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UNSYMMETRICAL ORGANOTIN COMPOUNDS
CONTAINING FUNCTIONAL GROUPS

by

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INTRODUCTION

Organotin compounds are those which have a direct union of carbon with tin. The first such compound was prepared by Löwig (82), in 1852, when he reacted ethyl iodide with a sodium-tin alloy to form diethyltin. Many of the early workers, Grimm (48), Cahours (13) and Ladenburg (78), used this method to obtain a mixture of products containing the tetraalkyltin compound. The preparation of organotin compounds through an organic halide and a sodium-tin alloy is still in use, and it is probably the most desirable commercial method available at present.

Frankland and Lawrence (26) prepared tetraethyltin by reaction of stannous chloride with diethylzinc, and found this method superior to the direct reaction of stannic chloride and diethylzinc which was quite vigorous and difficult to control. Pope and Peachey (100) introduced a more convenient method of preparation through the use of a Grignard reagent with a stannic halide. This reaction is easily controlled and is a most convenient laboratory method. Austin (5) has supplemented the use of the Grignard reagent with organolithium compounds thereby extending the versatility of the method.

The organolithium compounds possess greater reactivity than Grignard reagents and have found application in the introduction of sterically hindered groups into organotin compounds. This higher level of reactivity is emphasized in the preparation of organotin compounds reported by Talalaeva and Kocheshkov (113) by reaction of organolithium compounds with finely divided tin. Grignard reagents apparently do not enter into this reaction.

Recently Yakubovich and co-workers (126) reported a novel method of preparation for organotin compounds by the reaction of stannic halides with diazomethane and diazoethane. The course of the reaction can be controlled to yield mono-, di-, tri- and tetrasubstituted compounds, and appears to be a promising method of preparation.

The first organotin compound containing an aromatic group, triethylphenyltin, was prepared by Ladenburg (77) in 1871 by the addition of metallic sodium to an ethereal solution of triethyltin iodide and bromobenzene. This is a Wurtz type reaction and has received little attention as a preparative method. The best laboratory method for the preparation of unsymmetrical organotin compounds is the reaction of an organotin halide with a Grignard reagent (100), a method which has been widely used (9, 11, 49, 61, 75, 79, 107).

Kraus and Bullard (67) have reversed the Grignard approach by reacting an organotin halide with sodium metal in liquid ammonia to form an organotin-sodium intermediate which, after ammonia removal, is reacted with an organic halide to form the unsymmetrical organotin compound. Bobashinskaya and Kocheshkov (9) have supplemented the Grignard reagent with organolithium compounds to prepare certain organotin compounds, and recently (29, 40) organolithium compounds have been used to excellent advantage in the preparation of unsymmetrical organotin compounds containing functional groups such as hydroxyl, hydroxymethyl and dimethylamino.

Use of the "Random Distribution" reaction, as introduced by Calingaert and Beatty (15), for the preparation of organotin compounds is probably of commercial interest only, since a very efficient fractionating column is necessary to separate the products. The reaction is carried out by refluxing two symmetrical tetraalkyltin compounds in pentane in the presence of aluminum chloride. All the possible compounds are formed in yields which closely approximate those obtained by calculation according to the law of probability (14, 28).

The purpose of this study is the exploration of the reaction mechanism, scope and limitations of the preparation of symmetrical and unsymmetrical organotin compounds by way of an organotin-lithium complex of the type triphenyltinlithium (39, 41, 120, 123). Of primary interest is the preparation of organotin compounds which contain water-solubilizing groups or reactive groups that might be utilized in subsequent reactions with water-soluble compounds, thereby rendering the tin-containing compound water-soluble.

In connection with the study of the preparation of water-soluble organotin compounds several azo tin dyes have been prepared (40). These dyes have been tested as anticarcinogenic agents and for their substantivity as dyes.

HISTORICAL

Survey of the Chemical Literature on Organotin Compounds from 1941 to the Present Time

Investigators in this Laboratory have available an excellent and thorough bibliography of the organotin literature by Clyde E. Arntzen (3), in which publications through 1940, and some dated 1941, are listed. There is given also, in tabular form, a list of all organotin compounds known up to that time.

A thorough search of the chemical literature beginning with January 1941 and ending with the time of this writing has been made with the purpose of outlining the methods of preparation, both new and those previously described, now in use. In order to simplify the presentation of this data, it has been divided into five major sections, each of which covers a specific type of compound. At the end of each section is a table listing all compounds of the type discussed which were mentioned in the articles reviewed, no matter how brief the description of the compound may have been. Complete coverage of the chemical literature for the years 1941 through 1951, inclusive, and as complete coverage as possible for 1952 through the month of September has been made.

Compounds of the general formulae R_4Sn, R_3SnR', $R_2SnR'_2$, $R_2SnR'R''$, and R_2Sn

Methods of preparation. In this discussion organotin molecules in which the central tin atom is bonded only to carbon and all four organic groups are the same will be referred to as symmetrical compounds; where the groups are not all the same, the term unsymmetrical compounds will be used.

The best industrial method available for the preparation of symmetrical compounds is the reaction of an organic halide with a sodium-tin alloy. In many instances the reaction has been improved by the addition of zinc to the alloy. Tetraethyltin has been prepared by reacting a 60% excess of ethyl bromide with a sodium-zinc-tin alloy (29). Talalaeva and Kocheshkov (113) obtained tetra-p-tolyltin [39%] by refluxing a tin amalgum [0.02 g. atom of Sn plus 0.04 g. atom of Hg], lithium metal and p-bromotoluene in ether for 16 hours. Under corresponding conditions, tetraphenyltin was prepared in a 69% yield. While investigating the mechanism of this reaction, they found that tetraphenyltin [68%] could be prepared from phenyllithium and the amalgum, and the same compound was obtained in a 46% yield simply by shaking phenyllithium with tin powder in ether for 185 hours.

In the laboratory symmetrical organotin compounds are best prepared by reaction of a stannic halide with a reactive organometallic compound such as a Grignard reagent or organolithium compound. Unsymmetrical compounds are usually obtained from organotin halides and Grignard reagents. In some cases an organolithium compound may be substituted for the Grignard reagent to good advantage. Manulkin (85, 86, 87, 88a) has prepared tetra-n-heptyltin [89%] and tetra-n-octyltin [59%] by reacting stannic chloride with n-heptyl- and n-octylmagnesium bromides, respectively (87). Similarly dimethyldiethyltin [62%] was obtained from diethyltin dichloride and methylmagnesium iodide (88a), and some fifteen compounds of the type R_3SnR' were prepared from the appropriate trisubstituted organotin halide and a Grignard reagent in yields ranging from 78% to 91% (85, 86, 87).

Talalaeva and Kocheshkov (113) prepared tetra-p-methoxyphenyltin [55%], tetra-p-ethoxyphenyltin [78%] and tetra-p-biphenylyltin [69%] by refluxing stannic chloride with the appropriate organolithium compound in an ether-benzene solution for 1.5 hours. Meals (89) used stannic chloride and Grignard reagents to obtain four symmetrical long chain aliphatic tin compounds in yields ranging from 45% to 76%, and Vijayaraghavan (116) prepared tetraallyltin [80%] in the same manner.

Using a slightly less direct method Harris (53) obtained tetraphenyltin [67%] from stannic chloride, chlorobenzene and sodium metal. The reaction probably proceeds by formation of phenylsodium which then attacks the stannic chloride to form the final product.

Recently, during the course of some research on the introduction of water solubilizing groups into organotin compounds, it was found that if triphenyltin chloride was reacted with organolithium compounds which were prepared by halogen-metal interconversion (29) some tetraphenyltin was formed as a by-product. Therefore the organolithium compounds were converted to Grignard reagents by reaction with anhydrous magnesium bromide, and the Grignard reagents were, in turn, added to the organotin halide to prepare the unsymmetrical compounds (29).

$$\underline{o}\text{-}BrC_6H_4OH + 2\underline{n}\text{-}C_4H_9Li \longrightarrow \underline{o}\text{-}LiC_6H_4OLi + \underline{n}\text{-}C_4H_{10} + \underline{n}\text{-}C_4H_9Br$$

$$\underline{o}\text{-}LiC_6H_4OLi + MgBr_2 \longrightarrow \underline{o}\text{-}BrMgC_6H_4OLi + LiBr$$

$$\underline{o}\text{-}BrMgC_6H_4OLi + (C_6H_5)_3SnCl \longrightarrow (C_6H_5)_3Sn(\underline{o}\text{-}LiOC_6H_4)$$

$$(C_6H_5)_3Sn(\underline{o}\text{-}LiOC_6H_4) \xrightarrow[NH_4Cl]{\text{aqueous}} (C_6H_5)_3Sn(\underline{o}\text{-}HOC_6H_4)$$

In this manner triphenyl-o-hydroxyphenyltin [57%], triphenyl-p-hydroxyphenyltin [10%], diphenyldi-o-hydroxyphenyltin [68%], triethyl-*o*-hydroxyphenyltin [54%], triphenyl-*o*-hydroxymethylphenyltin [64%] and triphenyl-*p*-hydroxymethylphenyltin [66%] were prepared.

In cases where the organolithium compound was prepared by direct reaction of lithium metal with an organic halide, the reactive organometallic compound was added directly to triphenyltin chloride in ether without conversion to the Grignard reagent. Triphenyl-*o*-dimethylaminophenyltin [64%] and triphenyl-*p*-dimethylaminophenyltin [62%] were prepared by this shortened procedure. Triphenyl-*p*-carboxyphenyltin was obtained in a 44% yield by oxidation of triphenyl-*p*-hydroxymethylphenyltin with potassium permanganate (29).

Organotin complexes of the type R_3SnM [where M is lithium or sodium] have been used to prepare symmetrical and unsymmetrical compounds. Triphenyltin-sodium adds to ethylene oxide to yield, on hydrolysis, triphenyl-2-hydroxyethyltin in good yield (29), and triphenyltin-lithium has been reacted with appropriate organic halides to prepare tetraphenyltin [66%], triphenylbenzyltin [22%] and triphenylethyltin [36%] (39).

Tabulation of compounds.

Table 1

R_4Sn, R_3SnR', $R_2SnR'_2$, $R_2SnR'R''$, and R_2Sn Compounds

Compound	m.,b., and n_D, °C.*	References
Diallyldi-n-butyl-	145-146/17mm.	(62)
Diallyldiethyl-	99-100/17mm.	(62)
Dichloromethyldi-1-chloroethyl-	141-142/5mm. n 1.5478	(126)
Diethylcyclopentamethylene-		(119)
Diethyldi-1-chloroethyl-	114-115/5mm. n 1.5083	(126)
Diethyldiisoamyl-		(119)
Diethyldiisobutyl-		(119)
Diethyldimethyl-	131-132/760mm. n^{19} 1.4650	(87)
Diisoamylethyl-n-propyl-		(119)
Dimethylcyclopentamethylene-		(119)
Dimethyldiisobutyl-		(119)
Diphenyldibenzyl-		(101)

*In these tables, unless a pressure in millimeters is given, the data in the physical constants column are melting points. Where more than one value for a constant is reported, the highest value is recorded here, unless later investigations indicate the highest value reported is very questionable. Unless otherwise indicated n represents n_D^{20}.

Table 1 (continued)

Compound	m.,b., and n_D,°C.	References
Diphenyldi-p-dimethylamino-phenyl-		(125)
Diphenyldi-p-dimethylamino-phenyltin dimethiodide	164-168	(125)
Diphenyldiethyl-		(101)
Diphenyldi-o-hydroxyphenyl-	136-138	(4,29)
Diphenyl-		(60,123)
Sodium p-(2'-triphenylstannyl-4'-dimethylamino)phenylazobenzoate		(This thesis)
Tetraallyl-	69-70/1.5mm. n^{32} 1.533	(116)
Tetra-dl-amyl-		(119)
Tetra-n-amyl-		(119)
Tetra-p-biphenylyl-	260	(113)
Tetrabromomethyl-	57	(126)
Tetra-n-butyl-	127/1.7mm. n 1.4727	(88b,119)
Tetra-1-chloroethyl-	142/2mm.	(126)
Tetrachloromethyl-	49-49.5 148.5/5mm.	(126)
Tetra-p-chlorophenyl-		(38)
Tetra-p-dimethylaminophenyl-	196-198	(125)
Tetra-p-dimethylaminophenyl-tin tetramethiodide	dec. 190	(125)
Tetra-n-dodecyl-	15-16 n 1.4736	(89)

Table 1 (continued)

Compound	m.,b., and n_D,°C.	References
Tetra-p-ethoxyphenyl-	104	(113)
Tetraethyl-	180.5-181/760mm. n^{25} 1.4693	(4,27,29, 65,88b, 106,109, 110,119)
Tetra-n-heptyl-	219-221/2mm. n 1.4702	(86,119)
Tetra-n-hexadecyl-	41.5-42.5	(89)
Tetra-n-hexyl-		(119)
Tetraisoamyl-		(119)
Tetraisobutyl-	155-155.5/24mm. n 1.4760	(27)
Tetraisopropyl-		(105b)
Tetra-p-methoxyphenyl-	134.8	(113,127)
Tetramethyl-	n^{25} 1.4386	(65,110, 118,119)
Tetra-n-octadecyl-	47	(89)
Tetra-n-octyl-	250-255/5mm. n 1.4681	(86,119)
Tetraphenyl-	229	(27,32,37, 39,45,53, 106,113, 120,123, 127)
Tetra-n-propyl-		(52b,116)
Tetra-n-tetradecyl-	33-34	(89)
Tetra-o-tolyl-	216-217	(This thesis)

Table 1 (continued)

Compound	m.,b., and n_D,°C.	References
Tetra-*m*-tolyl-	122-123	(This thesis)
Tetra-*p*-tolyl-	234-235	(113)
Tri-*n*-amyl-*n*-propyl-		(119)
Tri-*n*-butylallyl-	155/17mm.	(62)
Tri-*n*-butyl-*sec*-butyl-	143-144/3mm. n^{18} 1.4796	(119)
Tri-*n*-butylethyl-		(119)
Tri-*n*-butyl-*n*-hexyl-	165/7mm. n^{17} 1.4762	(86,119)
Tri-*n*-butylisoamyl-	177-178/20mm. n 1.4715	(85,119)
Tri-*n*-butylmethyl-		(119)
Tri-*n*-butylphenyl-	139/0.6mm. n 1.5155	(This thesis)
Triethylallyl-	76-77/10mm.	(62)
Triethyl-*n*-amyl-		(119)
Triethyl-*n*-butyl-	99-101/15mm. n 1.4736	(85)
Triethyl-*o*-hydroxyphenyl-	155-156/15mm. n^{25} 1.5379	(4,29,119)
Triethylisoamyl-		(119)
Triethylisobutyl-		(119)
Triethylisopropyl-	192-194/719mm. n^{12} 1.4772	(86,119)

Table 1 (continued)

Compound	m.,b., and n_D,°C.	References
Triethylmethyl-	159/745mm. n 1.5653	(85,119)
Triethyl-n-propyl-	112/50mm. n 1.4726	(62,85,119)
Triisoamyl-n-heptyl-	158-160/3mm. n 1.4696	(86,119)
Triisoamylmethyl-	138-140/4mm. n^{15} 1.4700	(86,119)
Triisobutylethyl-		(119)
Triisobutylisoamyl-		(119)
Trimethyl-n-amyl-	171-172/721mm. n 1.4559	(85)
Trimethyl-n-butyl-	149-150/726mm. $n^{21.5}$ 1.4560	(85,119)
Trimethylethyl-	106/746mm. n 1.4527	(85)
Trimethylisoamyl-	162-164/725mm. n^{21} 1.4470	(85,119)
Trimethylisobutyl-	140-141/726mm. $n^{21.5}$ 1.4544	(85,119)
Triphenylbenzyl-	90-91	(39)
Triphenyl-p-bromophenyl-	133-135	(34,125)
Triphenyl-p-carboxyphenyl-	166-168	(4,29)
Triphenyl-p-chlorophenyl-	139-140	(This thesis)
Triphenyl-3-diethylamino-propyl-		(125)

Table 1 (continued)

Compound	m.,b., and n_D,°C.	References
Triphenyl-3-diethylamino-propyltin methiodide	173-175	(125)
Triphenyl-3-dimethylamino-6-(4'-bromophenylazo)phenyl-	199-200	(This thesis)
Triphenyl-4-dimethylamino-3-(4'-bromophenylazo)phenyl-	170-172	(This thesis)
Triphenyl-3-dimethylamino-6-(4'-carboxyphenylazo)phenyl-	dec. 358	(This thesis)
Triphenyl-4-dimethylamino-3-(4'-chlorophenylazo)phenyl-	162-165	(This thesis)
Triphenyl-3-dimethylamino-6-(4'-nitrophenylazo)phenyl-	205-206	(This thesis)
Triphenyl-4-dimethylamino-3-(4'-nitrophenylazo)phenyl-	187-189	(This thesis)
Triphenyl-o-dimethylamino-phenyl-	110-112	(4, 29)
Triphenyl-m-dimethylamino-phenyl-	90-91	(This thesis)
Triphenyl-p-dimethylamino-phenyl-	132-134	(4, 29)
Triphenyl-p-dimethylamino-phenyltin methiodide	164	(125)
Triphenyl-p-dimethylamino-phenyltin methosulfate	244-246	(125)
Triphenyl-2,4-dimethylphenyl-	113-115	(This thesis)
Triphenyl-2,5-dimethylphenyl-	97-99	(This thesis)
Triphenyl-2,6-dimethylphenyl-	118-119	(This thesis)

Table 1 (continued)

Compound	m.,b., and n_D,°C.	References
Triphenylethyl-	56-58	(32,39)
Triphenyl-2-furyl	158-159	(34)
Triphenyl-2-hydroxy-3-chlorophenyl-	97-99	(This thesis)
Triphenyl-2-hydroxyethyl-	67-68	(29)
Triphenyl-o-hydroxymethylphenyl-	158-159	(4,29)
Triphenyl-p-hydroxymethylphenyl-	98-100	(4,29)
Triphenyl-o-hydroxyphenyl-	dec. 176-177	(4,29)
Triphenyl-p-hydroxyphenyl-	201-203	(4,29)
Triphenylmesityl-	157-158	(This thesis)
Triphenyl-o-methoxymethylphenyl-	94.5-95.5	(4,28b)
Triphenyl-o-methoxyphenyl-	130-131	(This thesis)
Triphenyl-p-methoxyphenyl-	151-152	(This thesis)
Triphenylmethyl-	60-61	(98)
Triphenyl-2-pyridyl-	178-179	(34)
Triphenyl-3-pyridyl-	220	(34)
Triphenyl-3-pyridyltin methiodide	183-184	(34)
Triphenyl-o-tolyl-	165	(This thesis)
Triphenyl-p-tolyl-	124	(This thesis)

Table 1 (continued)

Compound	m.,b., and n_D,°C.	References
Tri-n-propyl-n-butyl-	137-138/37mm. n 1.4741	(85,88b,119)
Tri-n-propylethyl-		(119)
Tri-n-propylisobutyl-		(119)
Tri-o-tolylbenzyl-	108-109	(This thesis)

Compounds of the general formulae R_3SnX, $R_2R'SnX$, R_2SnX_2, and $RSnX_3$ [X = F, Cl, Br, or I]

Methods of preparation. Organotin halides are usually prepared by cleavage of a symmetrical or unsymmetrical organotin compound with acidic agents such as halogens, halogen acids, stannic halides, aluminum chloride or mercuric chloride. In order to systematize the review of this method of preparation, each cleavage agent will be discussed under a separate heading.

Halogen. Manulkin (84, 85, 86, 87, 88) has made an extensive study on the cleavage of organic groups from tin in organotin compounds, and in the course of this work has prepared many organotin halides. Most of the reactions studied involved cleavage of alkyl groups from both symmetrical and unsymmetrical compounds with iodine. The reactions were carried out by refluxing the tin compound with iodine in ether for 1-12 hours. In this manner some twenty organotin iodides have been prepared in yields ranging from 60%

$$R_4Sn + I_2 \longrightarrow R_3SnI + RI$$

$$R_3SnR' + I_2 \longrightarrow R_2R'SnI + RI$$

to 90% (84, 85, 86, 87). Manulkin has developed a series on the ease of cleavage of alkyl groups from tin based on these iodine cleavage reactions. The group most easily cleaved is methyl, and the one least easily cleaved is *n*-octyl: methyl > ethyl > *n*-propyl > isobutyl > *n*-butyl isoamyl > amyl > *n*-hexyl > *n*-heptyl > *n*-octyl.

Vijayaraghavan (116) attempted to prepare triallyltin bromide by reaction of tetraallyltin with bromine at -15°, but instead isolated an inseparable mixture of diallyltin dibromide and triallyltin bromide. In a reaction with iodine, under the same conditions, a similar mixture of mono- and dihalide compounds was formed. In contrast with this, triethyltin bromide was prepared in an 88% yield by the addition of bromine to tetraethyltin at -10° in a 1:1 molar ratio (29). From these results it is apparent that the allyl group is much more easily cleaved from tin by bromine than is the ethyl group.

Halogen acid. Meals (89) prepared tri-n-dodecyltin chloride, tri-n-tetradecyltin chloride [85%], tri-n-hexadecyltin chloride [74%], and tri-n-octadecyltin chloride [62%] by saturating an ethereal solution of the appropriate tetrasubstituted compound with hydrogen chloride and allowing the resulting mixture to stand overnight.

$$R_4Sn + HCl \longrightarrow R_3SnCl + RH$$

Manulkin (87) prepared trimethyltin chloride [70%] and dimethylethyltin chloride [80%] by passing dry hydrogen chloride into a refluxing chloroform solution of tetramethyltin and trimethylethyltin, respectively. These results show that the methyl group is more easily cleaved by halogen acid than is the ethyl group. Continuing the study of cleavage reactions, Razuvaev and Fetyukova (101) prepared dibenzyltin dichloride [80%] by dissolving diphenyldibenzyltin in ethanol saturated with hydrogen chloride, demonstrating that the phenyl group is more easily cleaved than the benzyl group.

Stannic halide. The preparation of organotin halides by reaction of an organotin compound with stannic halide has an advantage over other cleavage methods in that none of the substituents attached to the tin atom is lost.

$$3R_4Sn + SnX_4 \longrightarrow 4R_3SnX$$

$$R_4Sn + SnX_4 \longrightarrow 2R_2SnX_2$$
$$R_4Sn + 3SnX_4 \longrightarrow 4RSnX_3$$

Vijayaraghavan (116) successfully prepared diallyltin dibromide by reacting tetraallyltin with stannic bromide in a sealed tube at 20 mm. pressure and 50° for 10 hours. Pavlovskaya and Kocheschkov (98) found that compounds of the type $RSnCl_3$ [where R is an alkyl group] are best prepared from Ar_3SnR compounds [where Ar is an aromatic group] and stannic chloride. In this manner methyltin trichloride [65%] was prepared from triphenylmethyltin and stannic chloride.

Talalaeva, Zaiteseva and Kocheshkov (114) heated the appropriate tetrasubstituted compound with a stannic halide in a sealed tube for 3 hours at 160° to prepare di-p-methoxyphenyltin dichloride [87%], di-p-methoxyphenyltin dibromide [74%], di-p-ethoxyphenyltin dichloride [66%], di-p-biphenylyltin dichloride [80%] and di-p-biphenylyltin dibromide [71%]. Using the same method Jones and co-workers (62) prepared tri-n-butyltin chloride, di-n-butyltin dichloride and ethyltin trichloride, and triphenyltin chloride was prepared in a 72% yield (37). For an improved procedure for the preparation of the latter compound see the Experimental part.

Aluminum chloride. In extending his studies to other cleavage agents Manulkin (88a) found that tetraethyltin in chloroform is readily cleaved by aluminum chloride. After 7 hours at room temperature diethyltin dichloride was obtained in a 71% yield. Under comparable conditions, tri-*n*-butyltin chloride [22%] and di-*n*-butyltin dichloride [29%] were prepared from tetra-*n*-butyltin, and tetraphenyltin was completely degraded to benzene and stannic chloride. These results convincingly substantiate previous evidence which showed that aromatic groups are more readily cleaved from tin than aliphatic groups by acidic reagents (9).

Mercuric chloride. Manulkin (87) found that mercuric chloride was less active as a cleavage agent than aluminum chloride, but, surprisingly enough, a more active agent than hydrogen chloride in refluxing chloroform. Trimethyltin chloride [70%] and dimethyltin dichloride [13%] were prepared by adding mercuric chloride to an alcoholic solution of tetramethyltin at room temperature. Under similar conditions, tetraethyltin yielded triethyltin chloride [35%] and diethyltin dichloride [10%].

In conclusion, it appears that aromatic groups are more easily cleaved from tin than aliphatic groups by acidic agents; the longer the aliphatic group is, the more difficult it is to cleave; the branched chain isomer is more readily cleaved than the normal isomer where the number of carbon atoms in the chain is the same.

These conclusions are in agreement with those of Kharasch and his associates based on the reaction of hydrogen chloride with unsymmetrical organomercury compounds (28a). Kharasch deduced that the more electronegative radical unites with the hydrogen thereby providing a measure of the relative electronegativity of various aryl and alkyl groups. The results of the cleavage of groups from organotin compounds by acidic reagents substantiate the conclusions of these earlier workers.

Another method of preparation of organotin halides is the direct reaction with an alloy. Nesmeyanov, Borisov and Abramova (94) prepared trans-tri-2-chlorovinyltin chloride [40%] by stirring trans-2-chlorovinylmercuric chloride with a sodium-tin alloy [15% sodium] in benzene for 3 hours. Under comparable conditions, cis-2-chlorovinylmercuric chloride gave cis-tri-2-chlorovinyltin chloride in a 50% yield. Heating tin powder with trans-di-2-chlorovinylmercury in ethanol for 4.5 hours at 50° gave trans-tri-2-chlorovinyltin chloride [29%] and trans-2-chlorovinyltin trichloride [1.3%]. In another reaction with tin powder, dicarbethoxymethyltin dibromide [16%] was prepared by refluxing ethyl bromoacetate with the powder for 5.5 hours (36). Several other reactions with tin powder and similar haloesters failed to give isolable products.

_n_-Butyltin triiodide [25%] was formed by reacting $KSnCl_3$ with _n_-butyl iodide in a sealed Carius tube for 72 hours at 90° (36). Recently Yakubovich and co-workers (126) reported that stannic halides react progressively with aliphatic diazo compounds to yield halogen substituted organotin derivatives. Yields ranging from 40% to 80% were reported for the numerous compounds prepared by this method. The preparation of compounds with different aliphatic groups attached to tin was achieved by starting with substituted organotin halides and reacting them with a diazo compound containing another group.

The reactions with stannic halides were run at a temperature range of 0° to 5° using benzene as the solvent. Stannic chloride and bromide reacted satisfactorily, but stannic fluoride did not enter into the reaction.

$$
\begin{aligned}
SnX_4 &+ CH_2N_2 \longrightarrow XCH_2SnX_3 + N_2 \\
XCH_2SnX_3 &+ CH_2N_2 \longrightarrow (XCH_2)_2SnX_2 + N_2 \\
(XCH_2)_2SnX_2 &+ CH_2N_2 \longrightarrow (XCH_2)_3SnX + N_2 \\
(XCH_2)_3SnX &+ CH_2N_2 \longrightarrow (XCH_2)_4Sn + N_2
\end{aligned}
$$

Just before the report of Yakubovich and co-workers it was shown that tri-_n_-propyltin bromide reacted with diazoethane to form a compound which contained bromine, but, unfortunately, it decomposed before being completely analyzed (36).

Tabulation of compounds.

