn, 28.2.

Several attempts to prepare the methiodide of this compound were not successful. An intractable mass which could not be purified was obtained.

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[4] All melting points are uncorrected.

A micro test for tin in organotin compounds. Approximately 10 mg. of tetraphenyltin was dissolved in 1 ml. of carbon tetrachloride in a small test tube. Three drops of liquid bromine were added and the mixture was boiled until it was just at the point of dryness. The excess bromine which remained in the upper part of the test tube was blown off and four drops of distilled water were added. The aqueous mixture was warmed for about 10 seconds, then three drops of a 1:1 concentrated hydrochloric acid-water solution and a small piece of

TABLE I

Some Attempted Reactions with Triphenyltin Compounds

ORGANOTIN COMPOUND	REACTION ATTEMPTED	RESULT OBTAINED[a]
Triphenyl-2-furyltin	Cleavage of the furan ring.	Triphenyltin group was cleaved and the furyl ring probably was opened.
Triphenyl-2-furyltin	Condensation of the furyl ring with maleic anhydride and crotonaldehyde.	A 95% recovery of triphenyl-2-furyltin.
Triphenyl-*p*-bromophenyltin	Halogen-metal interconversion with *n*- and *tert*-butyllithium, followed by carbonation.	No tin-containing acid was isolated.
Triphenyl-*p*-bromophenyltin	Formation of an active organometallic compound with magnesium and lithium metal, followed by carbonation.	No tin-containing acid was isolated.
Triphenyl-3-pyridyltin	Addition of methyllithium to the azomethine linkage.	A 50% recovery of triphenyl-3-pyridyltin.

[a] Results were checked by duplicate reactions.

TABLE II

Organotin Compounds Tested[a] by the Micro Method

Tetra-*p*-dimethylaminophenyltin tetramethiodide
Triphenyl-*p*-dimethylaminophenyltin methosulfate
Triphenyl-*p*-dimethylaminophenyltin methiodide
Triphenyl-*p*-dimethylaminophenyltin
Triphenyl-*p*-bromophenyltin
Diphenyldi-*p*-dimethylaminophenyltin dimethiodide
Triphenyl-γ-diethylaminopropyltin methiodide
Triphenyltin bromide
Phenyltin trichloride
Triphenylbenzyltin
Tetraphenyltin
Triphenyl-2-furyltin
Triphenyl-3-pyridyltin
Triphenyltin chloride
Triphenylethyltin
Triphenylsilyltriphenyltin
Triphenylsiloxytriphenyltin
Triphenyl-6-(2-hydroxynaphthyl)tin
Triphenyl-4-dimethylamino-3-(4′-nitrophenylazo)phenyltin
Tetra-*n*-butyltin
Triphenyl-β-hydroxyethyltin
Triphenyl-2,6-dimethylphenyltin
Triphenyl-2,4-dimethylphenyltin
Triphenylmesityltin
Triphenyl-*o*-hydroxyphenyltin

[a] All of the above compounds gave a positive test for tin.

magnesium metal were added. The mixture was allowed to react for about 30 seconds before a test was made by dipping a stirring rod into the solution and then touching it to a strip of ammonium phosphomolybdate paper.[5] A blue spot, indicating a positive test, appeared on the paper.[6] The specific organotin compounds which were tested are listed in Table II.

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SUMMARY

The failure of triphenyl-2-furyltin to condense with either maleic anhydride or crotonaldehyde suggests a deactivating effect of the tin on the chemical reactivity of the rings bonded to the tin atom. The idea is supported by the failure of triphenyl-3-pyridyltin to add methyllithium to the azomethine linkage and by the apparent inability of triphenyl-*p*-bromophenyltin to undergo formation of an active organometallic compound by customary reactions with magnesium or *n*-butyllithium. A micro test for tin in organotin molecules is described and the preparation of several organotin compounds containing functional groups is reported.

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[5] The test paper was prepared by saturating a piece of filter paper with a 5% solution of phosphomolybdic acid [Linz, *Ind. Eng. Chem., Anal. Ed.*, **62**, 459 (1943)]. The wet paper was treated with ammonia until a yellow precipitate formed. The paper was then dried in a 110° oven.

[6] The authors wish to thank S. D. Rosenberg and T. C. Wu for furnishing and testing some of the compounds listed in Table II.