Table 2

R_3SnX, $R_2R'SnX$, R_2SnX_2, and $RSnX_3$ Compounds
(X = F, Cl, Br, or I)

Compounds	m.,b., and n_D,°C.*	References
Bromomethyltin tribromide	109/5mm.	(126)
_n_-Butyl-_n_-propyltin dichloride	67-68	(88b)
_n_-Butyltin triiodide	154/5mm.	(36, 80)
Chloromethyltin trichloride	72.5-73/5mm. n 1.5689	(126)
2-Chlorovinyltin trichloride	63-65/4mm. n^{29} 1.5602	(94, 119)
Diallyltin dibromide	77-79/2.0mm.	(116)
Dibenzyltin dichloride	163	(101)
Di-_p_-biphenylyltin dibromide	144-145	(114)
Di-_p_-biphenylyltin dichloride	140	(114)
Dibromomethyltin dibromide	87	(126)
Di-_n_-butyl-_n_-hexyltin iodide	180/8mm. n^{15} 1.5246	(86, 119)
Di-_n_-butylisoamyltin iodide	195/12mm. n 1.5254	(85, 119)

*See Table 1.

Table 2 (continued)

Compound	m.,b., and n_D,°C.	References
Di-n-butyltin dichloride	153-156/5mm. 41-42	(62, 88a, 88b, 97)
Di-1-carbethoxyethyltin dibromide$^{(?)}$	82-85/1.5mm.	(36)
Dicarbethoxymethyltin dibromide	139	(36, 80)
Di-1-chlorobutyltin dichloride	134/5mm. 53	(126)
Di-1-chloroethylchloromethyltin chloride	128/3mm. n 1.555	(126)
Di-1-chloroethyltin dichloride	112/4mm. 12 n 1.5535	(126)
Dichloromethyltin dichloride	89.5-90	(126)
cis-Di-2-chlorovinyltin dichloride	100-102/3mm. n 1.5675	(93, 94, 95, 119)
trans-Di-2-chlorovinyltin dichloride	77.5-78.5	(93,94,95)
Di-p-ethoxyphenyltin dichloride	46	(114)
Diethyl-n-amyltin bromide		(119)
Diethyl-5-bromoamyltin bromide		(119)
Diethyl-n-butyltin iodide	134-135/13mm. n 1.5460	(85,119)

(?) In this table a question mark following any compound signifies that its composition as indicated is not definite.

Table 2 (continued)

Compound	m.,b., and n_D,°C.	References
Diethylisoamyltin bromide		(119)
Diethylisoamyltin chloride		(119)
Diethylisobutyltin bromide		(119)
Diethyl-*n*-propyltin bromide		(119)
Diethyl-*n*-propyltin chloride		(119)
Diethyl-*n*-propyltin iodide	132-134/16mm. n 1.5582	(85,119)
Diethyltin dibromide		(63)
Diethyltin dichloride	227/760mm. 84-85	(2,15,21, 62,64,87, 88a,88b, 102,106)
Diethyltin diiodide	30-31	(84)
Diisoamylethyltin bromide		(119)
Diisobutylethyltin bromide		(119)
Dilauryltin dichloride	19.4	(108)
Di-*p*-methoxyphenyltin didibromide	102	(114)
Di-*p*-methoxyphenyltin dichloride	76	(114)
Dimethyl-*n*-amyltin iodide	132-133/23mm. n^{18} 1.5440	(85,119)
Dimethyl-*n*-butyltin iodide	118-120/25mm. n 1.5478	(85,119)

Table 2 (continued)

Compound	m., b., and n_D, °C.	References
Dimethylethyltin chloride	166-168/760mm. n 1.5082	(87)
Dimethylethyltin iodide	78/13mm. n 1.5705	(85)
Dimethylisoamyltin iodide	115/15mm. n^{21} 1.5410	(85,116)
Dimethylisobutyltin iodide	95/15mm. n 1.5082	(85,116)
Dimethyltin dichloride	185-190/760mm. 107-108	(2,64,87)
Dimethyltin diiodide	44	(84,119)
Diphenyl-*o*-carbomethoxyphenyltin chloride	168-169	(29)
Diphenyl-*o*-carboxyphenyltin chloride(?)		(29)
Diphenyltin dichloride	42	(29,64, 106,125)
Di-*n*-propyl-*n*-butyltin iodide	159-160/24mm. n 1.5320	(85,119)
Di-*n*-propyltin dibromide		(52b)
Di-*n*-propyltin diiodide		(52b)
Ethyltin trichloride	196-198/760mm. -10 n 1.5408	(21a,62)
Methyltin trichloride	45-46	(98)
Phenyltin tribromide		(119)
Phenyltin trichloride	96/1.4mm.	(10,119,125)

Table 2 (continued)

Compound	m.,b., and n_D,°C.	References
Tri-*n*-amyltin bromide		(119)
Tri-*n*-amyltin iodide	168/4mm.	(84)
Tribenzyltin chloride		(81)
Tri-*n*-butyltin bromide		(119)
Tri-*n*-butyltin chloride	145-147/5mm. n^{21} 1.4908	(19,62, 88a,119)
Tri-*n*-butyltin iodide	168/8mm. n 1.5345	(84,86)
Tri-1-chloroethyltin chloride	130/3mm. n 1.5450	(126)
Trichloromethyltin chloride	138-140/5mm. n 1.593	(126)
cis-Tri-2-chlorovinyltin chloride	119.5/1mm. n 1.5821	(94,95,119)
trans-Tri-2-chlorovinyltin chloride	121	(94,95)
Tri-*n*-dodecyltin chloride	33	(89)
Triethyltin bromide	105-107/15mm. n 1.5240	(19,29,119)
Triethyltin chloride	95/15mm. 15 n 1.5055	(2,19,21a,62, 63,87,88b, 119)
Triethyltin fluoride		(19)
Triethyltin iodide	117-118/15mm. n^{18} 1.5653	(19,84, 85,119)
Tri-*n*-heptyltin iodide	235-240/12mm. n^{30} 1.4732	(86)

Table 2 (continued)

Compound	m.,b., and n_D,°C.	References
Tri-n-hexadecyltin chloride	55.5-56.5	(89)
Triisoamyltin bromide		(119)
Triisoamyltin chloride		(119)
Triisoamyltin iodide	178-179/11mm. n^{18} 1.5209	(85,119)
Triisobutyltin bromide		(119)
Triisobutyltin chloride		(119)
Triisobutyltin iodide		(119)
Trimethyltin bromide		(63)
Trimethyltin chloride	152-154/760mm. 42	(2,87)
Trimethyltin fluoride		(63)
Trimethyltin iodide	69/15mm.	(84,119)
Tri-n-octadecyltin chloride	61-62	(89)
Tri-n-octyltin iodide	215-220/5mm. n 1.5181	(86,119)
Triphenyltin bromide	119-120	(120)
Triphenyltin chloride	106	(6,21b,29, 37,96,101, 123,125)
Triphenyltin fluoride		(21b)
Triphenyltin iodide	119-121	(29,83)
Tri-n-propyltin bromide		(52b,119)

Table 2 (continued)

Compound	m.,b., and n_D,°C.	References
Tri-n-propyltin chloride		(19,119)
Tri-n-propyltin iodide	140-141/15mm.	(52b,84,119)
Tri-n-tetradecyltin chloride	46-47	(87)

Compounds of the general formulae $(R_3Sn)_2Y$, R_3SnY, R_3SnYR, R_2SnY_2, R_2SnY, $R_2Sn(YR)_2$, $R_2Sn(YR')_2$, and SnY_4 [Y = OH, O, S, RCO_2, or $(RO)_2PO$]

Methods of preparation. The reaction of a disubstituted organotin halide, R_2SnX_2, with an inorganic base is the method of choice for the preparation of organotin oxides of the type R_2SnO. Talalaeva, Zaitseva and Kocheshkov (114) prepared

$$R_2SnCl_2 + 2OH^- \longrightarrow R_2SnO + H_2O + 2Cl^-$$

di-p-methoxyphenyltin oxide, di-p-ethoxyphenyltin oxide and di-p-biphenylyltin oxide in 100% yields by dissolving the appropriate organotin dihalide in alcohol saturated with ammonia. By reacting dilauryltin dichloride with sodium hydroxide in refluxing ether, Solerio (108) isolated some dilauryltin oxide.

Harada (51, 52a) prepared trimethyltin sulfide by reacting trimethyltin iodide with sodium sulfide in ethanol.

$$2(CH_3)_3SnI \quad + \quad Na_2S \longrightarrow [(CH_3)_3Sn]_2S \quad + \; 2NaI$$

Molecular weight determinations show this compound to be a monomer. Reaction of dimethyltin diiodide and diethyltin diiodide with potassium bisulfide or sodium sulfide in ethanol led to the recovery of dimethyltin sulfide and diethyltin sulfide. From molecular weight determinations it

$$(CH_3)_2SnI_2 \quad + \quad Na_2S \longrightarrow (CH_3)_2SnS \quad + \quad 2NaI$$

was decided that these sulfides must be trimers and the proposed formula for their structure is $R_2S\underline{nSSn(R_2)SSn(R_2)S}$, a six membered heterocycle. Talalaeva, Zaitseva and Kocheshkov (114) prepared di-p-methoxyphenyltin sulfide [71%], di-p-ethoxyphenyltin sulfide and di-p-biphenylyltin sulfide [72%] by reacting the appropriate organotin dichloride with potassium hydroxide in ethanol saturated with hydrogen sulfide.

Arbuzov and Grechin (1) prepared compounds of the type $R_2Sn(PO_3R_2)_2$ [where R is a short chain alkyl group] by mixing an organotin dihalide, R_2SnX_2, with a phosphorus ester, $P(OR)_3$, and heating to 100°. The compounds thus formed are

$$R_2SnX_2 \quad + \quad P(OR)_3 \longrightarrow R_2Sn(PO_3R_2)_2 \quad + \quad 2RX$$

soluble in hot butanol and chloroform, but are almost completely insoluble in other organic solvents. Molecular weight determinations by the Rast method show these compounds to be dimeric in structure. The phosphorus-tin bond is extremely sensitive, and it is readily cleaved by dilute hydrochloric acid, 10% sodium hydroxide solution or halogen. In an analogous reaction, Arbuzov and Pudovik (2) have prepared compounds of the type $R_3SnPO_3R_2$ by mixing an organotin halide, R_3SnX, with a phosphorus ester. These compounds are

$$R_3SnX + P(OR)_3 \longrightarrow R_3SnPO_3R_2 + RX$$

readily soluble in organic solvents, are monomeric in structure, and are easily cleaved by dilute acid, halogens and acetyl chloride.

Tabulation of compounds.

Table 3

$(R_3Sn)_2Y$, R_3SnY, R_3SnYR, R_2SnY_2, R_2SnY, $R_2Sn(YR)_2$, $R_2Sn(YR')_2$, and SnY_4 Compounds
[Y = OH, O, S, RCO_2, or $(RO)_2PO$]

Compound	m.,b., and n_D,°C.*	References
Di-p-biphenylyltin oxide		(114)
Di-p-biphenylyltin sulfide	134.5-135	(114)
Di-n-butyldi-n-butoxy-		(17)
Di-n-butyldiethoxy-		(17)
Di-n-butyldimethoxy-		(17)
Di-n-butyldi-n-octoxy-		(17)
Di-n-butyltin diacetate		(119)
Di-n-butyltin diundecate		(119)
Di-1-chloroethyltin sulfide	180	(126)
Di-p-ethoxyphenyltin oxide		(114)
Di-p-ethoxyphenyltin sulfide	127	(114)
Diethyltin sulfide	219-221/760mm. 24	(52a)
Diethyltin tetraethyldiphosphorate	249-251	(1)

*See Table 1.

Table 3 (continued)

Compound	m.,b., and n_D,°C.	References
Diethyltin tetramethyldiphosphorate	263.5-265	(1)
Diethyltin tetra-n-propyldiphosphorate	262-264	(1)
Dilauryltin oxide	dec. 110	(105)
Di-p-methoxyphenyltin oxide		(114)
Di-p-methoxyphenyltin sulfide	95	(114)
Dimethyltin sulfide	149	(52a)
Dimethyltin tetramethyldiphosphorate	245-247	(1)
Diphenyl-o-carboxyphenyl-, inner salt(?)		(29)
Diphenyltin oxide		(105,123)
Di-n-propyltin oxide		(52b)
Di-n-propyltin sulfide		(52b)
Di-n-propyltin tetra-n-propyldiphosphorate	251-253	(1)
Ethyl triphenylstannylacetate		(83)
Tin tetraacetate	253	(104)
Tri-n-butyltin hydroxide		(119)
Triethylethoxy-	82-84/11mm. n^{15} 1.4842	(2,116)

Table 3 (continued)

Compound	m.,b., and n_D,°C.	References
Triethyltin diethylphosphorate	210-220/2.5mm. n^{14} 1.4858	(2)
Triethyltin sulfide	187-188/20mm.	(51)
Trimethyltin dimethylphosphorate	96	(2)
Trimethyltin hydroxide	118	(2)
Trimethyltin sulfide	118/18mm.	(51)
Triphenylsiloxytriphenyl-	141-142	(This thesis)
_N_-Triphenylstannylbenzenesulfonamide		(83)
Triphenyltin _n_-butyrate		(83)
Triphenyltin hydroxide		(6)
Triphenyltin oxide	124	(105)
Tri-_n_-propyltin hydroxide		(52a)
Tri-_n_-propyltin oxide		(52a)
Tri-_n_-propyltin sulfide	215-219/19mm.	(51)

Compounds of the general formulae R_3SnSnR_3, $R_2R'SnSnR'R_2$, $R_3SnR'SnR_3$, and R_3SiSnR_3

Methods of preparation. The most direct method for the preparation of ditin compounds of the type R_3SnSnR_3 is the reaction of a trisubstituted organotin halide with sodium metal in refluxing xylene. Harada (50) used this method to prepare hexaethylditin.

$$2(C_2H_5)_3SnX \quad + \quad 2Na \longrightarrow (C_2H_5)_3SnSn(C_2H_5)_3 \quad + \quad 2NaX$$

Wittig, Meyer and Lange (123) reacted triphenyltin bromide with the intermediate, triphenyltin-lithium, to prepare hexaphenylditin in a 48% yield. Triphenylsilyltriphenyltin [71%] has been prepared by reacting triphenylchlorosilane with triphenyltin-lithium in ether at reflux for 3 hours (39). This compound has also been prepared by reacting triphenylsilyl-potassium with triphenyltin chloride (125). Attempts to prepare triphenylleadtriphenyltin by reacting triphenyltin-lithium with triphenyllead chloride, and triphenyllead-lithium with triphenyltin chloride were unsuccessful (125).

Tabulation of compounds.

Table 4

R_3SnSnR_3, $R_2R'SnSnR'R_2$, $R_3SnR'SnR_3$, and R_3SiSnR_3 Compounds

Compound	m.,b., and n_D,°C.*	References
Decamethylenedi-(triethyltin)		(119)
Hexaethyldi-	153-155/17mm.	(50,119)
Hexaisobutyldi-		(119)
Hexamethyldi-		(91)
Hexaphenyldi-	229-231	(39,120,123)
Hexa-n-propyldi-		(119)
Hexa-o-tolyldi-	298-300	(87, This thesis)
Pentamethylenedi-(triethyltin)		(119)
1,1,2,2-Tetraethyl-1,2-diisobutyldi-		(119)
1,1,2,2-Tetraethyl-1,2-di-n-propyldi-		(119)
Triphenylsilyltriphenyl-	289-291	(39,125)

*See Table 1.

Compounds of the general formulae R_3SnH, R_2SnH_2, and $RSnH_3$

Methods of preparation. Finholt, Schlesinger and coworkers (21a, 23) found that organotin halides are readily reduced by lithium aluminum hydride to organotin hydrides in excellent yields, and the products are obtained in a high state of purity. The reduction is carried out by stirring the organotin halide with lithium aluminum hydride in dioxane for 1 hour at 25°. Under comparable conditions no reduction is achieved when lithium hydride is substituted for lithium aluminum hydride.

$$4R_ySnX_{4-y} + (4-y)LiAlH_4 \longrightarrow 4R_ySnH_{4-y} + (4-y)LiX + (4-y)AlX_3$$

This method has been used to prepare silanes and germanes in good yields.

Triphenyltin hydride was prepared in a 42% yield (37) using the method of Chambers and Scherer (16) by ammoniating triphenyltin-sodium in liquid ammonia with ammonium bromide.

$$(C_6H_5)_3SnBr + 2Na \longrightarrow (C_6H_5)_3SnNa + NaBr$$

$$(C_6H_5)_3SnNa + NH_4Br \longrightarrow (C_6H_5)_3SnH + NH_3 + NaBr$$

Wittig, Meyer and Lange (123) reduced triphenyltin bromide directly with lithium aluminum hydride in ether to prepare triphenyltin hydride in 34% yield. Detailed directions for the preparation of this hydride by reduction of triphenyltin iodide with lithium aluminum hydride are included in the Experimental part.

Tabulation of compounds.

Table 5

R_3SnH, R_2SnH_2, and $RSnH_3$ Compounds

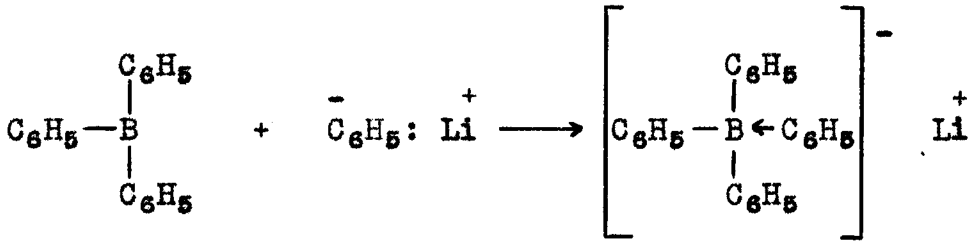
Compound	m.,b., and n_D,°C.*	References
Dimethyltin hydride	35/760mm. n 1.4480	(24)
Methyltin hydride	0/760mm.	(24)
Trimethyltin hydride	59/760mm.	(24)
Triphenyltin hydride	155-157/0.1mm.	(37,123)

*See Table 1.

Organometallic Complexes

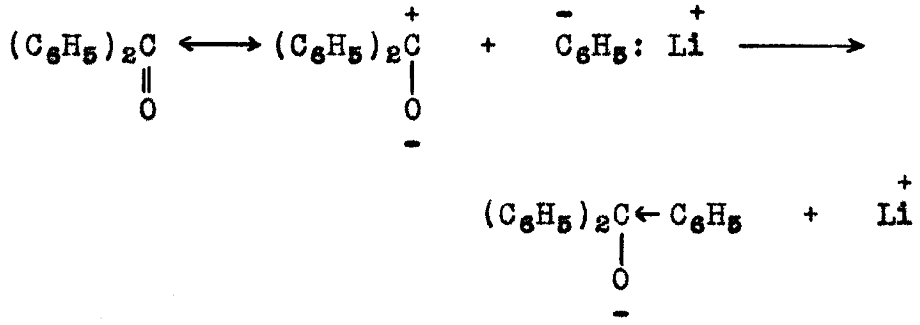
Since the preparation of lithium boron hydride by Schlesinger and Brown (103) about a dozen articles dealing with organometallic complexes have been published. These papers, together with all prior publications covering this field, will be reviewed herein in order to systematize the information now at hand.

The question arises as to how boron can, with a normal oxidation state of three, accommodate the five atoms apparently around it in lithium boron hydride. The answer to this question is found in the reports of Wittig and coworkers (120, 121, 122, 123, 124). They substituted phenyl groups for the hydrogen of lithium boron hydride, and studied the physical and chemical behavior of the more easily handled tetraphenylboron-lithium. The boron atom in triphenylboron has an open octet in that its outer shell contains but six electrons. In its need to fill its octet, the boron will share a pair of electrons donated by a nucleophilic group which the boron can accommodate. If phenyllithium is looked upon as a tight ion pair (18, 92), then it is apparent that the phenyl group can readily share its electron pair with the boron atom. This sharing leaves the newly formed tetraphenylboron group with a formal negative charge, enabling it to hold the lithium ion close by electrostatic interaction.



$$C_6H_5-\underset{C_6H_5}{\overset{C_6H_5}{B}} + \overset{-}{C_6H_5}:\overset{+}{Li} \longrightarrow \left[C_6H_5-\underset{C_6H_5}{\overset{C_6H_5}{B}}\leftarrow C_6H_5\right]^{-} \overset{+}{Li}$$

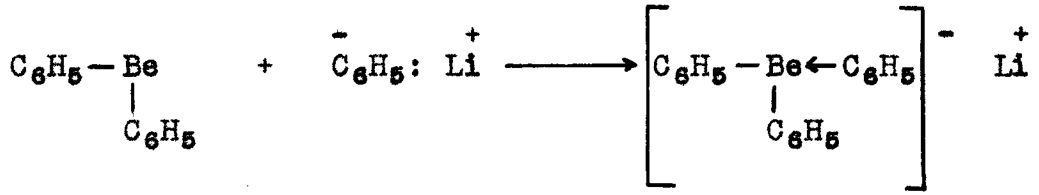
Wittig has compared this complex formation with the addition of phenyllithium to the polar form of benzophenone.



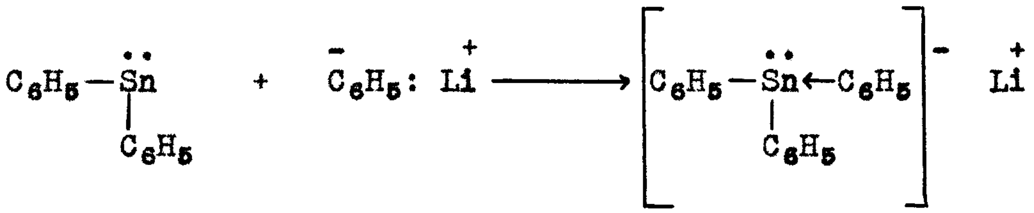
$$(C_6H_5)_2\underset{O}{\overset{}{\underset{\|}{C}}} \longleftrightarrow (C_6H_5)_2\underset{\overset{|}{\underset{-}{O}}}{\overset{+}{C}} + \overset{-}{C_6H_5}:\overset{+}{Li} \longrightarrow (C_6H_5)_2\underset{\overset{|}{\underset{-}{O}}}{C}\leftarrow C_6H_5 + \overset{+}{Li}$$

The carbon atom bonded to the oxygen atom in the polar form possesses an open octet which is quickly filled by the phenyl anion.

The same reasoning can be used to explain complexes like triphenylberyllium-lithium and triphenyltin-lithium. It will



$$C_6H_5-\underset{C_6H_5}{Be} + \overset{-}{C_6H_5}:\overset{+}{Li} \longrightarrow \left[C_6H_5-\underset{C_6H_5}{Be}\leftarrow C_6H_5\right]^{-} \overset{+}{Li}$$



$$C_6H_5-\underset{\underset{C_6H_5}{|}}{\ddot{Sn}} + \overset{-}{C_6H_5}{:}\,\overset{+}{Li} \longrightarrow \left[C_6H_5-\underset{\underset{C_6H_5}{|}}{\ddot{Sn}}\leftarrow C_6H_5\right]^{-}\overset{+}{Li}$$

be noted that in the case of the beryllium-complex, the beryllium atom still has an open octet. This accounts for some reactions into which it enters. These will be discussed in detail in the next section.

<u>Complexes of Group II metals</u>

In 1858 Wanklyn (117) attempted to prepare ethylsodium by the cleavage of diethylzinc with sodium metal but was not successful. Instead he had prepared triethylzinc-sodium from which the desired ethylsodium could not be obtained. Much later Hein (54, 55, 56, 58) showed that the addition of one equivalent of ethylsodium to one equivalent of diethylzinc in an inert solvent formed a solution with a conductivity equal to that of a 0.1 N potassium chloride solution, and that sodium ion migrates to the negatively charged electrode and triphenylzinc ion migrates to the positively charged electrode.

More recently it was reported (31) that an attempt to prepare diethylstrontium by the action of strontium metal on diethylzinc resulted in the preparation of a complex, tetraethylzinc-strontium. A similar reaction was carried out

$$2(C_2H_5)_2Zn \quad + \quad Sr \longrightarrow (C_2H_5)_2Zn{\cdot}Sr(C_2H_5)_2 \quad + \quad Zn$$

between barium metal and diethylzinc, and diethylbarium was prepared in good yield. De Postin (20) used the cleavage method to prepare triethylzinc-cesium from diethylzinc and cesium metal. Hurd (59) found that one equivalent of dimethylzinc in ether will take up two equivalents of methyllithium to form tetramethylzinc-dilithium.

$$(CH_3)_2Zn \quad + \quad 2CH_3Li \longrightarrow (CH_3)_4ZnLi_2$$

Wittig and co-workers have made an intensive study (120, 121, 122, 123, 124) on the nature of organometallic complexes and in the course of their research prepared triphenylberyllium-lithium, triphenylmagnesium-lithium, triphenylzinc-lithium, heptaphenyldizinc-trilithium, and triphenylcadmium-lithium. In each case the complex was prepared by adding an ethereal solution of phenyllithium to a solution of the diphenylmetallic compound in ether.

$$(C_6H_5)_2M \quad + \quad C_6H_5Li \longrightarrow (C_6H_5)_3MLi$$
$$(M = Be,\ Mg,\ Zn \text{ and } Cd)$$

It was not possible to prepare a complex from diphenylmercury and phenyllithium. Further study showed that the complex, triphenylmercury-lithium, could not be prepared by several different approaches.

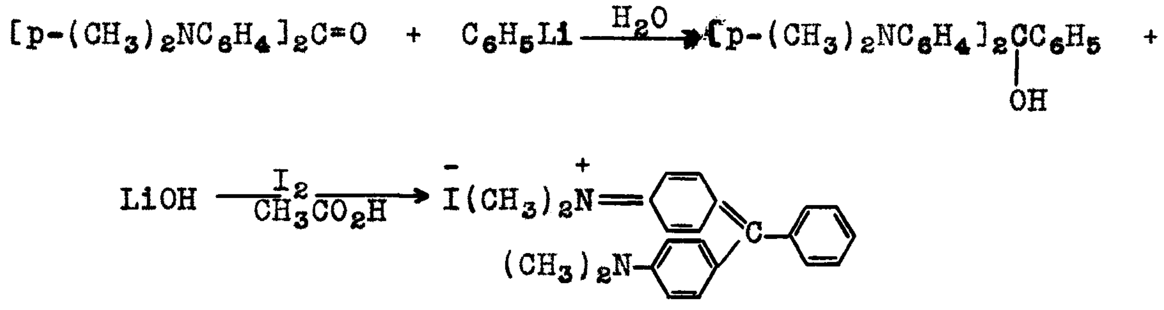
Triphenylberyllium-lithium is a colorless solid which is stable up to 200°. Diphenylberyllium, in contrast, begins to decompose at 160°. The complex can be crystallized from dioxane with four molecules of solvent, and from xylene solvent-free. Triphenylmagnesium-lithium decomposes at 212° while diphenylmagnesium is stable up to 250°. The complex can be crystallized from dioxane with two molecules of solvent, and from xylene solvent-free. Triphenylzinc-lithium decomposes at 165°, and heptaphenyldizinc-trilithium is stable up to 215°. Diphenylzinc is readily vacuum distilled without decomposition. Both complexes can be crystallized solvent-free from xylene. From dioxane, the former crystallizes with four molecules of solvent and the latter, with five. Investigations (123) have shown that the addition of phenyllithium to diethylzinc in a 1:1 ratio results in the preparation of triphenylzinc-lithium. The further addition of 0.5 equivalent of phenyllithium leads to the formation of the second complex, heptaphenyldizinc-trilithium.

$$(C_6H_5)_2Zn \quad + \quad C_6H_5Li \longrightarrow (C_6H_5)_3ZnLi$$

$$2(C_6H_5)_3ZnLi \quad + \quad C_6H_5Li \longrightarrow (C_6H_5)_7Zn_2Li_3$$

Triphenylcadmium-lithium is unstable, blackening slowly in the dark and rapidly in the presence of light. The addition of dioxane to an ethereal solution of the complex precipitates the triphenylcadmium-lithium with four solvating molecules of dioxane.

Reaction with Michler's ketone. Color Test I (42) is based on the fact that moderately active organometallic compounds add to the carbonyl double bond of Michler's ketone to form, upon hydrolysis, a tertiary carbinol which is converted to a di- or triphenylmethane type dye by iodine in acetic acid. For phenyllithium the reaction is:



$$[p\text{-}(CH_3)_2NC_6H_4]_2C{=}O \ + \ C_6H_5Li \xrightarrow{H_2O} [p\text{-}(CH_3)_2NC_6H_4]_2\underset{\displaystyle OH}{\underset{|}{C}}C_6H_5 \ + \ LiOH \xrightarrow[CH_3CO_2H]{I_2}$$

Malachite Green

Therefore Color Test I provides a good method for following the course of complex formation and for qualitatively estimating complex stability. If the complex were part of an equilibrium system, some phenyllithium would be present in solution and the equilibrium mixture would give a positive Color Test.

$$(C_6H_5)_3MLi \longrightarrow (C_6H_5)_2M \ + \ C_6H_5Li$$

The latter is valid, of course, only if the complex itself does not add as a unit to the carbonyl double bond, thereby giving a positive test. Fortunately, none of the complexes tested has sufficient activity to add as a unit. Table 6 outlines the results of Color Tests I with ethereal solutions of these complexes.

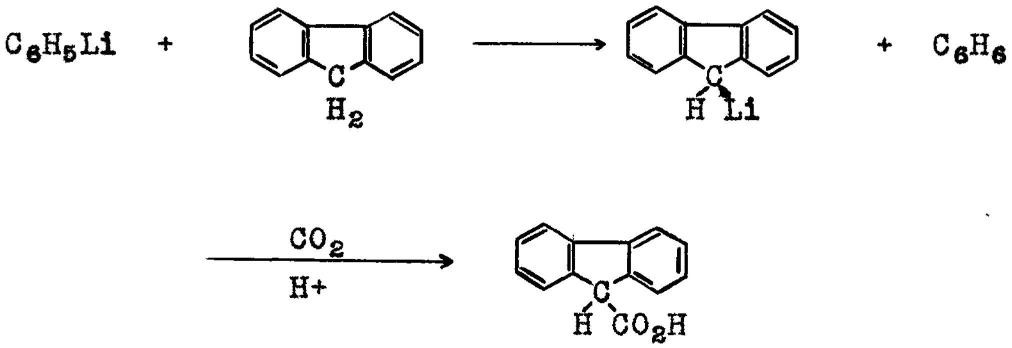
Table 6

Reaction of Group II Complexes with Michler's Ketone

$(C_6H_5)_3MLi$	Color Test I
Be	Negative
Mg	Positive
Zn	Negative
Cd	Positive
$(C_6H_5)_7Zn_2Li_3$	Negative

The results indicate that the complexes of magnesium and cadmium are involved in equilibrium systems, and those of beryllium and zinc are not.

Reaction with fluorene. Phenyllithium metalates fluorene promptly to form 9-fluorenyllithium which on carbonation yields diphenyleneacetic acid. Diphenylberyllium, -magnesium, -zinc, and -cadmium do not metalate fluorene. This reaction,



therefore, provides an excellent method to gain an insight into the stability of these complexes provided that any 9-fluorenyllithium formed does not itself form a stable complex with the diphenylmetallics. Fortunately the latter happens only in the case of diphenylcadmium, and the resulting complex, diphenyl-9-fluorenylcadmium-lithium, is so weakly formed that it does not interfere with the carbonation reaction. Table 7 summarizes the results of the reaction of fluorene with ethereal solutions of these complexes.

Table 7

Reaction of Group II Complexes with Fluorene

$(C_6H_5)_3MLi$	Number of days reacted	% yield of diphenyleneacetic acid
Be	14	0
Mg	3	47
Zn	10	16
Cd	3	64
$(C_6H_5)_7Zn_2Li_3$	10	44

From these results a series of complex-stability, $(C_6H_5)_3BeLi > (C_6H_5)_3ZnLi > (C_6H_5)_3MgLi > (C_6H_5)_3CdLi$, may be made. The exact position of $(C_6H_5)_7Zn_2Li_3$ cannot be decided on, but it is apparent that the complex first dissociates into $(C_6H_5)_3ZnLi$ and C_6H_5Li, and that this step is fairly rapid. Note that although the zinc-complexes do not give a positive Color Test I they do metalate fluorene.

Reaction with benzophenone. The addition of phenyllithium to the carbonyl double bond of benzophenone is quite prompt, thereby providing another method for measuring the stability of these complexes. Unfortunately this method is complicated by the fact that some of the diphenylmetallics possess sufficient activity to add to benzophenone. Table 8 shows the yield of triphenylcarbinol (tritanol) when each of the diphenylmetallics was reacted with benzophenone for 1 hour.

Table 8

Reaction of Diphenylmetallic Compounds with Benzophenone

$(C_6H_5)_2M$	% tritanol
Be	55
Mg	67
Zn	0
Cd	0
[C_6H_5Li]	[99]

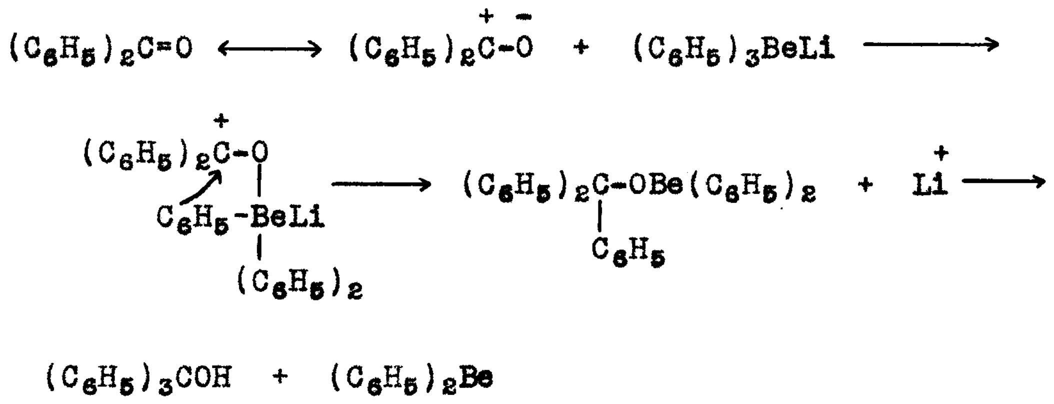
Table 9 outlines the results obtained when each of the complexes was reacted with benzophenone for 1 hour.

Table 9

Reaction of Group II Complexes with Benzophenone

$(C_6H_5)_3MLi$	% tritanol based on the addition of one phenyl group
Be	45
Mg	100
Zn	54
Cd	96
$(C_6H_5)_7Zn_2Li_3$	100

Surprisingly enough triphenylberyllium-lithium and benzophenone react to form tritanol in fair yield. Since this complex does not give a positive Color Test I and does not metalate fluorene, it is thought that the carbinol arises not from phenyllithium addition but, instead, by direct reaction of the complex with benzophenone.



$$(C_6H_5)_2C{=}O \longleftrightarrow (C_6H_5)_2\overset{+}{C}-\overset{-}{O} + (C_6H_5)_3BeLi \longrightarrow$$

$$(C_6H_5)_2\overset{+}{C}-O \cdots C_6H_5-BeLi(C_6H_5)_2 \longrightarrow (C_6H_5)_2C(C_6H_5)-OBe(C_6H_5)_2 + \overset{+}{Li} \longrightarrow$$

$$(C_6H_5)_3COH + (C_6H_5)_2Be$$

The energy necessary for the direct addition of the complex to the polar form of benzophenone is believed (123) to come from the desire of the beryllium atom to add two electrons to complete its octet. The intermediate thus formed then rearranges to form the carbinol.

As it is known that triphenylmagnesium-lithium is part of an equilibrium system the question arises whether the carbinol is formed by direct addition of the complex to benzophenone or from diphenylmagnesium and phenyllithium adding separately. Table 10 summarizes the results of series of additions to benzophenone.

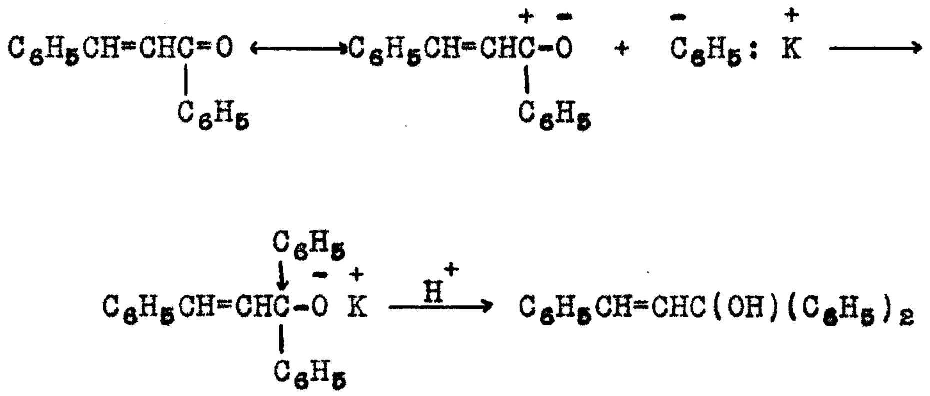
Table 10

Reaction of Organometallic Compounds with Benzophenone

Compound added	% tritanol after five minutes	% tritanol after one hour
$(C_6H_5)_2Mg$	44	67
$(C_6H_5)_3MgLi$	60	81
C_6H_5Li	78	99

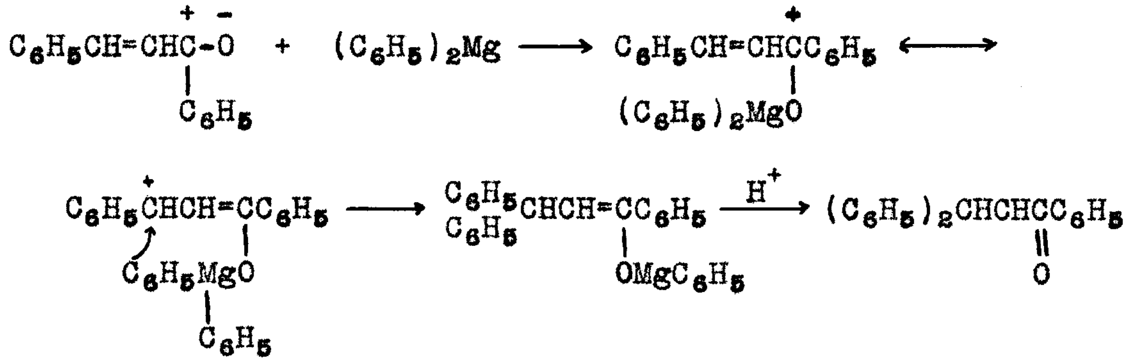
The yield of tritanol from the complex represents the mean between the diphenylmagnesium and phenyllithium, and from this it was concluded that the carbinol arises from addition of the latter pair of compounds to benzophenone and not from complex addition (123).

Reaction with benzalacetophenone. Organometallic compounds with high reactivity, such as phenylpotassium, add 1,2 to benzalacetophenone to form diphenyl-β-styrylcarbinol, while moderately active compounds, like diphenylmagnesium, add 1,4 to form diphenyl propiophenone.



$$C_6H_5CH{=}CH\underset{C_6H_5}{C}{=}O \longleftrightarrow C_6H_5CH{=}CH\underset{C_6H_5}{\overset{+}{C}}-\overset{-}{O} + \overset{-}{C_6H_5}:\overset{+}{K} \longrightarrow$$

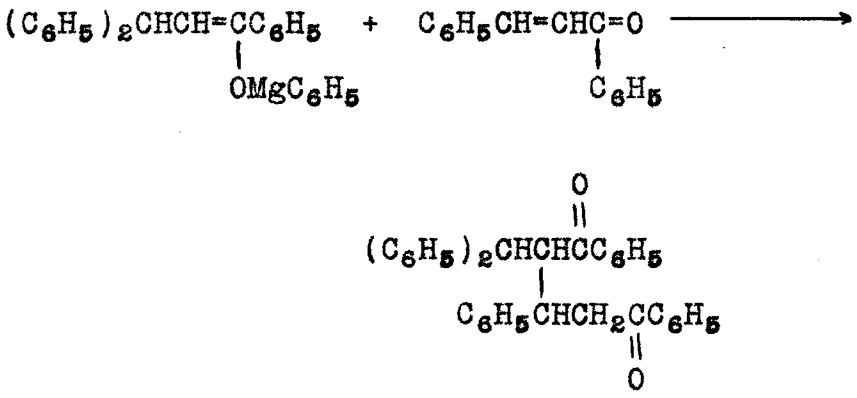
$$C_6H_5CH{=}CH\underset{C_6H_5}{\overset{C_6H_5}{C}}-\overset{-}{O}\ \overset{+}{K} \xrightarrow{H^+} C_6H_5CH{=}CHC(OH)(C_6H_5)_2$$



$$C_6H_5CH{=}CH\underset{C_6H_5}{\overset{+}{C}}-\overset{-}{O} + (C_6H_5)_2Mg \longrightarrow C_6H_5CH{=}CH\underset{(C_6H_5)_2MgO}{\overset{+}{C}}C_6H_5 \longleftrightarrow$$

$$C_6H_5\overset{+}{C}HCH{=}\underset{\underset{C_6H_5}{C_6H_5MgO}}{C}C_6H_5 \longrightarrow {}^{C_6H_5}_{C_6H_5}CHCH{=}\underset{OMgC_6H_5}{C}C_6H_5 \xrightarrow{H^+} (C_6H_5)_2CHCH\underset{O}{\overset{\|}{C}}C_6H_5$$

In some additions a secondary reaction takes place which leads to the formation of β-phenyl-γ-benzoyl-γ-benzhydrylbutyrophenone.



$$(C_6H_5)_2CHCH{=}\underset{\displaystyle OMgC_6H_5}{\underset{|}{C}}C_6H_5 + C_6H_5CH{=}CH\underset{\displaystyle C_6H_5}{\underset{|}{C}}{=}O \longrightarrow$$

$$(C_6H_5)_2CH\underset{\displaystyle C_6H_5CHCH_2\underset{\displaystyle O}{\underset{\|}{C}}C_6H_5}{\underset{|}{C}H}\overset{\displaystyle O}{\overset{\|}{C}}C_6H_5$$

Phenyllithium adds to benzalacetophenone to form diphenyl-β-styrylcarbinol [1,2-addition] in an 84% yield and diphenyl propiophenone [1,4-addition] in a 16% yield. The diphenylmetallics in their reactions with benzalacetophenone form only diphenyl propiophenone [1,4-addition], except diphenylcadmium, which does not react at all. Table 11 summarizes the results of the reaction between some of these complexes with benzalacetophenone, under comparable conditions.

Table 11

Reaction of Group II Complexes with Benzalacetophenone

$(C_6H_5)_3MLi$	% carbinol	% ketone	% diketone
Be	0	41	0
Mg	0.4	95	0
Zn	10	0	24
Cd	7	22	1.8
$(C_6H_5)_7Zn_2Li_3$	12	0	32

As with benzophenone, triphenylberyllium-lithium must add to benzalacetophenone as a unit, or else some carbinol would have been isolated. The same reasoning must follow for triphenylmagnesium-lithium, which also adds to benzalacetophenone as a unit. The zinc-complexes must first dissociate into diphenylzinc and phenyllithium which then add to the ketone. It is interesting to note that triphenylcadmium-lithium must add as a unit to the ketone while diphenylcadmium shows no reaction. This may be due to the desire of the cadmium in the complex to complete its open octet.

Complexes of Group III metals

In 1933 Thomson and Stevens (115) tried to prepare trimethylethylboron-lithium from trimethylboron and ethyllithium in ligroin at 120° without success. An attempt to prepare tetraphenylboron-lithium from triphenylboron and phenyllithium, under the same conditions, was also unsuccessful. Seven years later Schlesinger and Brown (103) announced the preparation of lithium boron hydride by reaction of diborane with ethyllithium, and, in order to prove that this type of complex was not unique, successfully synthesized and fully described trimethylethylboron-lithium. The latter complex was prepared by adding an ethereal solution of ethyllithium to trimethylboron in ether, at room temperature.

$$B_2H_6 + C_2H_5Li \longrightarrow LiBH_4 + C_2H_6$$

$$(CH_3)_3B + C_2H_5Li \longrightarrow (CH_3)_3(C_2H_5)BLi$$

Hurd (59), using the method of Schlesinger and Brown, prepared tetramethylboron-lithium and tetramethylaluminum-lithium from the trimethyl organometallic compounds and methyllithium in ether. Wittig and co-workers, along with their studies on the nature of the complexes of Group II metals, have prepared and fully described tetraphenylboron-lithium and tetraphenylaluminum-lithium (120, 121, 122, 123).

These complexes were prepared by the method of Schlesinger and Brown.

$$(C_6H_5)_3B + C_6H_5Li \longrightarrow (C_6H_5)_4BLi$$

$$(C_6H_5)_3Al + C_6H_5Li \longrightarrow (C_6H_5)_4AlLi$$

Tetraphenylboron-lithium can be recrystallized solvent-free from cyclohexane plus ether or from di-n-propyl ether to yield shiny colorless needles. The great stability of this complex is highlighted by the fact that it does not react with water, and water solutions of tetraphenylboron-lithium are stable. The complex does not give a positive Color Test I, and it does not react with benzophenone or acetone.

Tetraphenylaluminum-lithium can be recrystallized from dioxane. Like tetraphenylboron-lithium, this complex will not give a positive Color Test or react with benzophenone, but tetraphenylaluminum-lithium does react with water immediately on contact to yield benzene, aluminum hydroxide and lithium hydroxide. Analogous reactions with water are entered into by the Group II complexes.

$$(C_6H_5)_4AlLi + 4HOH \longrightarrow 4C_6H_6 + Al(OH)_3 + LiOH$$

Starting with tetraphenylboron-lithium it is possible to prepare tetraphenylboron-complexes with other alkali metals and the pseudoalkali, the ammonium ion. Tetraphenylboron-potassium, -rubidium, -cesium, and -ammonium are formed by reacting an aqueous solution of tetraphenylboron-lithium with a very concentrated salt solution of the appropriate ion [*e.g.*, potassium chloride]. Tetraphenylboron-sodium is prepared from the lithium complex and sodium methoxide.

$$(C_6H_5)_4BLi + K^+ \longrightarrow (C_6H_5)_4BK + Li^+$$

$$(C_6H_5)_4BLi + NaOCH_3 \longrightarrow (C_6H_5)_4BNa + LiOCH_3$$

An interesting complex, $(C_6H_5)_4BP(C_6H_5)_4$, is formed by reacting tetraphenylboron-lithium with tetraphenylphosphorus bromide in ether.

$$(C_6H_5)_4BLi + (C_6H_5)_4PBr \longrightarrow (C_6H_5)_4BP(C_6H_5)_4 + LiBr$$

Triphenylboron and triphenylaluminum react with hydrides of the alkali metals to form stable complexes.

$$(C_6H_5)_3B + AH \longrightarrow (C_6H_5)_3BHA$$

$$[A = Li, Na \text{ or } K]$$

$$(C_6H_5)_3Al + LiH \longrightarrow (C_6H_5)_3AlHLi$$

Complexes of Group IV metals

It has been known for some time that reactive intermediates of the type R_3MA [where R may be an aliphatic or aromatic group, M is Si (7, 32, 46, 68, 72), Ge (66, 69, 70, 74), Sn (11, 12, 16, 71, 73) or Pb (25, 30, 57), and A is Li, Na of K] can be prepared by the reaction of alkali metals or their alloys with compounds of the type R_3MX [where X may be an aliphatic, aromatic, alkoxy, R_3M, halogen, oxygen, hydrogen, and possibly nitrogen].

In 1941 it was reported that three equivalents of phenyllithium react with one equivalent of lead chloride in ether at -10° to form triphenyllead-lithium (43). The reaction has been shown to be a two step process, the first being simple nucleophilic displacement of chloride ion by phenyllithium and the second, complexation of the diphenyllead, thus formed, with phenyllithium (43).

$$2C_6H_5Li + PbCl_2 \longrightarrow (C_6H_5)_2Pb + 2LiCl$$

$$(C_6H_5)_2Pb + C_6H_5Li \longrightarrow (C_6H_5)_3PbLi$$

Wittig (120, 123) has prepared triphenyltin-lithium from diphenyltin and phenyllithium in ether. The complex may be crystallized solvent-free from dioxane to yield brilliant yellow needles. As with the lead-complex, triphenyltin-lithium has been prepared by direct reaction of three equivalents of phenyllithium with one equivalent of stannous chloride (39).

$$2C_6H_5Li \ + \ SnCl_2 \longrightarrow (C_6H_5)_2Sn \ + \ 2LiCl$$

$$(C_6H_5)_2Sn \ + \ C_6H_5Li \longrightarrow (C_6H_5)_3SnLi$$

Complexes of tin containing aliphatic groups, tri-<u>n</u>-butyltin-lithium and triethyltin-lithium, have been prepared by reacting the appropriate alkyllithium compound with stannous chloride (41).

Triphenylgermanium-lithium has been prepared, in like manner, by reacting germanium diiodide with phenyllithium, but little information is available on this complex at this writing.

<u>Reaction with Michler's ketone</u>. Triphenylsilyl-potassium (125) gives a positive Color Test I but the result is a blue color which is remindful of Michler's hydrol and not the usual green of Malachite Green. Triphenyltin-lithium does not give a positive Color Test, but triphenyllead-lithium does give a positive Test. From this result and other data cited below it has been concluded that triphenyllead-lithium is part of an equilibrium system, with the equilibrium displaced at least 80% toward the lead complex (43).

$$(C_6H_5)_2Pb \ + \ C_6H_5Li \rightleftarrows (C_6H_5)_3PbLi$$

Reaction with unsaturated linkages. Triphenylsilylpotassium reacts with Dry Ice to form triphenylsilylacetic acid. This acid is metastable, and on warming to 135° liberates carbon monoxide with formation of triphenylsilanol (7).

$$(C_6H_5)_3SiK \ + \ CO_2 \xrightarrow{H^+} (C_6H_5)_3SiCO_2H$$

$$(C_6H_5)_3SiCO_2H \longrightarrow (C_6H_5)_3SiOH \ + \ CO$$

The high reactivity of this intermediate is emphasized by its addition to trans-stilbene to yield β-triphenylsilyl-α,β-diphenylethylpotassium which on hydrolysis forms triphenyl-α,β-diphenylethylsilane (47).

$$(C_6H_5)_3SiK \ + \ C_6H_5CH{=}CHC_6H_5 \longrightarrow (C_6H_5)_3SiCH(C_6H_5)CH(C_6H_5)K$$

$$\xrightarrow{H_2O} \quad (C_6H_5)_3SiCH(C_6H_5)CH_2(C_6H_5)$$

Triphenyltin-lithium does not react with Dry Ice, gaseous carbon dioxide, benzophenone, benzalacetophenone, or trans-stilbene. From these results it has been concluded that, like triphenylberyllium-lithium, tetraphenylboron-lithium and tetraphenylaluminum-lithium, this tin-complex is not part of an equilibrium system.

Triphenyllead-lithium reacts with gaseous carbon dioxide to form benzoic acid and a diphenyllead polymer. Apparently the carbon dioxide combines with the phenyllithium present in the equilibrium mixture giving rise to the benzoic acid (43).

$$(C_6H_5)_3PbLi \longrightarrow (C_6H_5)_2Pb + C_6H_5Li$$

$$C_6H_5Li + CO_2 \xrightarrow{H^+} C_6H_5CO_2H$$

Reaction with water. Each of the three complexes discussed in this section reacts with water in a different manner. Triphenylsilyl-potassium yields triphenylsilane, which immediately hydrolyzes to triphenylsilanol, and potassium hydroxide; triphenyltin-lithium yields hexaphenylditin, hydrogen, and lithium hydroxide; triphenyllead-lithium yields a diphenyllead polymer, benzene, and lithium hydroxide.

$$\begin{aligned}(C_6H_5)_3SiK + HOH &\longrightarrow (C_6H_5)_3SiH + KOH\\ &\qquad \llcorner\!\!\longrightarrow (C_6H_5)_3SiOH\end{aligned}$$

$$(C_6H_5)_3SnLi + HOH \longrightarrow (C_6H_5)_6Sn_2 + H_2 + LiOH$$

$$(C_6H_5)_3PbLi + HOH \longrightarrow [(C_6H_5)_2Pb]_X + C_6H_6 + LiOH$$

Reaction with organic halides. The complexes discussed in this section are formed from compounds in which the metallic element has oxidation state of two. Unlike the metals of Group II and III complexes, the Group IV metals can rearrange their electronic configuration and assume an oxidation state of four. These Group IV complexes react promptly with aliphatic and aromatic halides to form compounds of the types, R_4M and R_3MR' [where R and R' may be aliphatic and/or aromatic groups], in good yields. Triphenyllead-lithium, although part of an equilibrium system, reacts as a unit with organic halides.

$$(C_6H_5)_3PbLi + C_6H_5CH_2Cl \longrightarrow (C_6H_5)_3PbCH_2C_6H_5 \ (70\%) + LiCl$$

In conclusion it may be said that triphenylsilyl-potassium and triphenyltin-lithium are not involved in equilibrium systems, and that the former is much more reactive than the latter. Triphenyllead-lithium is part of an equilibrium system and its reactivity is about the same as that of the tin-complex.

Analytical Procedures

The most convenient qualitative test for tin, although not the most accurate, in organotin compounds is to ignite a small sample of the compound on a clean spatula or crucible cover. The gray-white residue of stannic oxide indicates the presence of tin. This test may be ineffective with volatile organotin compounds, and decomposition of a sample of the compound with bromine followed by precipitation of the tin as the sulfide can be used as an alternative test for the presence of tin. Recently another test for tin has been developed based on the fact that Mo^{+6}, as in the Yellow precipitate, is reduced to Mo^{+5} by Sn^{+2}. Mo^{+5} compounds are blue in color, and the change in color from yellow to blue is indicative of tin (22, 34).

Quantitatively, tin in organotin compounds is determined as stannic oxide. Pfeiffer (99) introduced a method which involves decomposition of the sample by the use of fuming nitric acid in a sealed tube, followed by evaporation of the product with concentrated sulfuric acid and ignition to stannic oxide. A more convenient method (76) uses fuming nitric plus fuming sulfuric acid in a covered porcelain crucible to decompose the sample, followed by ignition to stannic oxide. Concentrated sulfuric acid plus 30% hydrogen peroxide has been used in place of fuming nitric plus fuming sulfuric acid (111). Volatile organotin compounds usually give low results by the fuming acid procedure. A method has been introduced whereby the volatile organotin compound is first decomposed with bromine in carbon tetrachloride, followed by treatment with concentrated nitric plus concentrated sulfuric acid and finally ignition to stannic oxide (35). It has been found that organotin compounds can be completely decomposed simply by treatment with concentrated sulfuric acid followed by ignition to stannic oxide. This method can be applied to volatile as well as non-volatile compounds.

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EXPERIMENTAL

Organotin Reactions

Studies on the nature and reactions of triphenyltin-lithium in ether

Preparation of triphenyltin-lithium in ether. The general procedure which was used for the preparation of triphenyltin-lithium on a 0.045 mole scale was as follows: the calculated volume of solution necessary to give 0.135 mole of phenyllithium[1,2] was added dropwise, over a period of about 1.5 hours, to 8.54 g. (0.045 mole) of finely ground anhydrous stannous chloride[3] suspended in 100 ml. of ether in a 500 ml., four-necked flask. The operations were carried out under nitrogen. During the addition the mixture was cooled in an ice-salt bath whose temperature was maintained

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[1] H. Gilman, E. A. Zoellner and W. M. Selby, J. Am. Chem. Soc., 55, 1252 (1933); see also ibid., 54, 1957 (1932).

[2] R. G. Jones and H. Gilman, "Organic Reactions", Vol. 6, John Wiley and Sons, Inc., New York, N.Y., 1951, p. 353.

[3] "Stannochlor" purchased from Metal and Thermit Corporation.

at -10°. Mechanical stirring, one of the most important points in the technique, was employed. A glass blade stirrer (*e.g.*, Ace Glass Co. stirrer, catalog number 8245) was found to be very efficient. The stirrer blade must fit the bottom of the flask closely, otherwise the dense stannous chloride collects on the bottom of the flask and the reaction proceeds irregularly.

The phenomena which occurred during the addition of the phenyllithium 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 phenyllithium, orange at 1.0 equivalent, red at 1.9 equivalents, deep red at 2.1 equivalents, rust at 2.5 equivalents, and tan at 3.0 equivalents. The deep red color is believed to indicate diphenyltin[4], and the tan color, triphenyltin-lithium[5]. Color Test I[6] for reactive organometallic compounds remained nega-

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[4] See E. Krause and A. von Grosse, "Die Chemie der metallorganischen Verbindungen", Gebruder Borntraeger, Berlin, 1937, p. 355, for a discussion of the color of solutions of diaryltin compounds in organic solvents.

[5] G. Wittig, *Angew. Chem.*, *62*, 231 (1950); G. Wittig, F. J. Meyer and G. Lange, *Ann.*, *571*, 167 (1951).

[6] H. Gilman and F. Schulze, *J. Am. Chem. Soc.*, *47*, 2002 (1925).

tive until 3.05-3.10 equivalents of phenyllithium had been added. At no time during the addition was there a homogeneous solution. The triphenyltin-lithium was ready for subsequent use as soon as the addition of the phenyllithium solution was completed. These phenomena were confirmed carefully in at least four different runs, and were observed in general in numerous other experiments.

It was found that the rate of addition of the phenyllithium solution to the stannous chloride was particularly critical. If the phenyllithium solution was added too rapidly, Color Test I remained positive throughout the addition and the color changes described above did not take place. Color Test I remained positive even 5 hours after the rapid addition of three equivalents was completed. A dropwise addition, at a rate where each drop can be seen distinctly, was found to give optimum results.

Hydrolysis of reactions involving triphenyltin-lithium. After the desired reaction time had elapsed the mixture was hydrolyzed by pouring it into 400 ml. of saturated ammonium chloride solution contained in a 1 liter beaker. The contents of the beaker were stirred efficiently during the hydrolysis by the use of a magnetic stirrer (*e.g.*, Precision Scientific Co. Mag-Mix, catalog number 65904). Any solid which may have come out of solution upon hydrolysis was filtered off and air-dried. The ether and water layers were separated, the ether layer dried over anhydrous sodium sulfate, and the water layer discarded. After drying, the ethereal solution was filtered from the sodium sulfate, the ether was removed by distillation from a water bath, the last traces of the solvent were removed at water pump pressure, and the residue worked up as required by the nature of the expected product.

It was found that the symmetrical organotin compounds were best recrystallized from benzene, petroleum ether (b.p. 77-120°), or a mixture of both. Unsymmetrical compounds were best recrystallized from ethanol or a mixture of methanol and benzene.

Hydrolysis of triphenyltin-lithium. Triphenyltin-lithium 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 stannous chloride suspended in 100 ml. of ether at -10°. The reaction mixture was hydrolyzed, as soon as the addition of the phenyllithium was completed, by pouring it into 400 ml. of water. Upon hydrolysis the ether layer became orange colored and had an orange solid suspended in it. On standing, a yellow solid precipitated from the ether layer.

The solid recovered on hydrolysis was crystallized from petroleum ether (b.p. 77-120°) to yield 2.1 g. (14.6%) of tetraphenyltin melting at 222-225°[7]. A mixed melting point with an authentic specimen showed no depression.

The ether layer yielded a yellow solid which when crystallized from petroleum ether (b.p. 77-120°) yielded 2.1 g. (10.9%) of hexaphenylditin melting at 226-229°[8]. A mixed melting point with an authentic specimen showed no depression. A mixed melting point with tetraphenyltin melted at 190-200°, showing a drastic depression.

Run 2. A second run carried out exactly as the first led to the recovery of 1.5 g. of tetraphenyltin (10.0%) melting at 224-226° and 2.2 g. of hexaphenylditin (14.0%) melting at 226-228°. Mixed melting points with authentic specimens showed no depression.

Carbonation of triphenyltin-lithium with gaseous carbon dioxide. The theory was developed that in the triphenyltin-lithium preparations there existed an equilibrium between diphenyltin and phenyllithium, on the one hand, and triphenyl-tin-lithium on the other,

$$(C_6H_5)_2Sn + C_6H_5Li \rightleftharpoons (C_6H_5)_3SnLi$$

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[7] D. Goddard and A. E. Goddard, J. Chem. Soc., 121, 256 (1922).

[8] E. Krause and R. Becker, Ber., 53, 173 (1920).

ordinarily far displaced toward the triphenyltin-lithium[9]. Such an equilibrium would help to explain the formation of tetraphenyltin in the reaction of triphenyltin-lithium with benzyl chloride (see pp. 91) by proposing a metal-metal interconversion between triphenylbenzyltin, as formed, and phenyllithium,

$$(C_6H_5)_3SnCH_2C_6H_5 \quad + \quad C_6H_5Li \longrightarrow (C_6H_5)_4Sn \quad + \quad (C_6H_5)_2(C_6H_5CH_2)SnLi$$

to yield tetraphenyltin and a new intermediate. For characterization of the phenyllithium the carbonation reaction was employed.

Triphenyltin-lithium was prepared by addition of 0.135 mole (3 equivalents) of phenyllithium in 162 ml. of ether to 8.54 g. (0.045 mole) of stannous chloride suspended in 100 ml. of ether at -10°. Color Test I was very weakly positive after the addition of the phenyllithium was completed, and the reaction mixture was tan colored. Dry carbon dioxide gas was then passed over the surface of the solution, still stirred in the cold, for 4 hours. The reaction mixture did not change in appearance in any way, and was hydrolyzed by pouring it into 100 ml. of water.

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[9] H. Gilman, L. Summers and R. W. Leeper, _J_. _Org_. _Chem_., _17_, 630 (1952).

On hydrolysis a yellow-brown solid came out of solution. The solid was filtered off and air-dried, and the layers were separated. The ether layer was extracted with three 15 ml. portions of 15% potassium hydroxide solution, and then dried over sodium sulfate. The potassium hydroxide layers were combined with the water layer of the hydrolysis mixture. The water layer was acidified with dilute hydrochloric acid, and the solution became faintly cloudy. The aqueous solution was extracted three times with 25 ml. portions of ether. The portions of ether were combined and dried over sodium sulfate.

The ether was removed from the layer which should contain the benzoic acid leaving a small amount of oily residue. No benzoic acid or addition products of benzoic acid were isolated from the oil.

The solid (10.7 g.) 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. A mixed melting point with an authentic specimen showed no depression.

The ether layer from the hydrolysis yielded a solid on distillation. Crystallization of the solid from petroleum ether (b.p. 77-120°) yielded 2.5 g. (15.9%) of hexaphenylditin melting at 227-230°. A mixed melting point with an authentic specimen showed no depression.

A check run gave essentially the same results, and no benzoic acid or addition products of benzoic acid were isolated. These results tend to eliminate the hypothesis that an equilibrium exists between diphenyltin and phenyllithium, on the one hand, and triphenyltin-lithium on the other.

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. The reaction mixture was then carbonated directly by pouring it onto 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 mixed melting point with an authentic specimen showed no depression.

The ethereal solution was evaporated to dryness, and the oily 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 extracted with 50 ml. of water and filtered hot. Acidification of the aqueous solution with concentrated hydrochloric acid yielded no acid. The petroleum ether solution yielded no tetraphenyltin or hexaphenylditin.

Reaction of triphenyltin-lithium with benzophenone. The purpose for carrying out this reaction was twofold. First, it was used to measure the reactivity of triphenyltin-lithium toward a carbon-oxygen double bond; second, it was used to further test the possibility that triphenyltin-lithium is in equilibrium with diphenyltin and phenyllithium, as previously mentioned. Wittig and co-workers[5] have used this method very successfully in the measurement of the stability of various organometallic complexes.

Triphenyltin-lithium was prepared by the addition of 0.330 mole (3 equivalents) of phenyllithium in 250 ml. of ether to 20.9 g. (0.110 mole) of stannous chloride suspended in 100 ml. of ether at -10°. Color Test I was very weakly positive after the addition of phenyllithium was completed, and the reaction mixture was tan colored. Then 20.0 g. (0.110 mole) of benzophenone was added in one portion. The reaction mixture became chocolate brown and increased in viscosity almost immediately. The ice-salt bath was maintained at -10° while the mixture was stirred for 2 hours. Hydrolysis was carried out as described above.

The solid recovered on hydrolysis was extracted with 500 ml. of petroleum ether (b.p. 77-120°), filtered hot, and the filtrate placed in a refrigerator to cool. On cooling, 3.5 g. (9.5%) of tetraphenyltin melting at 223-225° was obtained. A mixed melting point with an authentic specimen showed no depression.

The ether was removed leaving a yellow oil. On standing the oil solidified. The yellow solid was extracted with 100 ml. of petroleum ether (b.p. 28-36°) at reflux and the mixture was allowed to cool to room temperature. The solid was filtered off and dried while the petroleum ether was distilled from the filtrate leaving a yellow oil. The solid from the petroleum ether extraction was digested with 400 ml. of petroleum ether (b.p. 77-120°), filtered hot, and the filtrate placed in a refrigerator to cool. On cooling, 5.7 g. (14.8%) of hexaphenylditin melting at 226-229° was obtained. A mixed melting point with an authentic specimen showed no depression.

In order to determine the nature of the yellow oil recovered from the petroleum ether extraction a sample of it was reacted with phenylhydrazine to form a phenylhydrazone melting at 135-137° (the phenylhydrazone of benzophenone melts at 137°)[10]. A second sample was reacted with 2,4-dinitrophenylhydrazine to form a 2,4-dinitrophenylhydrazone melting at 236-238° (the 2,4-dinitrophenylhydrazone of benzophenone melts at 239°)[10].

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[10] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds", John Wiley and Sons, Inc., New York, 1948, 3rd Edition, p. 264.

The oil was extracted with 50 ml. of ethanol and filtered hot. The ethanol was removed by distillation at the water pump, and the residue was distilled at reduced pressure (124°/0.8 mm.). Only one fraction was obtained. A recovery of 12.6 g. (60.0%) of benzophenone melting at 46°[10] was made.

During the course of the work-up of the reaction particular attention was paid to the possible recovery of triphenylcarbinol but no trace of this compound was found. A check run was made and essentially the same results were obtained.

Reaction of triphenyltin-lithium with benzalacetophenone. 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 suspended in 100 ml. of ether. To this was added 9.4 g. (0.045 mole) of benzalacetophenone in 50 ml. of benzene. No apparent change took place upon addition or as the reaction progressed. The cooling bath was removed, the mixture was refluxed 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° (mixed melting point) was obtained.

The ether and benzene were removed by distillation leaving a brown gum. The gum was extracted with 225 ml. of methanol and filtered hot. On cooling, an oil came out of solution. Various attempts to crystallize the oil (10.0 g.) proved unsuccessful. In order to determine the nature of the oil a sample of it was reacted with phenylhydrazine to form a phenylhydrazone melting at 116-119° (the phenylhydrazone of benzalacetophenone melts at 120°)[10]. 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°)[10]. From these results it was concluded that the oil was principly unreacted benzalacetophenone.

<u>Preparation of triphenyl-2-hydroxyethyltin</u>. Triphenyltin-lithium was prepared from 8.54 g. (0.045 mole) of stannous chloride and 0.135 mole of phenyllithium in 150 ml. of ether. With the salt-ice bath (-10°) still in place 15.0 g. (750% excess of 0.045 mole) of ethylene oxide in 20 ml. of ether was added. The color 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 (1.3 g.) recovered on hydrolysis was extracted with 150 ml. of 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° (mixed melting point) was obtained.

The ether layer yielded an oil which was extracted with 100 ml. of methanol, and filtered hot. On cooling, a small amount of solid came out of solution. The methanol solution was decanted and the solid was ignored. The methanol was removed by distillation from a water bath, and the residue dissolved in a minimum amount of refluxing petroleum ether (b.p. 77-120°). On cooling, 8.3 g. (44.8%) of triphenyl-2-hydroxyethyltin melting at 66-67°[11] (mixed melting point) was obtained.

Preparation of triphenyl-2-hydroxy-3-chloropropyltin. Triphenyltin-lithium was prepared from 8.54 g. (0.045 mole) of stannous chloride and 0.135 mole of phenyllithium in 147 ml. of ether. With the salt-ice bath (*ca*. -10°) still in place 12.3 g. (0.045 mole plus 200%) of epichlorohydrin was added. 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 (2.6 g.) recovered on hydrolysis was extracted with 200 ml. of petroleum ether (b.p. 77-120°), treated with Norit A, and filtered hot. On cooling, 1.9 g. (9.9%) of

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[11] H. Gilman and C. E. Arntzen, *J. Org. Chem.*, *15*, 994 (1950).

tetraphenyltin melting at 224-226° (mixed melting point) was obtained.

The ether layer yielded an oil which was extracted with 100 ml. of methanol, and filtered hot. On cooling, a small amount of solid came out of solution. The methanol solution was decanted and the solid discarded. 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 triphenyl-2-hydroxy-3-chloropropyltin melting at 94-97° was 8.7 g. (43.5%). This crude product 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. Calcd. for $C_{21}H_{21}OClSn$: Sn, 26.76. Found: Sn, 26.77.

Run 2. This run was carried out exactly as the first. The yield of tetraphenyltin melting at 223-225° was 1.6 g. (8.4%) and of triphenyl-2-hydroxy-3-chloropropyltin melting at 97-99° was 4.7 g. (23.5%).

Reaction of triphenyltin-lithium with trans-stilbene. It was found that triphenylsilyl-potassium possesses sufficient reactivity to add to the carbon-carbon double bond of *trans*-stilbene[12], and this reaction was run to compare the reactivity of the two organometallic intermediates.

Triphenyltin-lithium was prepared from 8.54 g. (0.045 mole) of stannous chloride and 0.135 mole of phenyllithium in 144 ml. of ether. Color Test I was negative after the addition of the phenyllithium solution was completed. Then 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 remained negative throughout the course of the reaction. The mixture was stirred for 72 hours, and carbonated by pouring it onto 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 dried over sodium sulfate. Acidification of the aqueous layer gave 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 recovered.

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[12] T. C. Wu, Doctoral Dissertation, Iowa State College (1952).

Reaction of triphenyltin-lithium with iodine. The triphenyltin-lithium was prepared by reacting 8.54 g. (0.045 mole) of stannous chloride with 0.135 mole of phenyllithium in 125 ml. of ether. Then 11.4 g. (0.045 mole) of iodine in 100 ml. of ether was added, dropwise, to the reaction mixture. At first the iodine color was discharged as the ethereal solution was added but near the end of the addition the iodine color became permanent and was never 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 discharged immediately, and a white solid came out of solution.

The solid recovered on hydrolysis was extracted with 250 ml. of 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[13].

Run 2. This run was carried out exactly as the first except that 17.1 g. (0.0675 mole, 50% excess) of iodine was reacted with 0.045 mole of triphenyltin-lithium.

The solid recovered on hydrolysis was crystallized twice from petroleum ether (b.p. 77-120°) to yield 3.7 g. (23.5%) of hexaphenylditin melting at 226-229° (mixed melting point). The solid recovered from the ether layer was crystallized twice from petroleum ether (b.p. 77-120°) to yield 1.4 g. (6.5%) of triphenyltin iodide melting at 117-119°[14] (mixed melting point).

Run 3. 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 above, the layers were separated, and the ether-xylene layer dried over sodium sulfate.

The dried solution was concentrated to about 75 ml. by distillation and cooled to about 60°. Then 20 ml. of meth-

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

[14] E. Krause, Ber., 51, 912 (1918).

anol 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 recrystallized from petroleum ether (b.p. 77-120°) to yield 1.4 g. (7.3%) of tetraphenyltin melting at 223-225° (mixed melting point).

The mother liquor was evaporated to dryness by pulling a stream of air over the surface of the solution, and the solid residue was crystallized 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 triphenyltin iodide melting at 117-119°. The total yield of triphenyltin iodide was 12.0 g. (56.7%).

<u>Run 4</u>. This run was carried out exactly as the third except that the reflux time was lengthened from 4 hours to 18 hours. The yield of tetraphenyltin was 1.4 g. (7.3%), m. 223-225°, and of triphenyltin iodide was 8.5 g. (40.2%), m. 118-119°.

<u>Run 5</u>. In this run 5.7 g. (0.0225 mole) of iodine in 100 ml. of ether was added, dropwise, to 0.045 mole of triphenyltin-lithium, and the reaction mixture was refluxed for 18 hours. The iodine color was completely discharged. The reaction mixture was hydrolyzed and worked up in the usual manner.

The solid which was recovered on hydrolysis was extracted with 250 ml. of benzene and filtered hot. On cooling, 3.0 g. (20.0%) of hexaphenylditin melting at 332-334° (mixed melting point) was recovered. The mother liquor was evaporated to dryness by pulling a stream of air over the surface of the solution, and the solid residue was crystallized from 200 ml. of petroleum ether (b.p. 77-120°) to yield 6.0 g. of solid melting over the range 195-205°. Further attempts to purify the solid by recrystallization were unsuccessful. Infrared analysis showed the solid to be a mixture of tetraphenyltin and hexaphenylditin.

Reaction of triphenyltin-lithium with oxygen. Triphenyltin-lithium was prepared from 8.54 g. (0.045 mole) of stannous chloride and 0.135 mole of phenyllithium in 135 ml. of ether. Then oxygen was bubbled through the reaction mixture for 2 hours at room temperature, with good stirring, and the mixture was hydrolyzed. The color of the reaction mixture changed from tan to light yellow almost immediately after the admission of the oxygen.

The solid (9.5 g.) recovered on hydrolysis was crystallized from a petroleum ether (b.p. 77-120°)-benzene solvent pair to yield 8.1 g. of material melting over the range 180-190°.

The ether was removed by distillation leaving an oily solid which when crystallized from petroleum ether (b.p.

77-120°) yielded 1.0 g. of material melting over the range 170-190°. The two solids (9.1 g.) were combined and infrared absorption spectra showed the material to be a mixture of hexaphenylditin and tetraphenyltin. No triphenyltin hydroxide was isolated.

Preparation of triphenylbenzyltin. Benzyl chloride is usually the reagent of choice for the characterization of reactive organometallic intermediates, and it was thought that it would prove useful in the characterization of triphenyltin-lithium.

Triphenyltin-lithium was prepared from 8.54 g. (0.045 mole) of stannous chloride suspended in 100 ml. of ether at -10° and 0.135 mole of phenyllithium in 156 ml. of ether. Then, with the salt-ice bath in place, 5.2 g. (0.045 mole) of benzyl chloride in 20 ml. of ether was added. Color Test I was negative before the addition of the benzyl chloride, and was negative 1 minute after its addition. The reaction mixture was stirred for 15 minutes in the cold, refluxed for 1.5 hours, and hydrolyzed.

The solid (4.0 g.) recovered on hydrolysis was extracted with 250 ml. of petroleum ether (b.p. 77-120°), and filtered hot. On cooling, 3.3 g. of tetraphenyltin melting at 223-225° (mixed melting point) was obtained.

The ether layer yielded a yellow oil which was stirred with 15 ml. of ethanol, and the flask containing the mixture was placed on a cake of Dry Ice for 10 minutes. The oil solidified on cooling, and the solvent was decanted into a crystallization dish. The solidified oil was extracted with 100 ml. of methanol and filtered hot. Some of the solid (2.0 g.) did not dissolve in the methanol and it was crystallized from petroleum ether (b.p. 77-120°) to yield 1.9 g. of tetraphenyltin melting at 224-225°. On thorough cooling, the methanol solution yielded 4.6 g. of very crude triphenylbenzyltin melting over the range 80-84°. This was recrystallized from methanol to yield 1.9 g. of triphenylbenzyltin melting at 89-91°[15]. On standing, 2.0 g. of triphenylbenzyltin melting at 89-91° precipitated from the ethanol solution in the crystallization dish. Both triphenylbenzyltin samples were identified by a mixed melting point with an authentic specimen. The total yield of tetraphenyltin was 5.2 g. (36.1% based on the available phenyl groups), and of triphenylbenzyltin was 3.9 g. (19.7%).

Run 2. This run was carried out exactly as the first. The total yield of tetraphenyltin was 5.7 g. (39.6%),

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[15] R. A. Bullard, J. Am. Chem. Soc., 51, 3065 (1929).

and of triphenylbenzyltin was 1.5 g. (7.6%). The results of the two runs were somewhat erratic and it appeared as if some secondary reaction were taking place.

Run 3. This run was made at a lower temperature in order to minimize possible side reactions. Triphenyltinlithium was prepared from 8.54 g. (0.045 mole) of stannous chloride suspended in 100 ml. of ether at -10° and 0.135 mole of phenyllithium in 160 ml. of ether. The ice bath was then replaced by a Dry Ice-acetone bath at -35°. Then 5.7 g. (0.045 mole plus 10%) of benzyl chloride in 30 ml. of ether was added. The reaction mixture was stirred for 0.5 hour while the bath was maintained at -35°, and then for an additional hour while the bath slowly warmed to -10°. The reaction mixture was then hydrolyzed.

The solid (9.1 g.) recovered on hydrolysis was extracted in a Soxhlet with petroleum ether (b.p. 77-120°). A recovery of 8.7 g. of tetraphenyltin (60% based on the available phenyl groups) melting at 223-225° (mixed melting point) was made.

The ether layer yielded a yellow oil which, upon cooling in an ice bath, partially solidified. The solid was filtered off and dried on a suction filter. This solid (3.7 g., m. 88-91°) was crystallized from ethanol, and 3.4 g. (17.2%) of triphenylbenzyltin melting at 90-91° was recovered. Upon working up the remaining oil with the ethanol mother liquor, an additional 0.9 g. (4.5%) of triphenylbenzyltin melting at

90-91° (mixed melting point) was obtained.

Run 4. This run was made to investigate the effect of order of addition upon the relative yield of the products. Diphenyltin was prepared from 8.0 g. (0.042 mole) of stannous chloride suspended in 100 ml. of ether at -10° and 0.084 mole of phenyllithium in 100 ml. of ether. Then 5.7 g. (0.045 mole) of benzyl chloride was added. No apparent reaction took place upon the addition of the halide. Then an additional 0.042 mole of phenyllithium in 50 ml. of ether was added, dropwise and in the cold, to the reaction mixture. The color of the mixture lightened somewhat as the addition of the phenyllithium solution progressed but some red coloration remained when the addition was completed. The mixture was stirred for 15 minutes in the cold and hydrolyzed.

The solid (4.1 g.) recovered on hydrolysis was extracted with petroleum ether (b.p. 77-120°). On cooling, 3.4 g. (25.5%) of tetraphenyltin melting at 227-229° (mixed melting point) was obtained.

The ether layer yielded a yellow oil which was digested with 15 ml. of methanol and then cooled. The oil solidified yielding 3.9 g. (21.1%) of crude triphenylbenzyltin melting at 85-89°. The crude solid was recrystallized from methanol to yield 3.0 g. (16.2%) of triphenylbenzyltin melting at 90-91° (mixed melting point).

From these results it may be concluded that order of addition has little or no effect on the reaction as the yields of tetraphenyltin and triphenylbenzyltin are of the same order of magnitude as in the previous reactions.

Preparation of tetraphenyltin. For this preparation there were used 8.54 g. (0.045 mole) of stannous chloride in 100 ml. of ether, 0.135 mole of phenyllithium in 140 ml. of ether, and finally 10.1 g. (0.045 mole plus 10%) of iodobenzene. The mixture was refluxed for 1.5 hours and hydrolyzed. The solid recovered on hydrolysis was extracted in a Soxhlet with petroleum ether (b.p. 77-120°) for 12 hours. A total of 12.0 g. of tetraphenyltin melting at 224-225° (mixed melting point) was obtained.

An additional 0.7 g. of tetraphenyltin melting at 224-225° was recovered from the ether layer. The total yield of tetraphenyltin was 12.7 g. (66.2%).

Run 2. For this run 8.54 g. (0.045 mole) of stannous chloride in 100 ml. of ether, 0.135 mole of phenyllithium in 139 ml. of ether, and finally 10.1 g. (0.045 mole plus 10%) of iodobenzene were used. The reaction mixture was refluxed for 6 hours, stirred overnight, and hydrolyzed. The solid (25.9 g.) recovered on hydrolysis was refluxed with 300 ml. of benzene overnight, and filtered hot. On cooling, 13.2 g. of tetraphenyltin melting at 227-229° (mixed melting point) was obtained. Concentration of the benzene mother liquor led to the recovery of 2.3 g. of tetraphenyltin melting at 228-229°. The total yield of tetraphenyltin was 15.5 g. (80.8%).

In Table 12 there is a summary of the reaction of triphenyltin-lithium with a series of organic halides. These reactions were carried out as outlined above for benzyl chloride and iodobenzene with minor changes as noted in the table.

Preparation of triphenyl-2,6-dimethylphenyltin. Triphenyltin-lithium was prepared from 8.54 g. (0.045 mole) of stannous chloride and 0.135 mole of phenyllithium in 157 ml. of ether. Color Test I was negative after the addition of the phenyllithium 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 1 minute after the addition was very strongly positive. The ice bath was removed and the reaction mixture brought to reflux. Color Test I remained positive for 90 minutes after reflux started. The reaction mixture was refluxed for a total of 18 hours and hydrolyzed.

The solid (3.4 g.) recovered on hydrolysis was extracted with 300 ml. of petroleum ether (b.p. 77-120°). On cooling, 2.4 g. (12.5%) of tetraphenyltin melting at 227-228° (mixed melting point) was obtained.

Table 12

Preparation of $(C_6H_5)_3SnR$ from $(C_6H_5)_3SnLi$ and RX

Halide[a]	M.P. and yield $(C_6H_5)_3SnR$	M.P. and yield $(C_6H_5)_4Sn$	Reaction conditions
Ethyl iodide	56-58° 36.4%[b]	223-225° 26.9%	1.5 hours at reflux
Bromobenzene		227-229° 82.2%	6 hours at reflux
Chlorobenzene		228-229° 22.9%	6 hours at reflux
p-Iodotoluene[c]			1.5 hours at reflux
Bromomesitylene	155-157° 38.8%[d]	223-225° 12.4%	24 hours at reflux
p-Bromoanisole	151-152° 30.1%	225-226° 17.7%	6 days at 25°
p-Iodochlorobenzene[e]	136-139° 19.7%	222-224° 6.8%	24 hours at reflux
p-Bromodimethylaniline[f]		222-224° 25.5%	1.5 hours at reflux

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[a] None of these halides entered into the halogen-metal interconversion reaction reported below. [b] Recrystallized from ethanol. [c] No pure products were isolated. [d] Recrystallized from an ethanol-benzene solution (6:1). [e] A 14% recovery of this halide was made. [f] Apparently no reaction took place between this halide and triphenyltin-lithium, and 36.7% of the halide was recovered.

The ether layer yielded an oily solid which was recrystallized three times from a minimum amount of ethanol to yield 7.0 g. (34.1%) of triphenyl-2,6-dimethylphenyltin melting at 116-119° (mixed melting point).

Run 2. In order to identify the organometallic compound causing the positive Color Test I after the addition of 2,6-dimethyliodobenzene to triphenyltin-lithium the following reaction was carried out.

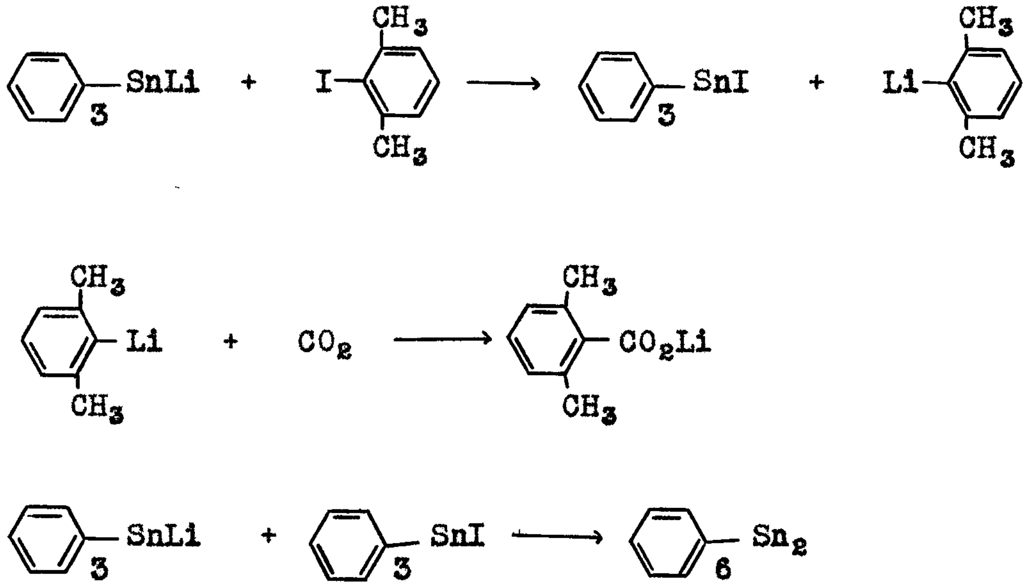
Triphenyltin-lithium was prepared from 8.54 g. (0.045 mole) of stannous chloride and 0.135 mole of phenyllithium in 115 ml. of ether. Color Test I was negative after the addition of the phenyllithium was completed. Then 10.5 g. (0.045 mole) of 2,6-dimethyliodobenzene was added. Color Test I made 10 minutes after the addition of the halide was very strongly positive, and the reaction mixture was carbonated by pouring it onto a Dry Ice-ether slurry with vigorous stirring.

On warming to room temperature the ether solution was decanted from the solid on the bottom of the flask. The solid was extracted with a mixture of water and benzene, and filtered hot. The layers were separated and the benzene layer dried over sodium sulfate. Acidification of the aqueous layer yielded nothing. The benzene was removed by distillation from a steam bath and the residue extracted with 100 ml. of petroleum ether (b.p. 77-120°). On cooling, 2.2

g. of solid melting over the range 195-215° was obtained. This was recrystallized from petroleum ether (b.p. 77-120°) to yield 2.0 g. of solid melting over the range 195-215°. Infrared analysis showed this solid to be a mixture of tetraphenyltin and hexaphenylditin.

The ether layer yielded an oily residue which was extracted with 100 ml. of petroleum ether (b.p. 60-70°). The solid which did not dissolve in the petroleum ether was extracted with 100 ml. of water, and filtered hot. Acidification of the aqueous solution with concentrated hydrochloric acid precipitated the crude 2,6-dimethylbenzoic acid which was recrystallized from petroleum ether (b.p. 60-70°) to yield 1.1 g. (16.2%) of 2,6-dimethylbenzoic acid melting at 116° (mixed melting point). The petroleum ether solution, on thorough cooling, yielded a small amount of solid. This was recrystallized twice from petroleum ether (b.p. 77-120°) to yield 0.7 g. (2.2%) of hexaphenylditin melting at 229-231° (mixed melting point).

Run 3. This run was made on a larger scale in order to isolate and identify all the secondary products. It was concluded that the 2,6-dimethylbenzoic acid arose by way of a halogen-metal interconversion between triphenyltin-lithium and 2,6-dimethyliodobenzene to form triphenyltin iodide and 2,6-dimethylphenyllithium, which on subsequent carbonation yielded the substituted benzoic acid. This reaction path would also explain the origin of the hexaphenylditin which would be brought about by reaction of triphenyltin-lithium with triphenyltin iodide, as formed.



Triphenyltin-lithium (0.10 mole) 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 Tests I made 1 and 10 minutes after addition of the halide were strongly positive. The reaction mixture was carbonated by pouring it onto a Dry Ice-ether slurry 10 minutes after the 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 2 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 crystallized from petroleum ether (b.p. 77-120°) to yield 1.3 g. of solid melting over the range 193-218°.

The ether layer yielded an oily residue which 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 the aqueous solution with concentrated hydrochloric acid precipitated 2.8 g. (18.7%) of 2,6-dimethylbenzoic acid melting at 115-116° (mixed melting point).

The benzene solution was evaporated to dryness and the residue crystallized from petroleum ether (b.p. 77-120°) 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 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 worked up by crystallization 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 obtained. Both compounds were identified by mixed melting points with authentic specimens.

In Table 13 there is a summary of the reaction of triphenyltin-lithium with a series of organic halides which entered into the halogen-metal interconversion reaction. These reactions were carried out as outlined above for 2,6-dimethyliodobenzene with minor changes as noted in the table. Two reactions were carried out between each halide and triphenyltin-lithium; first, to prepare the unsymmetrical organotin compound; second, to indirectly identify the organolithium compound formed during the halogen-metal interconversion reaction.

Preparation of hexaphenylditin. For this preparation 4.77 g. (0.023 mole) of stannous chloride in 100 ml. of ether, 0.069 mole of phenyllithium in 78 ml. of ether, and finally 8.86 g. (0.023 mole) of triphenyltin chloride in 250 ml. of ether were used. The reaction mixture was refluxed for 1.5 hours and hydrolyzed. The solid recovered on hydrolysis was extracted with 800 ml. of petroleum ether (b.p. 77-120°).

Table 13

Reaction of $(C_6H_5)_3SnLi$ with RX, Followed by Carbonation with Dry Ice

Halide	M.P. and yield $(C_6H_5)_3SnR$	M.P. and yield $(C_6H_5)_4Sn$	Reaction conditions	M.P. and yield acid	M.P. and yield $(C_6H_5)_3SnR$
2,4-Dimethyliodobenzene	112-115° 42.7%[a]	223-225° 13.0%	17 minutes at -10°	125-126° 9.3%[e]	113-115° 13.3%
2,5-Dimethyliodobenzene	97-99° 43.0%[a]	223-225° 8.3%	17 minutes at -10°	131-132° 3.7%[e]	96-99° 19.5%
o-Iodotoluene	163-165° 25.3%[b]	223-225° 24.5%	18 hours at reflux	103-104° 11.5%[e]	163-164° 19.2%
Iodomesitylene	156-158° 13.7%[b]	224-225° 7.8%	24 hours at reflux	152-155° 20.3%[f]	c
o-Iodoanisole	129-130° 24.3%[a]	d	17 minutes at -10°	100-102° 4.4%[e]	129-130° 12.1%

[a] Recrystallized from ethanol. [b] Recrystallized from an ethanol-benzene solution (6:1). [c] No unsymmetrical compound was isolated in the carbonation reaction. [d] No attempt was made to recover the tetraphenyltin. [e] Reaction time before carbonation was 2 minutes. [f] Reaction time before carbonation was 10 minutes.

On cooling, 3.6 g. of hexaphenylditin melting at 229-231° (mixed melting point) was obtained.

The ether layer yielded a solid which was crystallized from 800 ml. of petroleum ether (b.p. 77-120°). On cooling, 4.1 g. of hexaphenylditin melting at 229-231° was obtained. The total yield of hexaphenylditin was 7.7 g. (52.8%).

Run 2. For this preparation 8.54 g. (0.045 mole) of stannous chloride in 100 ml. of ether, 0.135 mole of phenyllithium in 152 ml. of ether, and finally 17.3 g. (0.045 mole) of triphenyltin chloride in 100 ml. of benzene were used. The reaction mixture was refluxed for 24 hours and hydrolyzed. The solid recovered on hydrolysis was extracted with 200 ml. of benzene for 3 hours, and filtered hot. On cooling, 9.4 g. of hexaphenylditin melting at 233-234° (mixed melting point) was obtained. Concentration of the mother liquor led to the recovery of 2.9 g. of hexaphenylditin melting at 232-234°.

The ether layer yielded a solid which was crystallized twice from a minimum amount of benzene to yield 4.6 g. of hexaphenylditin melting at 233-234° (mixed melting point). The total yield of hexaphenylditin was 16.9 g. (53.7%).

Preparation of triphenylsilyltriphenyltin. For this preparation there were used 8.54 g. (0.045 mole) of stannous chloride in 100 ml. of ether, 0.135 mole of phenyllithium in 101 ml. of ether, and finally 13.3 g. (0.045 mole) of triphenylchlorosilane in 100 ml. of ether. The color of the reaction mixture changed from tan to gray on addition of the silane. The mixture was refluxed for 3 hours and hydrolyzed.

The solid recovered on hydrolysis was extracted with benzene. On cooling, 21.3 g. of white solid melting at 282-287° was obtained. This was recrystallized from benzene to yield 19.5 g. (71.3%) of triphenylsilyltriphenyltin melting at 289-291°.

Anal. Calcd. for $C_{36}H_{30}SiSn$: Si, 4.61; Sn, 19.48. Found: Si, 5.09; Sn, 19.61.

A mixed melting point with a specimen prepared later by the reaction of triphenylsilyl-potassium with triphenyltin chloride showed no depression[12].

Reaction of triphenyltin-lithium with triphenylsilane. Triphenyltin-lithium was prepared from 3.65 g. (0.0193 mole) of stannous chloride in 100 ml. of ether and 0.0580 mole of phenyllithium in 52 ml. of ether. To this was added 5.0 g. (0.0193 mole) of triphenylsilane[16] in 100 ml. of ether, and the reaction mixture was refluxed for 3 hours and hydrolyzed.

The solid recovered on hydrolysis was extracted in a Soxhlet with benzene. A total of 1.7 g. (20.0%) of tetraphenyltin melting at 225-227° (mixed melting point) was obtained.

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[16] G. E. Dunn, Doctoral Dissertation, Iowa State College (1951).

The ether was removed leaving a yellow oil. This was extracted with 100 ml. of petroleum ether (b.p. 60-70°) and filtered hot. The solid which did not go into the petroleum ether was combined with the solid which came out of the petroleum ether on cooling, to yield 1.7 g. (32.0%) of triphenylsilanol melting at 148-151°[17] (mixed melting point).

Reaction of triphenyltin-lithium with triphenylchloromethane. For this preparation there was used 8.54 g. (0.045 mole) of stannous chloride in 100 ml. of ether, 0.135 mole of phenyllithium in 121 ml. of ether, and finally 12.0 g. (0.045 mole) of triphenylchloromethane in 100 ml. of ether. The mixture was refluxed for 3 hours and hydrolyzed.

The solid recovered on hydrolysis was extracted with 250 ml. of chloroform, and filtered hot. Then 250 ml. of ethanol was added to the filtrate and the solution placed in a refrigerator. On cooling, 14.5 g. of solid, which when heated turned red at 165° and melted at 174-179°, was obtained. This solid was recrystallized from a chloroform-ethanol solvent pair to yield 12.8 g. of material which when heated turned red at 169° and melted over the range 174-190°. Further attempts to purify this material by recrystallization failed. It has been reported that triphenylstannyltriphenyl-

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[17] H. Marsden and F. Kipping, J. Chem. Soc., 93, 198 (1908).

methane turns red at 260° and melts at 272-273°[18]. From these results it may be concluded that some triphenylstannyltriphenylmethane was formed, but that it was contaminated by secondary products, probably tetraphenyltin.

The ether layer yielded 1.3 g. of solid which turned red at 170° and melted at 172-178°. Attempts to purify this material failed.

Run 2. A second run carried out as the first was made with a fresh sample of triphenylchloromethane (Eastman Kodak white label, m.p. 112-113°) and, unfortunately, the results obtained were the same.

Reaction of triphenyltin-lithium with triphenylmethane. Triphenyltin-lithium was prepared from 8.54 g. (0.045 mole) of stannous chloride in 100 ml. of ether and 0.130 mole (2.9 equivalents) of phenyllithium in 121 ml. of ether. To this was added 11.0 g. (0.045 mole) of triphenylmethane in 50 ml. of ether. The reaction mixture was then refluxed for 18 hours. Color Test I remained negative for the entire reflux time. On completion of reflux the reaction mixture was carbonated by pouring it onto a Dry Ice-ether slurry with good mixing.

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[18] J. C. Bailie, Iowa State Coll. J. Sci., 14, 8 (1939).

On warming to room temperature the ethereal mixture was extracted with 100 ml. of water. The solid which did not go into solution was filtered off and air-dried. The layere were separated, the ether layer was dried over sodium sulfate, and the water layer acidified with dilute hydrochloric acid. No solid precipitated from the water solution on acidification.

The solid recovered on hydrolysis was extracted with 200 ml. of petroleum ether (b.p. 77-120°), and filtered hot. A total of 1.5 g. of tetraphenyltin (10.0%) melting at 224-226° (mixed melting point) was obtained.

The ether layer yielded a white solid which was extracted with 100 ml. of methanol, and filtered hot. The solid which did not go into solution was crystallized from petroleum ether (b.p. 77-120°) to yield 2.2 g. of hexaphenylditin (14.0%) melting at 227-229°. On cooling, 9.0 g. of triphenylmethane (81.8% recovery) melting at 93-94° was recovered from the methanol solution. Mixed melting points of the last two compounds with authentic specimens showed no depression.

<u>Preparation of bromobenzene-free phenyllithium</u>. In a 1 liter flask were placed 71.0 g. (0.2 mole) of diphenylmercury, 5.6 g. (0.8 g. atom) of lithium wire cut into 1/8 inch lengths, and 400 ml. of dry benzene. The mixture was stirred vigorously and maintained at an internal temperature

of 75° for 5 days. Then the benzene was distilled and, after the flask had cooled, 400 ml. of ether was added. The mixture was placed in a refrigerator for 12 hours. The ethereal solution was carefully decanted into a 500 ml. graduated dropping funnel leaving the black sludge behind. The yield, determined by acid titration of a 5 ml. aliquot, was 0.312 mole (78.5%)[19]. All of the above operations were carried out under nitrogen.

Preparation of bromobenzene-free triphenyltin-lithium in ether. The bromobenzene-free phenyllithium prepared above was used to synthesize three 0.033 mole runs of triphenyltin-lithium. The runs were carried out exactly as in all the previous preparations. It was noted that the color changes previously outlined took place once again, but that they were not as dramatic. The change in color from orange at the one equivalent's point to the deep red of the two equivalents' point was a gradual one, and once passed the two equivalents' point the change from deep red to the tan color present at the three equivalents' point takes place more promptly. In each run Color Test I was negative after the addition of the phenyllithium solution was completed.

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[19] Using essentially the same method W. Schlenk and J. Holtz, Ber., 50, 273 (1916) prepared phenyllithium but no yield was quoted.

Run 1. Triphenyltin-lithium was prepared from 6.27 g. (0.033 mole) of stannous chloride and 0.099 mole of bromobenzene-free phenyllithium in 135 ml. of ether. With the salt-ice bath (-10°) still in place, 15.0 g. 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 mixture was stirred for 1 hour with the cooling bath in place and hydrolyzed.

The solid (3.2 g.) recovered on hydrolysis was extracted with 150 ml. of petroleum ether (b.p. 77-120°), and filtered hot. On cooling, 1.3 g. (9.2%) of tetraphenyltin melting at 223-225° (mixed melting point) was obtained.

The ether layer yielded an intractable oil which could not be solidified though many different approaches were tried. This may have been due to the presence of some unreacted diphenylmercury which has a solubility in organic solvents similar to that of the expected product, triphenyl-2-hydroxyethyltin.

Run 2. As before, 0.033 mole of triphenyltin-lithium was prepared from 6.27 g. (0.033 mole) of stannous chloride and 0.099 mole of phenyllithium in 135 ml. of ether. Then 4.2 g. (0.033 mole) of benzyl chloride was added. Color Test I remained negative. The reaction mixture was refluxed for 1.5 hours and hydrolyzed.

The solid (2.8 g.) recovered on hydrolysis was extracted with 150 ml. of petroleum ether (b.p. 77-120°), and filtered hot. On cooling, 1.5 g. of tetraphenyltin melting at 223-225° (mixed melting point) was obtained.

The ether layer yielded an oil. To this oil was added 15 ml. of ethanol and the solution was permitted to cool slowly. The solid recovered by this treatment was recrystallized from 150 ml. of petroleum ether (b.p. 77-120°) to yield 0.5 g. of tetraphenyltin melting at 223-225°. Total yield of tetraphenyltin was 2.0 g. (14.2%).

To the ethanol mother liquor was added 75 ml. of methanol, and the mixture was placed on a block of Dry Ice for 10 minutes. The filtrate was then poured into a crystallization dish leaving most of the gummy solid behind; the filtrate was allowed to stand overnight. In this manner, 4.3 g. of crude triphenylbenzyltin melting at 81-84° was obtained. This crude product was recrystallized from methanol to yield 2.1 g. (14.4%) of triphenylbenzyltin melting at 89-91° (mixed melting point).

Run 3. Finally, 0.033 mole of triphenyltin-lithium was prepared from 6.27 g. (0.033 mole) of stannous chloride and 0.099 mole of phenyllithium in 135 ml. of ether. Then 6.6 g. (0.033 mole) of bromomesitylene was added. Color Test I remained negative. The reaction mixture was refluxed for 24 hours and hydrolyzed.

The solid (3.4 g.) recovered on hydrolysis was extracted with 150 ml. of petroleum ether (b.p. 77-120°), and filtered hot. On cooling, 1.3 g. of tetraphenyltin melting at 223-225° (mixed melting point) was obtained.

The ether layer yielded an oil which was dissolved in 100 ml. of methanol plus 50 ml. of benzene by refluxing the mixture for 1 hour. On cooling, a small amount of solid came out of solution. This solid was recrystallized from 50 ml. of petroleum ether (b.p. 77-120°) to yield 1.2 g. of tetraphenyltin melting at 224-225°. The total yield of tetraphenyltin was 2.5 g. (17.7%).

The methanol-benzene mother liquor was evaporated to dryness on a water bath and the residue was extracted with 100 ml. of methanol and filtered hot. On cooling, 4.6 g. (30.0%) of triphenylmesityltin melting at 155-157° (mixed melting point) was obtained.

It will be noted that in all three runs some tetraphenyltin was isolated, and the yield increased as the reaction time was lengthened. Apparently part or all of the tetraphenyltin isolated in previous runs may arise from some reaction path other than that of unreacted bromobenzene combining with triphenyltin-lithium as formed.

Preparation of triphenyltin hydride[5]. In a 250 ml. flask were placed 4.8 g. (0.01 mole) of triphenyltin iodide in 50 ml. of ether and 0.5 g. (0.01 mole plus 25%) of lithium aluminum hydride. The mixture was refluxed for 1 hour. Color Test I was positive at the end of the reflux period. Then some hydroquinone was cautiously added. A heavy white precipitate formed accompanied by a vigorous evolution of gas. The mixture was then extracted with 100 ml. of saturated sodium hydroxide solution and all the solid dissolved. The aqueous layer was removed by means of a pipet and the ether layer dried over sodium sulfate. All of the above was carried out under nitrogen.

The ethereal solution was filtered through a sintered glass plate into a distilling flask, and the ether was removed by distillation from a water bath. The residual oil was filtered through a sintered glass plate into a second distilling flask, and distilled under reduced pressure directly into a glass ampule. The yield of triphenyltin hydride was 1.8 g. (51.6%); b.p. 151°/0.05 mm. All of the above was carried out under a nitrogen atmosphere. Using this same method Wittig and co-workers[5] prepared triphenyltin hydride in 43% yield.

Run 2. This run was carried out exactly as the first. The yield of triphenyltin hydride was 1.8 g. (51.6%); b.p. 172°/0.5 mm.

Reaction of triphenyltin hydride with methyllithium[5]. A 250 ml. flask was equipped with a magnetic stirrer, a 100 ml. graduated dropping funnel, a nitrogen inlet tube and a gas outlet tube. The gas outlet tube was attached to a gas bubble counter filled with concentrated sulfuric acid; the counter was, in turn, attached to a Dumas tube filled with fine cupric oxide; the tube was attached to water- and carbon dioxide-absorption tubes used in micro carbon and hydrogen quantitative analysis.

About 50 ml. of ether was placed in the flask, gentle stirring was begun, and a very slow stream (ca. 1 bubble every 3 seconds) of nitrogen gas was passed through the entire system for 1 hour. The long burner under the Dumas tube was turned on during the sweep-through of the gas. The absorption tubes were then weighed.

After the absorption tubes were returned to their positions 1.6 g. (0.0046 mole) of triphenyltin hydride was added to the reaction flask and 0.0046 mole of methyllithium in 35 ml. of ether was placed in the dropping funnel. The same rate of nitrogen sweep-through and stirring as before were maintained while the methyllithium solution was added dropwise. There was no decernable increase in the bubble rate during the addition of the methyllithium solution and a white solid precipitated. No tan colored precipitate or yellow solution formed (indicative of triphenyltin-lithium). The system was swept with nitrogen for 0.5 hour after the addition was completed. The absorption tubes were then reweighed and, within limits of allowable error, there was no change in weight for either tube. A Color Test I made 1 hour after the addition was completed was negative.

The ethereal solution was filtered from the white solid, extracted with 50 ml. of water, and dried over sodium sulfate. The ether layer yielded an oil which was digested with 50 ml. of methanol, and the mixture was allowed to cool slowly. On cooling, 0.4 g. of solid melting over the range 170-225° was recovered. This solid was recrystallized from 25 ml. of petroleum ether (b.p. 77-120°) to yield 0.35 g. (25.0%) of tetraphenyltin melting at 224-225° (mixed melting point). The methanol was removed by distillation leaving an oil. Thorough cooling in a Dry Ice bath yielded an oily solid. This mass was extracted twice with 5 ml. portions of cold ethanol to yield 0.5 g. of crude triphenylmethyltin melting at 48-54°. This crude solid was recrystallized from 5 ml. of ethanol to yield 0.3 g. (18.1%) of triphenylmethyltin melting at 59-61°[20] (mixed melting point).

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[20] R. H. Bullard and W. R. Robinson, J. Am. Chem. Soc., 49, 1368 (1927).

Run 2. This run was carried out precisely as the first. Once again no gas evolution was noted and the weight of the gas absorption tubes remained constant. In this run 0.35 g. (25.0%) of tetraphenyltin melting at 222-225° and 0.25 g. (15.0%) of triphenylmethyltin melting at 60-61° were obtained. Both compounds were identified by mixed melting points with authentic specimens.

Studies on the nature and reactions of other organotin-lithium complexes in ether

Preparation of tri-p-tolyltin-lithium in ether. In order to explore the scope of the reaction of RM (where R may be alkyl or aryl and M may be Li, Na or MgX) with stannous chloride, a series of compounds was reacted with the tin halide, the first of these being p-tolyllithium. The calculated volume of solution necessary to give 0.135 mole of p-tolyllithium[1] was added dropwise, over a period of about 1.5 hours, 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 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 3.0 equivalents of p-tolyllithium had been added. The tri-p-tolyltin-lithium was ready for subsequent use as soon as the addition of the p-tolyllithium solution was completed.

Preparation of tetra-p-tolyltin. For this preparation there were used 8.54 g. (0.045 mole) of stannous chloride in 100 ml. of ether, 0.135 mole of p-tolyllithium in 141 ml. of ether, and finally 10.8 g. (0.045 mole plus 10%) of p-iodotoluene in 50 ml. of ether. The mixture was refluxed for 1.5 hours and hydrolyzed. The solid recovered on hydrolysis was extracted with benzene. On cooling, 11.1 g. of tetra-p-tolyltin melting at 233-235°[21] (mixed melting point) was obtained. Concentration of the benzene mother liquor led to the recovery of 4.3 g. of tetra-p-tolyltin melting at 232-234°.

An additional 1.0 g. of tetra-p-tolyltin melting at 232-234° was recovered from the ether layer. The total yield of tetra-p-tolyltin was 16.4 g. (74.2%).

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[21] P. Pfeiffer, Z. anorg. Chem., 68, 122 (1910).

Reaction of tri-p-tolyltin-lithium with 2,6-dimethyliodobenzene. Tri-p-tolyltin-lithium was prepared from 8.54 g. (0.045 mole) of stannous chloride and 0.135 mole of p-tolyllithium in 126 ml. of ether. Color Test I was negative after the addition of the p-tolyllithium solution was completed. Then 10.5 g. (0.045 mole) of 2,6-dimethyliodobenzene in 40 ml. of ether was added to the reaction mixture. No apparent change took place, but a Color Test I made 5 minutes after the addition was very strongly positive. The reaction mixture was then carbonated by pouring it onto a Dry Ice-ether slurry with vigorous stirring.

On warming to room temperature the ether solution was decanted from the solid on the bottom of the flask. The solid was extracted with 100 ml. of petroleum ether (b.p. 77-120°) and filtered hot. On cooling, 1.8 g. of solid melting over the range 210-215° was obtained. This was recrystallized from 50 ml. of petroleum ether (b.p. 77-120°) to yield 1.5 g. of tetra-p-tolyltin melting at 231-233° (mixed melting point).

The ether layer yielded an oily residue which was extracted with 100 ml. of petroleum ether (b.p. 77-120°). The solid which did not dissolve in the petroleum ether was extracted with 100 ml. of 5% potassium hydroxide solution, and filtered hot. Acidification of the aqueous solution with concentrated hydrochloric acid precipitated the crude 2,6-

dimethylbenzoic acid. This crude acid was recrystallized from petroleum ether (b.p. 60-70°) to yield 1.6 g. (23.7%) of 2,6-dimethylbenzoic acid melting at 115-116° (mixed melting point). The petroleum ether solution, on thorough cooling, yielded 0.2 g. of tetra-p-tolyltin melting at 233-235°. The total yield of tetra-p-tolyltin was 1.7 g. (7.8%).

Preparation of tri-m-tolyltin-lithium in ether. The calculated volume of solution necessary to give 0.135 mole of m-tolyllithium[1] was added dropwise, over a period of about 1.5 hours, to 8.54 g. (0.045 mole) of finely ground stannous chloride suspended in 100 ml. of ether at -10°.

The phenomena which occurred during the addition of the m-tolyllithium were as follows: 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 3.0 equivalents of m-tolyllithium had been added. The tri-m-tolyltin-lithium was ready for subsequent use as soon as the addition of the m-tolyllithium solution was completed.

Preparation of tetra-m-tolyltin. For this preparation there were used 8.54 g. (0.045 mole) of stannous chloride in 100 ml. of ether at -10°, 0.135 mole of m-tolyllithium in 141 ml. of ether, and finally 7.8 g. (0.045 mole) of m-bromotoluene in 20 ml. of ether. The mixture was refluxed for 24 hours and hydrolyzed. The solid (23.9 g.) 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°[22]. Concentration of the methanol-benzene mother liquor led to the recovery of an additional 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 in ether. The calculated volume of solution necessary to give 0.135 mole of o-tolyllithium[1] was added dropwise, over a period of about 1.5 hours, to 8.54 g. (0.045 mole) of finely ground anhydrous stannous chloride suspended in 100 ml. of ether at -10°.

The phenomena which occurred during the addition of the o-tolyllithium 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 o-tolyllithium, orange at 1.0 equivalent, deep red-brown at 2.0 equivalents, deep red-brown at 2.5 equivalents, red-brown at 2.8 equivalents, and deep brown at 3.0 equivalents. Color Test I remained negative until 3.1 equivalents of o-tolyllithium had been added. The tri-o-tolyltin-lithium

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[22] E. Krause and R. Becker, Ber., 53, 185 (1920).

was ready for subsequent use as soon as the addition of the o-tolyllithium solution was completed.

Preparation of tetra-o-tolyltin. For this preparation there were used 8.54 g. (0.045 mole) of stannous chloride in 100 ml. of ether at -10°, 0.135 mole of o-tolyllithium in 150 ml. of ether, and finally 10.8 g. (0.045 mole plus 10%) of o-iodotoluene. 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, and 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[23] and a sample was analyzed.

Anal. Calcd. for $C_{42}H_{42}Sn$: 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.

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[23] H. Morris, W. Byerly and P. W. Selwood, J. Am. Chem. Soc., 64, 1727 (1942).

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°[24] (mixed melting point) was obtained.

Preparation of tri-o-tolylbenzyltin. For this preparation there were used 8.54 g. (0.045 mole) of stannous chloride in 100 ml. of ether at -10°, 0.135 mole of o-tolyllithium in 150 ml. of ether, and finally 5.9 g. (0.045 mole plus 10%) of benzyl chloride. The mixture was brought to reflux and a gradual change in color from red to dark yellow took place. The mixture was refluxed for 5 hours, stirred overnight at room temperature, and hydrolyzed. The white solid recovered on hydrolysis was extracted with 500 ml. of benzene. The benzene solution was concentrated by distillation to about 250 ml. On cooling, 6.5 g. (37.6%) of hexa-o-tolylditin melting at 298-300° was obtained from the distillate. A mixed melting point with a sample of hexa-o-tolylditin isolated in the previous experiment showed no depression.

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

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[24] E. Krause and M. Schmitz, Ber., 52, 2159 (1919).

out of the mixture. It was filtered off, and crystallized from a benzene-methanol solution to yield 0.7 g. of tetra-o-tolyltin melting at 214-215° (mixed melting point).

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 & 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°. 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 benzene-methanol solution. A total of 0.5 g. (2.3%) of tri-o-tolylbenzyltin melting at 105-107° (mixed melting point) was obtained.

Attempted preparation of tri-p-dimethylaminophenyltin-lithium in ether. The calculated volume of solution necessary to give 0.135 mole of p-dimethylaminophenyllithium was added, dropwise, to 8.54 g. (0.045 mole) of finely ground anhydrous stannous chloride suspended in 100 ml. at -10°.

The phenomena which occurred during the addition of the p-dimethylaminophenyllithium were as follows: the first few drops produced a yellow color. The color changed rapidly and was pea green at 0.2 equivalent of p-dimethylaminophenyllithium, pea green at 0.5 equivalent, yellow at 1.0 equivalent. At this point Color Test I became positive and remained so for 1 hour. At 1.8 equivalents the color was golden, the ice bath was removed, and Color Test I remained positive for 2 hours. At 2.3 equivaltnts the color was tan and Color Test I remained positive even after 72 hours. At this point the reaction was abandoned because none of the third equivalent was taken up after 72 hours.

Preparation of tri-n-butyltin-lithium in ether. The general procedure which was used for the preparation of tri-n-butyltin-lithium on a 0.045 mole scale was as follows: the calculated volume of solution necessary to give 0.135 mole of n-butyllithium[8,25] was added dropwise, over a period of about 2.5 hours, to 8.54 g. (0.045 mole) of finely ground anhydrous stannous chloride suspended in 100 ml. of ether at -10°.

The phenomena which occurred during the addition of the n-butyllithium were as follows: the first few drops produced a yellow color. The color gradually increased in intensity and was light orange at 0.5 equivalent of n-butyllithium, orange at 1.0 equivalent, red at 1.5 equivalents, deep red at

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[25] H. Gilman and co-workers, J. Am. Chem. Soc., 71, 1499 (1949).

2.0 equivalents, deep red at 2.5 equivalents, deep brown at 2.8 equivalents, and deep brown at 3.0 equivalents. Color Test I for organometallic compounds remained negative until 2.0 equivalents of n-butyllithium had been added. At the 2.0 equivalents' point Color Test I became positive and remained positive for the rest of the addition[26]. Color Test II for very reactive organometallic compounds[27] remained negative until exactly 3.0 equivalents of n-butyllithium had been added. At no time during the addition was there a homogeneous solution. The tri-n-butyltin-lithium was ready for subsequent use about 15 minutes after the addition of the n-butyllithium solution was completed. These phenomena were confirmed carefully in at least four different runs, and were observed in general in other experiments.

Preparation of tetra-n-butyltin. Tri-n-butyltin-lithium was prepared by the addition of 0.135 mole (3 equivalents) of n-butyllithium in 112 ml. of ether to 8.54 g. (0.045 mole) of stannous chloride suspended in 100 ml. of ether at -10°. To this preparation there was then added 9.1 g. (0.045 mole plus 10%) of n-butyl iodide, still in the cold. The brown color

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[26] Color Test I at this point was not the usual dark green color but was remindful of the blue of Michler's hydrol.

[27] H. Gilman and J. Swiss, J. Am. Chem. Soc., 62, 1847 (1940).

of the reaction mixture changed to bright yellow immediately upon the addition of the halide, and Color Test I was negative 5 minutes after its addition. The reaction mixture was stirred for 15 minutes in the cold, refluxed for 3 hours, and hydrolyzed as described above.

The ether layer yielded about 15 ml. of a water-like liquid which was distilled under reduced pressure to yield 8.2 g. (52.2%) of tetra-n-butyltin distilling at 127°/1.7 mm.; n_D^{20} 1.4727[28].

Preparation of tri-n-butylphenyltin. Tri-n-butyltinlithium was prepared by the addition of 0.30 mole of n-butyllithium in 336 ml. of ether to 18.96 g. (0.10 mole) of stannous chloride suspended in 150 ml. of ether at -10°. To this preparation there was then added 20.4 g. (0.10 mole) of iodobenzene in 35 ml. of ether. The reaction mixture was stirred for 15 minutes in the cold, refluxed for 24 hours, and hydrolyzed.

The ether layer yielded a water-like liquid which was distilled under reduced pressure, and two fractions were collected. Fraction I distilled at 70-87°/0.1 mm., weighed 10.0 g., n_D^{20} 1.4780. Fraction II distilled at 94-110°/0.1

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[28] W. J. Jones and co-workers, J. Chem. Soc., 39 (1935).

mm., weighed 15.4 g., n_D^{20} 1.5094. Fraction II was redistilled under reduced pressure to yield a forerun distilling at 108-136°/0.6 mm., and 10.0 g. (27.6%) of tri-n-butylphenyltin distilling at 139°/0.6 mm., n_D^{20} 1.5155.

Anal. Calcd. for $C_{18}H_{32}Sn$: Sn, 32.33. Found: Sn, 32.37.

The forerun was combined with Fraction I which was then redistilled under reduced pressure to yield 7.2 g. (27.8%) of tetra-n-butyltin distilling at 109°/0.5 mm., n_D^{20} 1.4731.

Preparation of triethyltin-lithium in ether. The ethyllithium solution, about 1 M, was prepared as described above for n-butyllithium. The calculated volume of this solution necessary to give 0.135 mole of ethyllithium was added, dropwise, over a period of 2.5 hours, to 8.54 g. (0.045 mole) of finely ground anhydrous stannous chloride suspended in 100 ml. of ether at -10°.

The phenomena which occurred during the addition of the ethyllithium solution were as follows: the first few drops produced a yellow color. This color gradually increased in intensity and was light orange at 0.5 equivalent of ethyllithium, orange at 1.0 equivalent, red at 1.5 equivalents, deep red at 2.0, 2.5, and 3.0 equivalents. Color Test I remained negative until 2.0 equivalents of ethyllithium had been added. At the 2.0 equivalents' point Color Test I became positive and remained positive for the remainder of the addition[28]. Color Test II remained negative until exactly 2.5 equivalents of ethyllithium had been added, and was positive from this point to the completion of the addition. At no time during the addition was there a homogeneous solution. The triethyltin-lithium was ready for subsequent use 15 minutes after the addition of the ethyllithium solution was completed.

Preparation of tetraethyltin. Triethyltin-lithium was prepared by the addition of 0.135 mole (3 equivalents) of ethyllithium in 162 ml. of ether to 8.54 g. (0.045 mole) of stannous chloride suspended in 100 ml. of ether. To this preparation there was then added 10.0 g. (0.09 mole, 100% excess 0.045 mole) of ethyl bromide, still in the cold. The deep red color of the reaction mixture immediately changed to dark grey. The mixture was stirred overnight and hydrolyzed.

The ether layer yielded a water-like liquid which was distilled to yield 7.3 g. (68.6%) of tetraethyltin distilling at 178.5°, n_D^{20} 1.4691[29].

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[29] L. L. Gershbein and V. N. Ipatieff, J. Am. Chem. Soc., 74, 1540 (1952).

Run 2. This run was carried out exactly as the first. The yield of tetraethyltin was 7.7 g. (72.6%); b.p. 177°, n_D^{20} 1.4691.

Preparation of compounds for proof of structure

Preparation of 2,4-dimethylbenzoic acid. On a Dry Ice-ether slurry was dropped, with vigorous stirring, 0.048 mole of 2,4-dimethylphenyllithium[30] in 98 ml. of ether. On warming to room temperature the mixture was extracted once with 100 ml. of water and once with 50 ml. of 15% potassium hydroxide solution. The aqueous layers were combined and warmed on a steam plate for 1 hour to remove any traces of ether. Upon neutralization of the aqueous solution with concentrated hydrochloric acid, the crude 2,4-dimethylbenzoic acid precipitated from solution. This crude acid was crystallized from an ethanol-water solution to yield 6.4 g. (87.8%) of 2,4-dimethylbenzoic acid melting at 124-126°[31].

Preparation of triphenyl-2,4-dimethylphenyltin. In a 500 ml. flask was placed 19.25 g. (0.050 mole) of triphenyl-

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[30] Prepared in 99.4% yield by refluxing 23.2 g. (0.10 mole) of 2,4-dimethyliodobenzene (Eastman Kodak white label) in 200 ml. of ether with 1.7 g. (0.2 g. atom plus 20%) of sliced lithium wire for 1 hour.

[31] O. Jacobsen, Ber., 11, 18 (1878); W. H. Perkin and J. F. S. Stone, J. Chem. Soc., 127, 2283 (1925).

tin chloride in 100 ml. of ether. To this was added, dropwise and with good stirring, 0.050 mole of 2,4-dimethylphenyllithium in 102 ml. of ether. The reaction mixture was stirred for 2 hours and hydrolyzed. The layers were separated and the ether layer dried over sodium sulfate.

The ether layer yielded an oil which was digested with 25 ml. of methanol, and the oil solidified after several minutes' refluxing. The methanol solution was decanted, and the solid was recrystallized twice from a methanol-benzene solution to yield 16.2 g. (71.2%) of triphenyl-2,4-dimethylphenyltin melting at 113-115°.

Anal. Calcd. for $C_{26}H_{24}Sn$: Sn, 26.08. Found: Sn, 25.97.

Preparation of 2,5-dimethylbenzoic acid. On a Dry Ice-ether slurry was dropped, with vigorous stirring, 0.045 mole of 2,5-dimethylphenyllithium[32] in 92 ml. of ether. On warming to room temperature the mixture was extracted once with 100 ml. of water and once with 50 ml. of 15% potassium hydroxide solution. The aqueous layers were combined and warmed on a steam plate for 1 hour. Upon neutralization of

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[32] Prepared in 96.5% yield by refluxing 23.2 g. (0.10 mole) of 2,5-dimethyliodobenzene (Eastman Kodak white label) in 200 ml. of ether with 1.7 g. (0.2 g. atom plus 20%) of sliced lithium wire for 1 hour.

the aqueous solution with concentrated hydrochloric acid the crude 2,5-dimethylbenzoic acid precipitated from solution. This crude acid was crystallized from an ethanol-water solution to yield 6.5 g. (96.5%) of 2,5-dimethylbenzoic acid melting at 131-132°[33].

<u>Preparation of triphenyl-2,5-dimethylphenyltin</u>. In a 500 ml. flask was placed 19.25 g. (0.050 mole) of triphenyltin chloride in 100 ml. of ether. To this was added, dropwise and with good stirring, 0.050 mole of 2,5-dimethylphenyllithium in 103 ml. of ether. The reaction mixture was stirred for 2 hours and hydrolyzed. On hydrolysis a white solid came out of solution. It was filtered off, the layers were separated, and the ether layer dried over sodium sulfate.

The solid recovered on hydrolysis was crystallized from petroleum ether (b.p. 77-120°) to yield 4.0 g. (25.0%) of tetraphenyltin melting at 224-225° (mixed melting point).

The ether layer yielded a violet oil which was dissolved in 100 ml. of ethanol plus 30 ml. of benzene by vigorous refluxing. On cooling, a small amount of oil came out of solution. The oil was dissolved in 50 ml. of methanol by reflux-

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[33] O. Jacobsen, <u>Ber</u>., <u>14</u>, 2111 (1881).

ing. On cooling, 0.8 g. of triphenyl-2,5-dimethylphenyltin melting at 98-99° was obtained. Then the ethanol-benzene mother liquor was refluxed with some Norit A, filtered hot, and concentrated by distillation. The concentrated solution was seeded and allowed to cool slowly. On thorough cooling, 10.5 g. of triphenyl-2,5-dimethylphenyltin melting at 97-99° was recovered. Total yield of triphenyl-2,5-dimethylphenyltin was 11.3 g. (49.7%).

Preparation of 2,6-dimethylbenzoic acid. On a Dry Ice-ether slurry was dropped, with vigorous stirring, 0.042 mole of 2,6-dimethylphenyllithium[34] in 90 ml. of ether. On warming to room temperature the mixture was extracted once with 100 ml. of water and once with 50 ml. of 15% potassium hydroxide solution. The aqueous layers were combined and warmed on a steam plate for 1 hour. Upon neutralization of the aqueous solution with concentrated hycrochloric acid the crude 2,6-dimethylbenzoic acid precipitated from solution. This crude acid was crystallized from petroleum ether

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[34] Prepared in 93.0% yield by refluxing 23.2 g. (0.10 mole) of 2,6-dimethyliodobenzene (Eastman Kodak white label) in 200 ml. of ether with 1.7 g. (0.2 g. atom plus 20%) of sliced lithium wire for 1 hour.

(b.p. 60-70°) to yield 5.4 g. (86.0%) of 2,6-dimethylbenzoic acid melting at 115-116°[35].

Preparation of triphenyl-2,6-dimethylphenyltin. In a 500 ml. flask was placed 19.25 g. (0.050 mole) of triphenyltin chloride in 100 ml. of ether. To this was added, dropwise and with good stirring, 0.050 mole of 2,6-dimethylphenyllithium in 108 ml. of ether. The reaction mixture was refluxed for 30 hours and hydrolyzed. Color Test I was weakly positive just before hydrolysis. The layers were separated and the ether layer dried over sodium sulfate.

The ether layer yielded an oil which was digested with 25 ml. of methanol, and the oil solidified after several minutes' refluxing. The methanol solution was decanted and the solid was recrystallized twice from a methanol-benzene solution to yield 10.1 g. (44.5%) of triphenyl-2,6-dimethylphenyltin melting at 118-119°.

Anal. Calcd. for $C_{26}H_{24}Sn$: Sn, 26.08. Found: Sn, 26.13.

Preparation of mesityllithium. Mesityllithium was prepared on a 0.1 mole scale as follows: in a 250 ml, three-necked flask were placed 19.9 g. (0.10 mole) of bromomesityl-

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[35] R. W. Hufferd and W. A. Noyes, J. Am. Chem. Soc., 43, 929 (1921).

ene (Eastman Kodak white label), 1.7 g. (0.2 g. atom plus 20%) of sliced lithium wire and 200 ml. of ether. The mixture was stirred and refluxed for 48 hours, cooled, and then decanted through a thin glass wool plug into a 250 ml. graduated dropping funnel. The yield was determined by titration of a 2 ml. aliquot with standard acid, and was 90.3%.

Preparation of mesitoic acid. On a Dry Ice-ether slurry was dropped, with vigorous stirring, 0.039 mole of mesityllithium in 96 ml. of ether. On warming to room temperature the mixture was extracted once with 100 ml. of water and once with 50 ml. of 15% potassium hydroxide solution. The aqueous layers were combined and warmed on a steam plate for 1 hour. Upon neutralization of the aqueous solution with concentrated hydrochloric acid the crude mesitoic acid precipitated from solution. This crude acid was crystallized from an ethanol-water solution to yield 6.4 g. (98.9%) of mesitoic acid melting at 152-154°[36].

Preparation of triphenylmesityltin. In a 500 ml. flask was placed 19.25 g. (0.050 mole) of triphenyltin chloride in 200 ml. of ether. To this was added, dropwise and with good stirring, 0.050 mole of mesityllithium in 122 ml. of ether.

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[36] P. Jannasch and W. Weiler, Ber., 27, 3446 (1894).

The reaction mixture was refluxed for 15 hours and hydrolyzed. The layers were separated and the ether layer dried over sodium sulfate.

The ether layer yielded a light yellow solid which was extracted with 25 ml. of methanol for 10 minutes. The methanol solution was decanted and the residual solid was crystallized twice from a methanol-benzene solution to yield 17.4 g. (74.2%) of triphenylmesityltin melting at 157-158°.

Anal. Calcd. for $C_{27}H_{26}Sn$: Sn, 25.30. Found: Sn, 25.54.

Preparation of triphenyl-o-methoxyphenyltin. In a 500 ml. flask was placed 7.5 g. (0.020 mole) of triphenyltin chloride in 200 ml. of ether. To this was added, dropwise and with good stirring, 0.022 mole of o-methoxyphenylmagnesium iodide[37] in 50 ml. of ether. The reaction mixture was refluxed for 1 hour and hydrolyzed. The layers were separated and the ether layer dried over sodium sulfate.

The ether layer yielded a white solid which was crystallized twice from an excess of ethanol to yield 3.2 g. (36.0%) of triphenyl-o-methoxyphenyltin melting at 129-130°.

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[37] Prepared by refluxing 5.0 g. (0.022 mole) of o-iodoanisole in 50 ml. of ether with 1.0 g. (0.042 g. atom) of magnesium metal for 35 minutes.

Anal. Calcd. for $C_{25}H_{22}OSn$: Sn, 25.97. Found: Sn, 26.10.

Preparation of triphenyl-p-anisyltin. In a 500 ml. flask was placed 7.5 g. (0.20 mole) of triphenyltin chloride in 200 ml. of ether. To this was added, dropwise and with good stirring, 0.024 mole of *p*-methoxyphenylmagnesium bromide[38] in 50 ml. of ether. The reaction mixture was refluxed for 1 hour and hydrolyzed. The layers were separated and the ether layer dried over sodium sulfate.

The ether layer yielded an oil which solidified on thorough cooling. This solid was crystallized three times from an excess of ethanol to yield 3.3 g. (37.1%) of triphenyl-*p*-methoxyphenyltin melting at 151-152°.

Anal. Calcd. for $C_{25}H_{22}OSn$: Sn, 25.97. Found: Sn, 26.21.

Preparation of triphenylmethyltin. In a 500 ml. flask was placed 10.0 g. (0.026 mole) of triphenyltin chloride in 200 ml. of ether. To this was added, dropwise and with good stirring, 0.039 mole of methylmagnesium iodide in 50 ml. of ether. The reaction mixture was refluxed for 1 hour and hydrolyzed. The layers were separated and the ether layer

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[38] Prepared by refluxing 4.4 g. (0.024 mole) of *p*-bromoanisole in 50 ml. of ether with 1.0 g. (0.042 g. atom) of magnesium metal for 2 hours.

dried over sodium sulfate.

The ether layer yielded an oil which solidified on thorough cooling. The solid was crystallized twice from a minimum amount of ethanol to yield 1.2 g. (20.2%) of triphenylmethyltin[20] melting at 60-61°.

Preparation of triphenyl-p-tolyltin. In a 500 ml. flask was placed 5.0 g. (0.013 mole) of triphenyltin chloride in 200 ml. of ether. To this was added, dropwise and with good stirring, 0.024 mole of p-tolylmagnesium bromide in 50 ml. of ether. The reaction mixture was refluxed for 1 hour and hydrolyzed. The layers were separated and the ether layer dried over sodium sulfate.

The ether layer yielded an oil which solidified on thorough cooling. This solid was crystallized twice from an excess of ethanol to yield 2.1 g. (36.8%) of triphenyl-p-tolyltin melting at 123-124°[39].

Preparation of tetra-o-tolyltin. In a 2 liter flask was placed 39.15 g. (0.15 mole) of stannic chloride in 150 ml. of benzene. To this was added, with good stirring, 0.625 mole of o-tolyllithium in 630 ml. of ether at a rate to maintain gentle reflux. The addition took 4 hours to

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[39] E. Krause and M. Schmitz, Ber., 52, 2150 (1919).

complete, and when completed the mixture was stirred for 18 hours at room temperature. Color Test I was negative at the end of this time and the reaction mixture was hydrolyzed by cautious addition of water.

The solid (23.4 g.) recovered on hydrolysis was thoroughly air-dried and crystallized from petroleum ether (b.p. 77-120°) to yield 20.7 g. of product melting at 215-216°. The ether and benzene were removed by distillation, and the solid residue was crystallized from petroleum ether (b.p. 77-120°) to yield 28.6 g. of product melting at 214-216°. The total yield of tetra-o-tolyltin[22] was 49.3 g. (68.1%).

Preparation of hexa-o-tolylditin. In a 125 ml. flask were placed 4.0 g. (0.0094 mole) of tri-o-tolyltin chloride[14], 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 recrystallized twice from a minimum amount of benzene to yield 2.3 g. (62.1%) of hexa-o-tolylditin[22] melting at 298-300° (mixed melting point).

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 solvent was then distilled, and the solid residue was recrystallized from a 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. 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 layers were separated and the ether layer dried over sodium sulfate.

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. Calcd. for $C_{28}H_{28}Sn$: Sn, 24.73. Found: Sn, 24.96.

Studies of cleavage reactions with organolithium compounds

Reaction of triphenylbenzyltin with phenyllithium. In a 250 ml. flask was placed 2.0 g. (0.0046 mole) of triphenylbenzyltin in 150 ml. of ether. The flask was immersed in a Dry Ice-acetone bath which was maintained at -35°. Then 0.01 mole of phenyllithium in 10 ml. of ether was added. The solution turned bright yellow immediately. After 5 minutes of stirring a white solid precipitated from solution. The mixture was stirred for 1 hour and hydrolyzed. The solid which remained suspended in the ether layer was filtered off and air-dried. The layers were separated, and the ether layer dried over sodium sulfate.

The tetraphenyltin recovered on hydrolysis weighed 1.5 g. and melted at 223-225° (mixed melting point).

From the ether layer 0.3 g. of tetraphenyltin melting at 222-225° and 0.2 g. of triphenylbenzyltin melting at 89-91° were recovered. Total yield of tetraphenyltin was 1.8 g. (91.8%).

The triphenylbenzyltin used in this experiment was prepared as follows: in a 250 ml., three-necked flask was placed 15.0 g. (0.039 mole) of triphenyltin chloride in 100 ml. of ether. To this was added, dropwise and with good stirring, 0.08 mole of benzylmagnesium chloride. After addition was completed the mixture was refluxed for 1 hour and hydrolyzed. The layers were separated and the ether layer dried over sodium sulfate.

The ether layer yielded a solid residue which was crystallized from petroleum ether (b.p. 77-120°) to yield 13.8 g. (80.4%) of triphenylbenzyltin[15] melting at 90-91° (mixed melting point).

Run 2. A second run carried out as the first gave almost the same results: 4.41 g. (0.01 mole) of triphenylbenzyltin was reacted with 0.013 mole of phenyllithium at -35°. Total yield of tetraphenyltin melting at 223-225° was 3.8 g. (89.0%), and no triphenylbenzyltin was recovered.

Run 3. This run was devoted to identifying the benzyllithium which was formed by the metal-metal interconversion which took place in the formation of the tetraphenyltin (as was established by the following): 5.0 g. (0.0113 mole) of triphenylbenzyltin was reacted with 0.012 mole of phenyllithium at -35°. The yellow color (ether solutions of benzyllithium are yellow in color) was formed immediately and tetraphenyltin precipitated from solution a few minutes later. After 1 hour of stirring, the mixture was allowed to stand a few minutes while the solid settled from solution. The supernatant liquid was then decanted onto a Dry Ice-ether slurry with vigorous stirring, and the yellow color was discharged. Upon warming to room temperature the ether layer was extracted with 100 ml. of water and then with 50 ml. of 15% potassium hydroxide solution. The aqueous layers were combined and placed in a liquid-liquid extraction apparatus and extracted for 16 hours with petroleum ether (b.p. 60-70°). The basic aqueous layer was then acidified with concentrated hydrochloric acid, returned to the extraction apparatus and extracted with a new sample of petroleum ether (b.p. 60-70°)

for 16 hours. The petroleum ether was then placed in a crystallization dish, and the solvent was allowed to evaporate at room temperature. The white solid residue recovered in this manner was collected and crystallized from petroleum ether (b.p. 77-120°) to yield 0.6 g. of phenylacetic acid (39.0%) melting at 73-74° (mixed melting point).

The total yield of tetraphenyltin melting at 223-225° (mixed melting point) was 4.1 g. (88.0%).

Reaction of triphenylethyltin with phenyllithium. In a 100 ml. flask was placed 1.9 g. (0.005 mole) of triphenylethyltin in 50 ml. of ether. To this was added 0.005 mole of phenyllithium in 4.8 ml. of ether. The solution was stirred for 1 hour at room temperature (ca. 25°), no color change was noted, and no solid precipitated from solution. The solution was then poured onto a Dry Ice-ether slurry. Upon warming to room temperature the ether layer was extracted twice with 25 ml. of 10% potassium hydroxide solution. The aqueous layers were combined, made slightly acid with concentrated hydrochloric acid, then made alkaline by the addition of solid sodium bicarbonate, filtered, and finally acidified with concentrated hydrochloric acid.

The solid which precipitated from solution on the final acidification was filtered off and air-dried. The yield of benzoic acid melting at 120-122° (mixed melting point) was 0.4 g. (64.5%).

From the ether layer 0.2 g. (9.4%) of tetraphenyltin melting at 223-225° and 1.0 g. (52.6% recovery) of triphenylethyltin melting at 56-58° were recovered. Both samples were identified by mixed melting points with authentic specimens. No carbonation reaction was run to identify and ethyllithium that may have been formed.

Reaction of triphenylbenzyltin with triphenyltin-lithium. Triphenyltin-lithium was prepared by the addition of 0.0729 mole of phenyllithium in 72 ml. of ether to 4.6 g. (0.0243 mole) of stannous chloride suspended in 100 ml. of ether. Then 10.7 g. (0.0243 mole) of triphenylbenzyltin in 50 ml. of ether was added. The mixture was stirred for 2 hours at -10° and hydrolyzed.

The white solid recovered on hydrolysis was extracted with 300 ml. of petroleum ether (b.p. 77-120°). Upon cooling, 2.8 g. (26.9%) of tetraphenyltin melting at 223-225° (mixed melting point) was obtained.

The ether layer yielded a yellow oil which was extracted with 60 ml. of ethanol, and filtered hot. Upon cooling, 6.3 g. of triphenylbenzyltin melting at 90-91° was recovered. Concentration of the ethanol mother liquor led to the recovery of an additional 0.5 g. of triphenylbenzyltin melting at 89-91°. Total recovery was 6.8 g. (63.5%).

It is known that some tetraphenyltin accompanies all preparations of triphenyltin-lithium but the amount isolated under comparable conditions is not as great as that obtained above. A better recovery of triphenylbenzyltin, if it had not reacted with the triphenyl-lithium, could be hoped for. Therefore the triphenyltin-lithium may have reacted to a slight extent with the triphenylbenzyltin to form the tetraphenyltin.

Reaction of triphenylbenzyltin with phenylmagnesium bromide. In a 250 ml. flask was placed 4.41 g. (0.01 mole) of triphenylbenzyltin in 50 ml. of ether. The solution was brought to reflux, and 0.01 mole of phenylmagnesium bromide in 10 ml. of ether was added. Reflux was continued for 1 hour, no yellow color developed, and the solution was then carbonated by pouring it onto a Dry Ice-ether slurry. On warming the ethereal solution was extracted with 25 ml. of water, and then with 25 ml. of 10% sodium hydroxide solution. The aqueous layers were combined, placed in a liquid-liquid extraction apparatus, and treated as outlined on p.141. The ether layer was dried over sodium sulfate.

The ether layer yielded an oily solid which was crystallized from a minimum amount of ethanol to yield 3.6 g. (81.9% recovery) of triphenylbenzyltin melting at 90-91°. No phenylacetic acid was isolated by the extraction process.

Reaction of hexaphenylditin with phenyllithium. In a 250 ml. flask were placed 5.0 g. (0.00715 mole) of hexaphenylditin in 92 ml. of ether and 0.00715 mole of phenyllithium in 8 ml. of ether. The mixture was refluxed for 24 hours. The suspended solid was then allowed to settle out and the supernatant liquid was filtered off under nitrogen. The solid was crystallized from petroleum ether (b.p. 77-120°) to yield 4.7 g. (88.6%) of tetraphenyltin melting at 224-225° (mixed melting point).

The ether solution had a pale yellow color. When 5 ml. of bromobenzene were added to the ether solution the yellow color gradually faded and the solution became cloudy. Work up of this solution led to the recovery of 0.6 g. of solid which softened at 220° but did not completely melt up to 300°. In order to be sure that the starting material was hexaphenylditin and not tetraphenyltin, a sample of the starting material was used in a mixture melting point with an authentic specimen of tetraphenyltin. The mixture melted over the range 190-195°.

Preparation of azo tin dyes

Preparation of triphenyl-4-dimethylamino-3-(4'-nitrophenylazo)phenyltin[11]. In a 1 liter beaker, surrounded by an ice bath and equipped with a magnetic stirrer, were placed

3.5 g. (0.007 mole) of triphenyl-p-dimethylaminophenyltin[11], 4.1 g. of sodium acetate, 75 ml. of ethyl acetate and 50 ml. of water. A solution containing 0.007 mole of p-nitrobenzenediazonium chloride, to which enough sodium acetate had been added to neutralize the excess hydrochloric acid, was added dropwise and with vigorous stirring. A red color formed almost immediately. The solution was stirred for 2 hours, the ice bath was removed, and the mixture allowed to stand overnight. The water, in which a red oil was suspended, was decanted, and the red mass was digested with two 25 ml. portions of ethanol leaving a brown solid. This solid was dissolved in a minimum amount of refluxing chloroform, then ethanol was added at reflux until a trace of solid precipitated from solution. On cooling, 1.1 g. (24.0%) of triphenyl-4-dimethylamino-3-(4'-nitrophenylazo)phenyltin, a bright gold gilt color, melting at 187-189° (mixed melting point) was obtained.

Run 2. In this run 14.1 g. (0.03 mole) of triphenyl-p-dimethylaminophenyltin, 16.4 g. of sodium acetate, 300 ml. of ethyl acetate and 200 ml. of water were reacted with a solution containing 0.06 mole of p-nitrobenzenediazonium chloride exactly as outlined above. On working up the reaction 4.2 g. (22.9%) of triphenyl-4-dimethylamino-3-(4'-nitrophenylazo)phenyltin melting at 187-189° was obtained.

Preparation of triphenyl-4-dimethylamino-3-(4'-bromophenylazo)phenyltin. In a 1 liter beaker, surrounded by an ice bath and equipped with a magnetic stirrer, were placed 3.0 g. (0.0064 mole) of triphenyl-p-dimethylaminophenyltin, 75 ml. of ethyl acetate, 4.1 g. of sodium acetate and 50 ml. of water. A solution containing 0.008 mole of p-bromobenzenediazonium chloride, to which enough sodium acetate had been added to neutralize the excess hydrochloric acid, was added dropwise and with good stirring. A red color formed almost immediately, after 1 hour a deep red solid appeared, and after 2 hours all the ethyl acetate had evaporated and a deep red tar remained in the water. The water was decanted, and the tar digested with two 50 ml. portions of ethanol. The brown solid residue was crystallized twice from petroleum ether (b.p. 77-120°) to yield 0.3 g. (7.2%) of triphenyl-4-dimethylamino-3-(4'-bromophenylazo)phenyltin melting at 170-172°.

Anal. Calcd. for $C_{32}H_{28}N_3BrSn$: N, 6.43; Sn, 18.17. Found: N, 6.43; Sn, 18.36.

Run 2. A second preparation carried out exactly as the first except that 9.0 g. (0.0191 mole) of triphenyl-p-dimethylaminophenyltin was reacted with 0.040 mole (100% excess) of p-bromobenzenediazonium chloride. The yield of triphenyl-4-dimethylamino-3-(4'-bromophenylazo)phenyltin melting at 170-172° was 2.1 g. (16.8%). Note that in this reaction the yield of dye was increased by changing the relative amounts of the reactants, whereas there was no effect in the previous preparation.

Preparation of triphenyl-4-dimethylamino-3-(4'-chlorophenylazo)phenyltin. The same procedure as that outlined for the preparation of triphenyl-4-dimethylamino-3-(4'-bromophenylazo)phenyltin was followed except that 2.4 g. (0.0051 mole) of triphenyl-p-dimethylaminophenyltin was reacted with 0.006 mole of p-chlorobenzenediazonium chloride. The yield of triphenyl-4-dimethylamino-3-(4'-chlorophenylazo)phenyltin melting at 162-165° was 0.28 g. (4.5%).

Anal. Calcd. for $C_{32}H_{28}N_3ClSn$: N, 6.89; Sn, 19.47. Found: N, 7.00; Sn, 19.58.

Reaction of triphenyl-p-dimethylaminophenyltin with p-sulfobenzenediazonium chloride. In a 1 liter beaker, surrounded by an ice bath and equipped with a magnetic stirrer, were placed 5.9 g. (0.0125 mole) of triphenyl-p-dimethylaminophenyltin, 5.0 g. of sodium acetate, 125 ml. of ethyl acetate and 60 ml. of water. A solution containing 0.025 mole of p-sulfobenzenediazonium chloride was added, dropwise and with vigorous stirring. Upon addition of the diazonium solution a white solid precipitated, and the characteristic red color never developed although the reaction mixture was stirred overnight. This solid was then filtered off and crystallized from petroleum ether (b.p. 77-120°) to yield 3.7 g. (62.7% recovery) of triphenyl-p-dimethylaminophenyltin melting at 132-134°.

Preparation of p-nitrobenzenediazonium fluoborate[40]. In a 400 ml. beaker were placed 34.0 g. (0.25 mole) of p-nitroaniline and 110 ml. of 42-45% fluoboric acid. The amine was dissolved by warming the mixture on a steam bath. The beaker was then surrounded by an ice bath and the solution was stirred vigorously. On cooling, the amine salt precipitated from solution. Then a cold solution of 17.0 g. (0.25 mole) of sodium nitrite in 34 ml. of water was added dropwise. When the addition was completed the mixture was stirred for 10 minutes and then filtered by suction on a sintered glass filter. This solid was washed once with 25 ml. of cold fluoboric acid, twice with 15 ml. of cold alcohol, and three times with 10 ml. of ether. The yield of p-nitrobenzenediazonium fluoborate was 47.0 g. (79.5%).

Reaction of triphenyl-p-dimethylaminophenyltin with p-nitrobenzenediazonium fluoborate. In a 1 liter beaker was placed 8.0 g. (0.017 mole) of triphenyl-p-dimethylaminophenyltin in 100 ml. of dioxane. The beaker was surrounded

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[40] E. B. Starkey, Org. Syntheses, Coll. Vol. II, 225 (1943).

by an ice bath and 4.0 g. (0.017 mole) of p-nitrobenzenediazonium fluoborate dissolved in 250 ml. of dioxane and 50 ml. of water was added, dropwise and with good stirring. After addition was completed, the deep red mixture was stirred for 15 minutes, and then 400 ml. of water was added. The deep red solid which precipitated on addition of the water was filtered off and air-dried. The solid was then extracted with 125 ml. of chloroform, and filtered hot. On cooling, 2.1 g. of red solid melting at 228-231° was obtained.

If expulsion of the triphenylstannyl group was the main course of the reaction, the dye formed would be 4-dimethylamino-4'-nitroazobenzene. A mixed melting point between an authentic specimen of 4-dimethylamino-4'-nitroazobenzene and the red solid recovered above showed no depression. Total yield of 4-dimethylamino-4'-nitroazobenzene was 2.1 g. (45.7%)[41].

The following diagram outlines the course of the proposed expulsion reaction:

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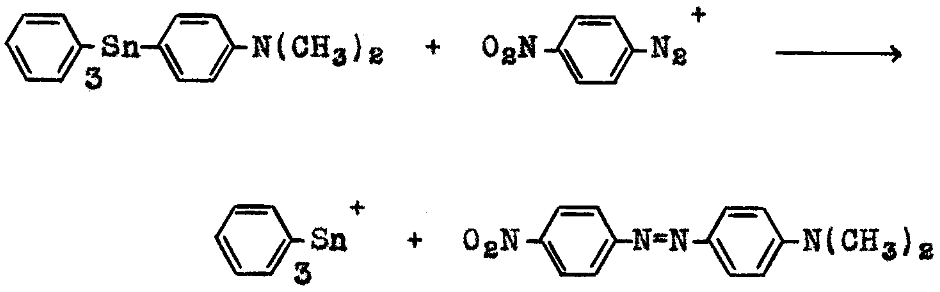
[41] R. Meldola, J. Chem. Soc., 45, 107 (1884).



The ultimate fate of the triphenylstannyl group has not been established.

Preparation of p-bromobenzenediazonium fluoborate[42]. In a 1 liter beaker were placed 37.0 g. (0.125 mole) of *p*-bromoaniline, 80 ml. of concentrated hydrochloric acid, and 25 ml. of water. The amine was dissolved by warming the mixture on a hot plate. The beaker was then surrounded by an ice-salt bath and 23.0 g. (0.333 mole) of sodium nitrite in 30 ml. of water was added, dropwise and with good stirring. After addition was completed the solution was stirred for 15 minutes, then 110 ml. of 42-45% fluoboric acid was added all at once. The solid which precipitated on the addition of the fluoboric acid was filtered off, washed twice with 20 ml. of water, twice with 20 ml. of ethanol, twice with ether, and

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[42] G. Schiemann and R. Pillarsky, *Ber.*, *64*, 1340 (1931).

was then thoroughly air-dried. Total yield of p-bromobenzenediazonium fluoborate was 34.7 g. (60.0%).

Reaction of triphenyl-p-dimethylaminophenyltin with p-bromobenzenediazonium fluoborate. In a 1 liter beaker was placed 8.0 g. (0.017 mole) of triphenyl-p-dimethylaminophenyltin in 100 ml. of dioxane. The beaker was surrounded by an ice bath and 4.6 g. (0.017 mole) of p-bromobenzenediazonium fluoborate dissolved in 250 ml. of dioxane and 50 ml. of water was added, dropwise and with good stirring. A deep red solution was formed almost immediately. After addition was completed the deep red mixture was stirred for 1 hour, then 600 ml. of water was added. The orange solid which precipitated from solution on addition of the water was filtered off and air-dried. The solid was then extracted with 150 ml. of ethanol, and filtered hot. On cooling, 3.0 g. of orange solid melting at 148-152° was obtained. Two recrystallizations of the solid from a minimum amount of ethanol yielded 2.3 g. (45.3%) of 4-dimethylamino-4'-bromoazobenzene melting at 151-153°[43].

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[43] H. Goldschmidt and B. Bardach, Ber., 25, 1375 (1892).

Preparation of triphenyltin chloride[44]. In a 1 liter flask equipped with an air condenser were placed 118.0 g. (0.276 mole) of tetraphenyltin which had been air-dried at 120° for 12 hours and 33.4 g. (0.09 mole) of anhydrous stannic chloride. The flask was placed in an oil bath which was maintained at 220° ± 10° for 1 hour. The flask was shaken occasionally. After the mass had cooled, it was extracted with 500 ml. of petroleum ether (b.p. 77-120°), treated with Norit A, and filtered hot. On cooling, 92.8 g. (65.5%) of triphenyltin chloride melting at 104-106° was obtained (mixed melting point). This reaction was repeated many times in the course of this research, and the yields were consistantly between 60% and 70%.

Preparation of m-bromodimethylaniline. In a 2 liter, three-necked flask were placed 100 g. (0.581 mole) of *m*-bromoaniline and 100 ml. of water. The flask was partially immersed in a running water bath and 70 ml. (91 g., 0.72 mole) of freshly redistilled dimethyl sulfate was added, dropwise and with good stirring. Ten minutes after addition was completed the solution was neutralized by adding 150 ml. of saturated sodium carbonate solution. A second and third

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[44] Private communication from Eastman Kodak Company.

addition of 70 ml. of dimethyl sulfate were made followed by neutralization with sodium carbonate solution after each addition (care was taken to make the mixture strongly basic after the third addition). The reaction mixture was then extracted with 500 ml. of ether, the layers were separated, and the ether layer was dried over sodium sulfate. To the water layer was added 500 ml. of saturated potassium iodide solution, and a voluminous white solid precipitated. The solid was filtered off and air-dried. The ether was removed by distillation from a water bath and the residue digested with 150 ml. of saturated sodium carbonate solution. The resulting mixture was poured into the potassium iodide mother liquor, and the precipitate thus formed was filtered off and air-dried. The solids were combined (158.5 g.) and distilled at water pump pressure (122.5°/15 mm., 136°/22 mm.); the total distillate was collected in one fraction. The distillate partially solidified on standing. The entire fraction was then redistilled under reduced pressure (78°/1.0 mm.) and two cuts were taken. Both fractions had the same index of refraction, $n_D^{17.1}$ 1.6011. Total yield of <u>m</u>-bromodimethylaniline was 79.2 g. (68.2%)

<u>Preparation of m-dimethylaminophenyllithium</u>. <u>m</u>-Dimethylaminophenyllithium was prepared on a 0.045 scale as follows: in a 250 ml., three-necked flask were placed 0.8 g. (0.09 g.

atom plus 20%) of sliced block lithium or lithium wire and 50 ml. of ether. In a dropping funnel was placed 9.0 g. (0.045 mole) of m-bromodimethylaniline in 40 ml. of ether. The halide solution was added to the reaction flask, with good stirring, at a rate to maintain very gentle reflux. When addition was completed the mixture was refluxed for 30 minutes, cooled, and then decanted through a glass wool plug into a 250 ml. graduated dropping funnel. The yield was determined by titration of a 1 ml. aliquot with standard acid using phenolphthalein as the indicator, and usually was between 97% and 105%[45].

Preparation of triphenyl-m-dimethylaminophenyltin. In a 500 ml., three-necked flask was placed 15.0 g. (0.039 mole) of triphenyltin chloride in 200 ml. of ether. The flask was immersed in a running water bath, and 0.046 mole of m-dimethylaminophenyllithium in 84 ml. of ether was added, dropwise and with good stirring. The mixture was stirred for 1 hour after addition was completed; Color Test I was negative at the end of this time. The reaction mixture was hydrolyzed by the addition of 150 ml. of water to the reaction flask, the layers were separated, and the ether layer dried over sodium sulfate.

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[45] Yields in excess of 100% were attributed to the presence of small amounts of m-bromo-N-methylaniline in the halide used.

The ether layer yielded an oil which was dissolved in 25 ml. of chloroform plus 100 ml. of methanol by vigorous refluxing. On cooling, 12.3 g. of white solid melting at 87-91° was obtained. The solid was again recrystallized from 25 ml. of chloroform plus 100 ml. of methanol. On cooling, 10.4 g. of triphenyl-*m*-dimethylaminophenyltin melting at 90-91° was obtained. Concentration of the mother liquor led to the recovery of 1.2 g. of triphenyl-*m*-dimethylaminophenyltin melting at 89-91°. Total yield of triphenyl-*m*-dimethylaminophenyltin was 11.6 g. (63.4%)

Anal. Calcd. for $C_{26}H_{25}NSn$: Sn, 25.24. Found: Sn, 25.28.

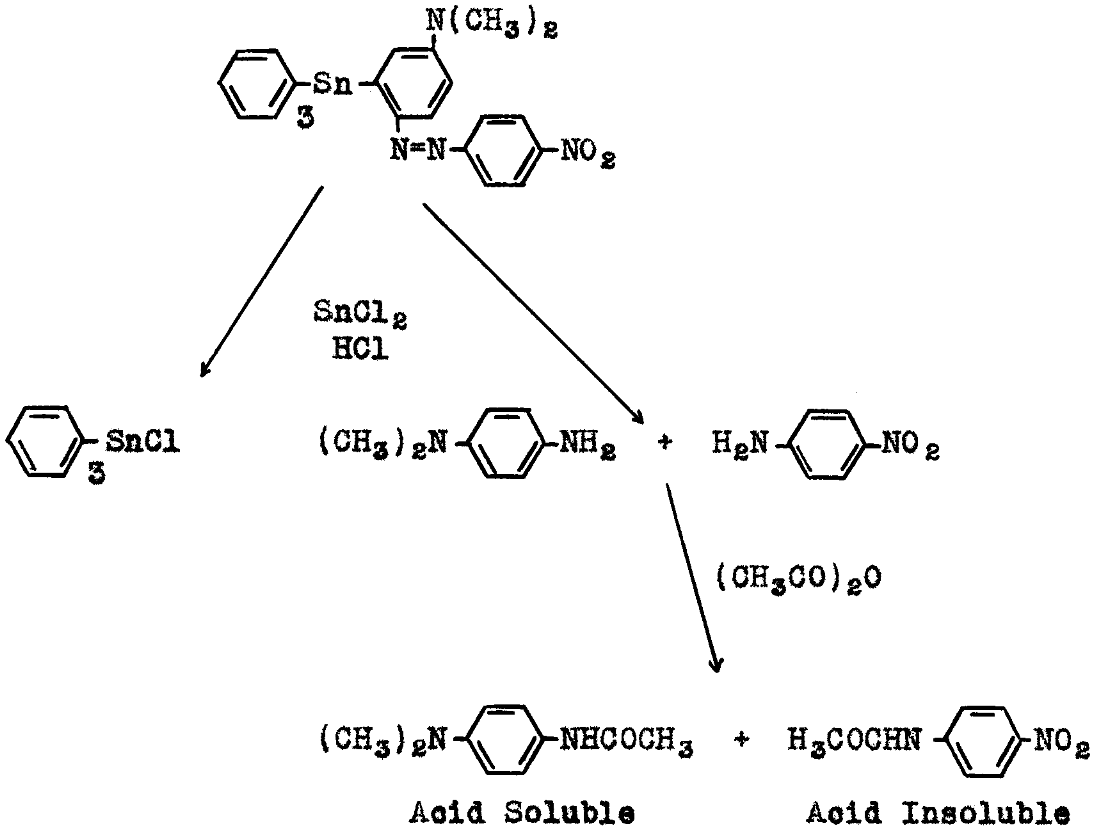
Preparation of triphenyl-3-dimethylamino-6-(4'-nitrophenylazo)phenyltin. In a 1 liter beaker, surrounded by an ice bath and equipped with a magnetic stirrer, was placed 8.0 g. (0.017 mole) of triphenyl-*m*-dimethylaminophenyltin in 100 ml. of dioxane. A solution of 4.0 g. (0.017 mole) of *p*-nitrobenzenediazonium fluoborate in 500 ml. of a 50% dioxane-water mixture was added, dropwise and with vigorous stirring. A deep red solution was formed almost immediately. Fifteen minutes after the addition was completed 400 ml. of water was added, and a deep red solid precipitated. The solid was filtered off and air-dried on a suction filter. Extraction of the solid with two 150 ml. portions of refluxing petroleum ether (b.p. 77-120°) yielded 5.7 g. of red solid melting at 205-206°. The solid, recovered on cooling the two petroleum ether mother liquors in an ice bath, was recrystallized twice from petroleum ether (b.p. 77-120°) to yield 1.3 g. of shiny green platelets melting at 205-205.5°. A mixed melting point between the red and green solids showed no depression. The total yield of triphenyl-3-dimethylamino-6-(4'-nitrophenylazo)phenyltin was 7.0 g. (66.6%)

Anal. Calcd. for $C_{32}H_{28}O_2N_4Sn$: Sn, 19.17. Found: Sn, 19.18.

In a 100 ml. flask were placed 4.0 g. (0.0065 mole) of the dye, 8.0 g. of stannous chloride, 10 ml. of water, and 30 ml. of concentrated hydrochloric acid. The mixture was stirred vigorously, and warmed on a hot plate until decolorized (*ca*. 3 hours). The solid residue was filtered off, and the filtrate was then made basic with 10% sodium hydroxide solution and extracted with ether. The ether layer was dried over sodium sulfate. The ether was evaporated by passing a gentle stream of air over the surface of the solution. The crude bases were warmed on a water bath with 1.0 g. of acetic anhydride for 5 minutes. This solution was then diluted with 25 ml. of water, and filtered.

The filtrate was neutralized with saturated sodium carbonate solution, and extracted with ether. The ether layer was dried over sodium sulfate. Then the ether was once again removed using a stream of air, and the residue was crystallized from water to yield 0.4 g. (35.0%) of p-dimethylaminoacetanilide melting at 131° (mixed melting point).

The following diagram shows the structure proof.



No effort was made to recover the organotin halide or p-nitroacetanilide.

Preparation of triphenyl-3-dimethylamino-6-(4'-bromophenylazo)phenyltin. In a 1 liter beaker, surrounded by an ice bath and equipped with a magnetic stirrer, was placed 4.0 g. (0.0085 mole) of triphenyl-*m*-dimethylaminophenyltin in 100 ml. of dioxane. A solution of 2.3 g. (0.0085 mole) of *p*-bromobenzenediazonium fluoborate in 100 ml. of dioxane plus 15 ml. of water was added, with good stirring. The solution was stirred for 4 hours while a deep red color gradually formed. Then 600 ml. of water was added, and the red solid which precipitated was filtered off and air-dried on a suction filter. The solid (3.7 g.) was extracted with 150 ml. of petroleum ether (b.p. 77-120°), and filtered hot. On cooling, 2.7 g. (48.6%) of triphenyl-3-dimethylamino-6-(4'-bromophenylazo)phenyltin melting at 199-200° was obtained.

Anal. Calcd. for $C_{32}H_{28}N_3BrSn$: Sn, 18.17. Found: Sn, 18.01.

Preparation of p-carboxybenzenediazonium fluoborate[46]. In a 400 ml. beaker were placed 34.3 g. (0.25 mole) of *p*-aminobenzoic acid and 100 ml. of 42-45% fluoboric acid. The amino acid was almost completely dissolved by warming on a steam bath. The beaker was then placed in an ice bath and cooled with vigorous stirring. On cooling the amine salt precipitated. A cold solution of 17.0 g. (0.25 mole) of sodium nitrite in 34 ml. of water was added dropwise. After addition was completed the mixture was stirred for 0.5 hour and filtered on a sintered glass filter. The solid was washed once with 15 ml. of iced fluoboric acid, once with 10 ml. of iced alcohol, and once with 20 ml. of ether. The total yield of p-carboxybenzenediazonium fluoborate was 35.4 g. (60.0%). The diazonium salt is very soluble in water and this tends to lower the yield when a pure product is desired. Using the same general procedure Dunker, Starkey and Jenkins[46] prepared this diazonium salt in 76% yield, and Ruddy, Starkey and Hartung[47] in 84% yield. Specific directions for the preparation of the salt were not included in either of the reports and no mention of the comparatively high water solubility of the salt was made.

Preparation of triphenyl-3-dimethylamino-6-(4'-carboxyphenylazo)phenyltin. In a 1 liter beaker, equipped as above, was placed 4.0 g. (0.0085 mole) of triphenyl-m-dimethylaminophenyltin in 50 ml. of dioxane. A solution of 2.0 g. (0.0085 mole) of p-carboxybenzenediazonium fluoborate in 200 ml. of dioxane plus 15 ml. of water was added. A deep red color developed almost immediately. The solution was stirred for

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[46] M. F. W. Dunker, E. B. Starkey and G. L. Jenkins, J. Am. Chem. Soc., 58, 2308 (1936).

[47] A. W. Ruddy, E. B. Starkey and W. H. Hartung, ibid., 64, 828 (1942).

4 hours, then 500 ml. of water was added. An oil, which quickly solidified, came out of solution. This solid (4.1 g.) was filtered off, air-dried and extracted with 100 ml. of petroleum ether (b.p. 77-120°) for 0.5 hour, and the hot solution was decanted. The solid residue was then crystallized from 250 ml. of ethanol. On cooling, 0.8 g. of solid was obtained from the ethanol solution. Concentration of the mother liquor led to the recovery of an additional 1.1 g. of solid. Both solids had the same decomposition point, 358°. The total yield of triphenyl-3-dimethylamino-6-(4'-carboxyphenylazo)phenyltin was 1.9 g. (36.2%).

<u>Anal</u>. Calcd. for $C_{33}H_{29}O_2N_3Sn$: Sn, 19.20. Found: Sn, 19.37.

<u>Run 2</u>. A second preparation carried out exactly as the first except that 3.5 g. (0.0074 mole) of triphenyl-<u>m</u>-dimethylaminophenyltin was reacted with 1.75 g. (0.0074 mole) of <u>p</u>-carboxybenzenediazonium fluoborate. The solid recovered from the reaction mixture was extracted with 100 ml. of petroleum ether (b.p. 77-120°), and filtered hot. The yield of triphenyl-3-dimethylamino-6-(4'-carboxyphenylazo)phenyltin was 2.2 g. (47.8%), dec. 356°.

The acid is insoluble in water, very slightly soluble in dilute hydrochloric acid and 5% sodium bicarbonate, slightly soluble in 5% sodium carbonate and 5% sodium hydroxide, and extremely soluble in ethanol.

Preparation of sodium p-(2'-triphenylstannyl-4'-dimethylamino)phenylazobenzoate. In a 250 ml. beaker was placed 2.0 g. (0.00324 mole) of triphenyl-3-dimethylamino-6-(4'-carboxyphenylazo)phenyltin in 100 ml. of ethanol. To this was added exactly 33.8 ml. of 0.096 N sodium hydroxide solution (0.00324 mole). The solution was then poured into a crystallization dish, and the ethanol permitted to evaporate. A recovery of 2.0 g. (96.5%) of sodium p-(2'-triphenylstannyl-4'-dimethylamino)phenylazobenzoate, orange in color, was made. This salt is very slightly soluble in water. Infrared studies indicated that the compound was the sodium salt of triphenyl-3-dimethylamino-6-(4'-carboxyphenylazo)phenyltin.

Preparation of p-dimethylaminobenzenediazonium fluoborate[48]. In a 600 ml. beaker were placed 17.0 g. (0.10 mole) of p-amino-N,N-dimethylaniline monohydrochloride and 100 ml. of concentrated hydrochloric acid. The beaker was placed in an ice bath and cooled with vigorous stirring. A cold solution of 6.9 g. (0.10 mole) of sodium nitrite in 14 ml. of water was added dropwise. The diazotization proceeded smoothly and, 5 minutes after the addition of the ni-

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[48] G. Schiemann and W. Winkelmüller, Ber., 66, 727 (1933).

trite solution was completed, 100 ml. of 42-45% fluoboric acid was added. The stirring was continued for an additional 15 minutes to ensure that the precipitation of the diazonium fluoborate was complete. The salt was filtered off on a sintered glass filter, washed once with 15 ml. of iced fluoboric acid, once with 15 ml. of iced alcohol, and twice with ether. Total yield of p-dimethylaminobenzenediazonium fluoborate was 9.5 g. (40.4%). This diazonium salt is very soluble in water. Using the general procedure Schiemann and Winkelmüller[48] prepared this diazonium salt in 56% yield. p-Aminodimethylaniline was used as the starting material in place of the p-aminodimethylaniline monohydrochloride used above. No mention of the comparatively high water solubility of the salt was made.

Attempted preparation of triphenyl-3-dimethylamino-6-(4'-dimethylaminophenylazo)phenyltin. In a 600 ml. beaker, equipped as above, was placed 2.0 g. (0.0042 mole) of triphenyl-m-dimethylaminophenyltin in 50 ml. of dioxane. A solution of 1.0 g. (0.0042 mole) of p-dimethylaminobenzenediazonium fluoborate in a dioxane-water mixture was added. The characteristic red color did not develop within 2 hours so the ice bath was removed and the solution was stirred overnight. A light red color developed on the long stirring. About 300 ml. of water was added to the beaker, and the solid which precipitated from solution was filtered off and air-dried. The solid was crystallized from 25 ml. of ethanol to yield 1.7 g. (85.0% recovery) of triphenyl-m-dimethylaminophenyltin melting at 90-91° (mixed melting point).

Other organotin reactions

Preparation of triphenylsiloxytriphenyltin. In a 250 ml. flask were placed 5.0 g. (0.018 mole) of triphenylsilanol[49] in 150 ml. of dry toluene and 1.0 g. (0.04 g. atom) of sliced sodium metal. The mixture was refluxed for 1 hour, then decanted hot through a glass wool plug into a 250 ml. flask, and 7.0 g. (0.018 mole) of triphenyltin chloride was added to the toluene solution. The mixture was refluxed for 1 hour and filtered hot to remove the insoluble sodium chloride which was formed during the reflux period. On cooling, 11.2 g. of white solid melting at 138-142° was obtained. The solid was crystallized from petroleum ether (b.p. 77-120°) to yield 10.6 g. (95.0%) of triphenylsiloxytriphenyltin melting at 141-142°. A mixed melting point with triphenylsilanol melted at 121-125°.

This compound was analyzed by decomposing a 0.2 g. sample with concentrated sulfuric acid in a 30 ml. vycor

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[49] F. Kipping and L. Lloyd, J. Chem. Soc., 79, 452 (1901).

crucible on a Rogers' ring burner, followed by ignition to the combined oxides (silicon dioxide plus stannic oxide). The combined oxides were then weighed and the percent combined Si-Sn determined. The stannic oxide was then removed by heating the combined oxides with 15 times its weight of ammonium iodide at 450° for 1 hour[50]. This treatment converts the stannic oxide to stannic iodide which is lost by volatilization leaving the silicon dioxide behind. The silicon dioxide was then weighed and the percent Si determined. The percent Sn was determined by the difference of percent combined Si-Sn and percent Si.

Anal. Calcd. for $C_{36}H_{30}OSiSn$: Combined Si-Sn, 23.46; Si, 4.48; Sn, 18.98. Found: Combined Si-Sn, 23.46; Si, 4.77; Sn, 18.69.

Reaction of phenyllithium with tin. Talalaeva and Kocheshkov[51] reported the preparation of tetraphenyltin in 46% yield simply by stirring phenyllithium with tin powder suspended in ether for 185 hours at room temperature. Because of the interest aroused by this report the reaction was investigated.

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[50] E. R. Caley and M. G. Burford, *Ind. Eng. Chem., Anal. Ed.*, *8*, 114 (1936).

[51] T. V. Talalaeva and K. A. Kocheshkov, *J. Gen. Chem.* (U.S.S.R.), *12*, 403 (1942) [*C.A.*, *37*, 3068 (1943)].

In a 500 ml. flask was placed 11.9 g. (0.1 g. atom) of tin powder (Metals Disintergrating Co. Inc., Lot 1007-F, Order 6540) suspended in 50 ml. of ether. To this was added 0.4 mole of phenyllithium in 325 ml. of ether, and the mixture was stirred vigorously and refluxed for 7 days. Color Test I was strongly positive at the end of the reflux period. The mixture was hydrolyzed, the black solid was filtered off and the ether layer dried over sodium sulfate.

The black solid was extracted in a Soxhlet with petroleum ether (b.p. 77-120°) for 24 hours. On concentration and cooling, 1.0 g. (2.5%) of tetraphenyltin melting at 224-225° (mixed melting point) was obtained.

Reaction of phenylmagnesium bromide with tin. This reaction was run to compare the reactivity of phenylmagnesium bromide with that of phenyllithium toward tin metal. In a 500 ml. flask was placed 11.9 g. (0.1 g. atom) of tin powder suspended in 50 ml. of ether. To this was added 0.4 mole of phenylmagnesium bromide in 350 ml. of ether, and the mixture was stirred vigorously and refluxed for 7 days. Color Test I was strongly positive at the end of the reflux period. The mixture was hydrolyzed, the black solid was filtered off, and the ether layer dried over sodium sulfate.

The black solid was placed in a Soxhlet and extracted with petroleum ether (b.p. 77-120°) for 24 hours. No solid was recovered from the petroleum ether on concentration and cooling. The ether layer yielded no solid material either.

Organolead Reactions

Studies on the nature and reactions of triphenyllead-lithium in ether

Preparation of triphenyllead-lithium in ether. In order to afford a ready means of comparison of the methods of preparation of triphenyltin-lithium and triphenyllead-lithium in ether the directions for the preparation of the latter complex are included here. For a more comprehensive coverage of triphenyllead-lithium, its chemical nature and reactions, the report of Gilman, Summers and Leeper[9] should be consulted. The calculated volume of solution necessary to give 0.120 mole of phenyllithium[1] was added dropwise, over a period of about 1 hour, to 11.1 g. (0.04 mole) of dry lead chloride in 30 ml. of ether at -10°.

The phenomena which occurred during the addition of the phenyllithium were as follows: the first few ml. produced no visible effect. Within a short time a yellow color developed and deepened to a bright orange-yellow. This color, which is believed to indicate diphenyllead[9], increased in amount up to 2 equivalents of phenyllithium, if the addition was made slowly enough so that the phenyllithium could react as added. If at any time the phenyllithium was added much faster than indicated above, the color would disappear and then reappear when addition was slowed. Color Test I remained negative up to about 2.75 equivalents of phenyllithium. Between 2.75 and 3.00 equivalents the yellow color disappeared and did not reappear. At the same time Color Test I became positive. The final mixture contained a gray-white precipitate in a light yellow solution, and was ready for subsequent use as soon as the addition of the phenyllithium solution was completed.

The most striking difference between the preparations of triphenyltin-lithium and triphenyllead-lithium is the results obtained with Color Test I. With the former complex Color Test I remains negative until a slight excess of 3.0 equivalents of phenyllithium had been added, but with the latter complex Color Test I becomes positive at the 2.75 equivalents' point.

<u>Preparation of triphenylbenzyllead</u>[9]. This experiment is included to highlight the great difference in reactivity of triphenyltin-lithium and triphenyllead-lithium toward benzyl chloride. In the reaction of the tin complex with this halide, under comparable conditions, triphenylbenzyltin was obtained in a 20% yield and a second product, tetraphenyltin, in a 36% yield. On the other hand, only one product, tri-

phenylbenzyllead, was isolated in a 71% yield in the reaction of the lead complex with this halide.

Benzyl chloride was the reagent employed for the characterization of triphenyllead-lithium. Triphenyllead-lithium was prepared, as described above, by the addition of 0.120 mole of phenyllithium in 112 ml. of ether to 11.1 g. (0.04 mole) of lead chloride in 30 ml. of ether. To this preparation there was then added 6.1 g. (0.04 mole plus 20%) of redistilled benzyl chloride in 50 ml. of ether, still in the cold. There was no visible heating effect. The mixture was stirred for 15 minutes in the cold, and then refluxed for 1.5 hours. The gray appearance gave way to the dead-white color of lithium chloride. The mixture was cooled and hydrolyzed by pouring it into 400 ml. of saturated ammonium chloride solution which had been previously cooled in an ice-salt bath. The hydrolysis left only traces of solid, which were filtered off. The ether layer was separated, washed with water, and dried over sodium sulfate. The ether was removed on a water bath, and finally by evacuation at a water pump at room temperature. This left a solid residue weighing 18.8 g., which was extracted with 175 ml. of 95% ethanol and filtered hot. On cooling, 14.4 g. of triphenylbenzyllead melting at 91-93°

(mixed melting point) was obtained[52]. Concentration of the mother liquor led to the recovery of an additional 0.6 g. of triphenylbenzyllead melting at 90-93°. The total yield of triphenylbenzyllead was 15.0 g. (71.0%).

Reaction of triphenyllead-lithium with 6-bromo-2-naphthol. It would be a distinct advantage if unsymmetrical organolead compounds containing functional groups could be prepared directly from triphenyllead-lithium and organic halides. For this reason an attempt to introduce a hydroxyl-containing group was made. To 0.04 mole of triphenyllead-lithium was added 9.0 g. (0.04 mole) of 6-bromo-2-naphthol[53] in 60 ml. of ether, still in the cold. There was no visible heating effect. The mixture was stirred in the cold for 15 minutes and then brought slowly to reflux. Just as the ether began to reflux a large amount of fine black solid precipitated on the sides of the flask. The flask was instantly cooled in an ice-salt bath. Working up the reaction mixture led to the recovery of a trace of hexaphenyldilead and some metallic lead. Apparently the presence of the active hydrogen decomposed the triphenyllead-lithium.

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[52] H. Gilman, E. B. Towne and H. L. Jones, J. Am. Chem. Soc., 55, 4689 (1933).

[53] H. Frazen and G. Staüble, J. prakt. Chem., 103, 352 (1922).

Reaction of triphenyllead-lithium with lithium o-bromophenoxide. To 0.04 mole of triphenyllead-lithium was added 0.04 mole of lithium o-bromophenoxide (prepared by reacting 0.04 mole of o-bromophenol with 0.04 mole of phenyllithium) suspended in 50 ml. of ether. The mixture was stirred for 4 hours at -10°, 8 hours at room temperature (ca. 20°), and then refluxed for 1.5 hours. The mixture was cooled and hydrolyzed by pouring into 400 ml. of saturated ammonium chloride solution which had been previously cooled in an ice-salt bath.

Upon hydrolysis a gray solid came out of solution. This solid was filtered off and air-dried, the layers were separated, and the ether layer dried over sodium sulfate. The ether layer was deep orange in color and, on standing, an orange solid precipitated from the ether solution. The solid recovered on hydrolysis was extracted with ethanol and filtered hot. On cooling, 0.5 g. (2.9%) of hexaphenyldilead, dec. 170-172°, was obtained.

The ether layer yielded a white solid which was extracted with ethanol, and filtered hot. On cooling, 1.0 g. (6.4%) of tetraphenyllead melting at 221-222° (mixed melting point) was obtained. An attempt to recover the o-bromophenol was unsuccessful.

Preparation of triphenyl-o-methoxyphenyllead. To 0.045 mole of triphenyllead-lithium was added 7.5 g. (0.04 mole) of o-bromoanisole in 50 ml. of ether, still in the cold. The mixture was stirred for 15 minutes in the cold, refluxed for 1.5 hours, cooled and hydrolyzed as outlined above.

Upon hydrolysis a small amount of solid came out of solution. This solid was filtered off and air-dried, the layers were separated, and the ether layer dried over sodium sulfate. The solid recovered on hydrolysis was extracted with ethanol and filtered hot. On cooling, 0.2 g. (2.5%) of tetraphenyllead melting at 224-225° (mixed melting point) was obtained.

The ether layer yielded a small amount of solid in a yellow oil. The mixture was dissolved in ethanol by vigorous refluxing. On cooling, 10.3 g. of white solid melting at 120-125° was obtained. This was recrystallized from petroleum ether (b.p. 77-120°) to yield 7.8 g. (35.8%) of triphenyl-o-methoxyphenyllead melting at 127-129° (mixed melting point)[54].

Reaction of triphenyllead-lithium with methyl o-bromobenzoate. To 0.045 mole of triphenyllead-lithium was added

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[54] D. S. Melstrom, Iowa State Coll. J. Sci., 18, 65 (1943) [C.A., 38, 728 (1944)]; H. Gilman and D. S. Melstrom, J. Am. Chem. Soc., 72, 2953 (1950).

9.5 g. (0.04 mole plus 10%) of methyl o-bromobenzoate in 50 ml. of ether. The reaction mixture became chocolate brown upon the addition of the ester. The mixture was stirred for 15 minutes in the cold, and then refluxed for 1.5 hours. The mixture was then cooled and hydrolyzed as above.

The solid recovered on hydrolysis was extracted with a petroleum ether (b.p. 77-120°)-chloroform solvent pair and filtered hot. On cooling, 7.5 g. of hexaphenyldilead, dec. 155°, was obtained.

The ether layer yielded a yellow solid which was extracted with petroleum ether (b.p. 60-70°), and filtered hot. The residue was then crystallized from a petroleum ether (b.p. 77-120°)-chloroform solution to yield 2.0 g. of hexaphenyldilead, dec. 155°. Total yield of hexaphenyldilead was 9.5 g. (54.0%). From the original petroleum ether extraction 0.8 g. of tetraphenyllead (3.7%) melting at 223-224° (mixed melting point) was obtained. An attempt to recover the methyl o-bromobenzoate was unsuccessful.

DISCUSSION

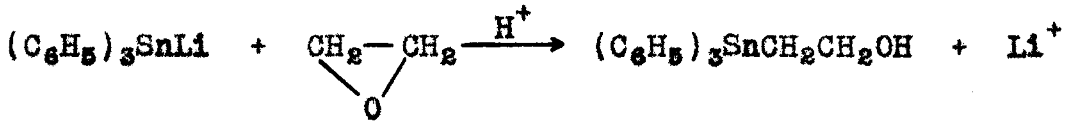
The preparation of triphenyltin-lithium from stannous chloride and phenyllithium is a two step process, the first step being nucleophilic displacement of the chlorine atoms bonded to the tin atom as chloride ions by the phenyl anion of phenyllithium to form diphenyltin. The second step involves addition of the phenyl anion to the open octet of the tin atom in diphenyltin to form the complex, triphenyltin-lithium. The energy for the second step must be provided by the necessity of the tin atom to fill its valence shell with a full quota of electrons.

$$\overset{\cdot\cdot}{\mathrm{Sn}}\mathrm{Cl}_2 \quad + \quad 2\overset{-}{\mathrm{C}_6\mathrm{H}_5}\mathrm{:}\ \overset{+}{\mathrm{Li}} \longrightarrow (\mathrm{C}_6\mathrm{H}_5)_2\overset{\cdot\cdot}{\mathrm{Sn}} \quad + \quad 2\overset{+}{\mathrm{Li}}\overset{-}{\mathrm{Cl}}$$

$$(\mathrm{C}_6\mathrm{H}_5)\overset{\cdot\cdot}{\mathrm{Sn}} \quad + \quad \overset{-}{\mathrm{C}_6\mathrm{H}_5}\mathrm{:}\ \overset{+}{\mathrm{Li}} \longrightarrow [(\mathrm{C}_6\mathrm{H}_5)_2\overset{\cdot\cdot}{\mathrm{Sn}}\ \ \mathrm{C}_6\mathrm{H}_5]^{-}\ \ \mathrm{Li}^{+}$$

The attraction of the phenyl anion for the diphenyltin must indeed 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, Dry Ice, benzophenone and benzalacetophenone. If the complex did dissociate into its component parts, it would be expected that the phenyllithium would react with the aforementioned compounds to form benzoic acid, triphenylcarbinol and diphenyl-β-styrylcarbinol, respectively. In each reaction the only compound formed was tetraphenyltin (ca. 10%), and in the last two, good recoveries of the ketones were made.

Several different types of reactions indicate that triphenyltin-lithium has a lower level of reactivity than phenyllithium. The complex does not add to carbon-carbon or carbon-oxygen double bonds, but it does possess sufficient activity to successfully attack the oxirane ring[55] as evidenced by the preparation of triphenyl-2-hydroxyethyltin and triphenyl-2-hydroxy-3-chloropropyltin, by reaction of ethylene oxide and epichlorohydrin, respectively, with the complex. Triphenyltin-lithium reacts promptly with iodine to form triphenyltin iodide but the reaction is complicated by the rapid attack on the iodide, as formed, by excess triphenyltin-lithium, resulting in the preparation of hexaphenylditin. Triphenyltin-lithium reacts promptly with organic iodides and



$$(C_6H_5)_3SnLi + \underset{O}{CH_2-CH_2} \xrightarrow{H^+} (C_6H_5)_3SnCH_2CH_2OH + Li^+$$

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[55] R. C. Elderfield, "Heterocyclic Compounds", John Wiley and Sons, New York, 1950, p. 2.

$$(C_6H_5)_3SnLi + I_2 \longrightarrow (C_6H_5)_3SnI + LiI$$

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

bromides to form unsymmetrical compounds of the type $(C_6H_5)_3SnR$ in fair yields. Aryl chlorides, such as chlorobenzene, apparently do not react readily with the complex, but, under corresponding conditions, more active organic chlorides, such as benzyl chloride, react promptly.

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

It was found that when o-substituted aryl iodides were reacted with triphenyltin-lithium a second reaction, along with that of the formation of the unsymmetrical compound, took place. This second reaction was first observed when 2,6-dimethyliodobenzene was reacted with the complex, and made itself apparent when Color Test I changed from negative before the addition of this halide to positive after its addition. The change is most directly explained by proposing a halogen-metal interconversion reaction[2] between the halide and triphenyltin-lithium. 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 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. 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.

The usual nucleophilic displacement reaction to form the unsymmetrical compound accompanies the halogen-metal interconversion reaction. The presence of this competing reaction is confirmed by the isolation of triphenyl-o-tolyltin from the reaction of o-iodotoluene with triphenyltin-lithium followed by carbonation just 2 minutes after halide addition. In reactions with 2,6-dimethyliodobenzene and iodomesitylene, where carbonation was carried out 10 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 acid and mesitoic acid. 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 cannot 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 aryl halide to form a substituted diphenyl compound; second, it may cleave the solvent, diethyl ether; third, it may enter into a metal-metal interconversion reaction[56] with the unsymmetrical 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 excellent yield, thereby supporting the fourth alternative.

Another reaction which indicates a lower order of activity for triphenyltin-lithium as compared to phenyllithium is that between triphenylsilane and the complex. Treatment

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[56] H. Gilman, F. W. Moore and R. G. Jones, J. Am. Chem. Soc., 63, 2482 (1941); see also H. Gilman, "Organic Chemistry", John Wiley and Sons, New York, 1943, 2nd ed., p. 572.

of this silane with phenyllithium results in the preparation of tetraphenylsilane and lithium hydride[57], whereas triphenyltin-lithium does not react with triphenylsilane. Similarly, the complex does not react with triphenylmethane, whereas phenyllithium reacts to form triphenylmethyllithium and benzene. Triphenyltin-lithium does react promptly with triphenylchlorosilane and triphenyltin chloride to form triphenylsilyltriphenyltin and hexaphenylditin, respectively, in good yields.

Complexes other than triphenyltin-lithium may be obtained by substituting other organolithium compounds for phenyllithium. The preparation of symmetrical alkyl and aryl organotin compounds by this method appears to be promising as the yields of tetraethyltin, tetra-n-butyltin, tetra-p-tolyltin and tetra-m-tolyltin were in excess of 70%. It would be of interest to see if long chain alkyl compounds, such as tetradodecyltin, and polyaryl compounds, such as tetra-p-biphenylyltin, can be prepared using this method. The preparation of compounds using these complexes as intermediates has distinct advantages over the usual laboratory method, which employs stannic chloride and an organolithium

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[57] H. Gilman and H. W. Melvin, J. Am. Chem. Soc., 71, 4050 (1949).

compound or Grignard reagent, in that the stannous chloride is much more easily handled than stannic chloride, and the overall preparation is less time consuming.

It was not possible to prepare tetra-o-tolyltin by treatment of tri-o-tolyltin-lithium with o-iodotoluene. The steric hindrance[58] presented by the three o-methyl groups probably prevents a successful attack on the halide from taking place. A reaction between this complex and benzyl chloride prepared the desired unsymmetrical compound in only a 2.3% yield. It would be of interest to see if the hindrance of the methyl groups would be great enough to prevent a successful reaction between the complex and methyl iodide. In the reactions of tri-o-tolyltin-lithium with o-iodotoluene and benzyl chloride, respectively, a considerable amount of solid which analyzed for hexa-o-tolylditin was isolated. This material melted at 298-300° and was almost completely insoluble in organic solvents. Morris, Byerly and Selwood[23] reported that they had prepared hexa-o-tolylditin by reduction of tri-o-tolyltin bromide in benzene with sodium metal and ethanol. Their product melted at 208-210°. In order to clear up this apparent

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[58] For a complete review of steric hindrance as applied to Group IVB elements see C. G. Brannen, Doctoral Dissertation, Iowa State College, 1951.

discrepancy another sample of hexa-o-tolylditin was prepared by reacting tri-o-tolyltin chloride with sodium shot in refluxing xylene. The compound thus obtained melted at 298-300°, showed no depression in a mixed 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.

Several investigators have studied the possible dissociation of hexaalkyl- and hexaarylditin compounds into free radicals of the type R_3Sn[23,59,60,61,62,63,64,65]. The experimental evidence is contradictory, and it is difficult to decide whether these ditin compounds actually do dissociate. Molecular weight determinations made by ebulliometric methods indicate that hexaethylditin is partially dissociated in ethereal solutions[59], hexacyclohexylditin to be completely

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[59] L. Rügheimer, Ann., 364, 51 (1909).

[60] G. Grüttner, Ber., 50, 1808 (1917).

[61] E. Krause and R. Becker, Ber., 53, 173 (1920).

[62] J. Böeseken and J. J. Rutgers, Rec. trav. chim., 42, 1017 (1923).

[63] E. Krause and R. Pohland, Ber., 57, 532 (1924).

[64] C. A. Kraus and W. V. Sessions, J. Am. Chem. Soc., 47, 2361 (1925).

[65] H. Morris and P. W. Selwood, ibid., 63, 2509 (1941).

dissociated in benzene[63], and hexamethylditin to be completely dissociated at a concentration of 0.4% and completely associated at 5.0% in benzene[64]. Using cryoscopic methods in benzene the following compounds have been shown to be completely associated, within limits of experimental error: hexaethylditin, hexa-n-propylditin, hexaisobutylditin, sym.-tetraethyldi-n-propylditin, sym.-tetraethyldiisobutylditin[60], and hexaphenylditin[61,62]. Using the Rast method hexacyclohexylditin in camphor was found to be completely associated[63]. Morris and Selwood[65], using magnetic susceptibility measurements, concluded that hexamethylditin does not exist as the monomer even in dilute benzene solutions. This method is sensitive enough to detect dissociation down to a minimum of less than 2%. In an attempt to investigate the reasons behind the apparent contradiction between ebulliometric measurements and the other methods cited above, Morris, Byerly and Selwood[23] made a series of ebullioscopic measurements using hexamethylditin in benzene. They concluded that ebulliometric measurements are of little value for the study of organometallic free radicals as the compound noticeably decomposes even before the apparatus can come into equilibrium. The reactions of hexaalkylditin compounds with halogens and moist air suggest that if there is no actual dissociation into free radicals, the tin-tin bond must, at best, be a weak one.

Hexa-o-tolylditin was reacted with oxygen in benzene in the hope that it would show free radical behavior but apparently no reaction took place as evidenced by almost quantitative recovery of the ditin compound.

Unsymmetrical compounds of the type R_3SnR' are more easily prepared by the usual laboratory procedure, which employs an organotin halide and an organolithium compound or Grignard reagent, than by using these complexes as intermediates. The reason for this is the formation of a small amount of symmetrical compound in all reactions in which these complexes are involved. The symmetrical by-product contaminates the desired unsymmetrical compound thereby rendering the latter more difficult to purify and lessening its yield. From the data available it is not possible to ascertain exactly how the symmetrical by-product is formed. In general, it appears that the longer a reaction is continued, the higher is the yield of the symmetrical compound. In reactions with triphenyltin-lithium it was thought that the tetraphenyltin arose from the reaction of the complex, as formed, with unreacted bromobenzene carried over from the preparation of phenyllithium. The reactions with bromobenzene-free triphenyltin-lithium demonstrated that this explanation cannot be the only mechanism involved in the formation of the by-product, as tetraphenyltin was isolated in yields comparable to those obtained with the usual complex preparation. The tetraphenyltin may also arise from disproportionation of diphenyltin, triphenyltin-lithium or the unsymmetrical compounds, as formed. A more intensive study of this phenomenon is needed to shed more light on this side reaction.

Another method of synthesis for unsymmetrical compounds which might prove to be interesting is the preparation of $R_2SnR'_2$ and $R_2SnR'R''$ compounds by reaction of mixed organotin-lithium complexes with appropriate organic halides. This method would afford a direct synthesis for these more complex

$$R_2Sn + R'Li \longrightarrow R_2R'SnLi$$

$$R_2R'SnLi + R'X \longrightarrow R_2SnR'_2 + LiX$$

$$R_2R'SnLi + R''X \longrightarrow R_2SnR'R'' + LiX$$

unsymmetrical organotin compounds as the reaction could be carried out in one flask and only the final product would actually be isolated and purified, thereby tending to increase the overall yield of desired compound.

In order to study the effect of substituents on the reactivity of organic halides toward triphenyltin-lithium, the complex was reacted with p-bromodimethylaniline, p-bromoanisole and p-iodochlorobenzene, respectively. The first halide apparently did not react at all, while the last two reacted to form triphenyl-p-methoxyphenyltin (30%) and triphenyl-pchlorophenyltin (20%), respectively. Bromobenzene, in contrast, reacts with triphenyltin-lithium to form tetraphenyltin in 82% yield. Complexes like triphenyltin-sodium and triphenyltin-potassium should prove to be more reactive than triphenyltin-lithium and thereby these former complexes, if they could be similarly prepared in ether, might be more useful in the preparation of unsymmetrical organotin compounds.

The preparation of triphenyltin hydride (52%) by reduction of triphenyltin iodide with lithium aluminum hydride proved to be a more efficient method of synthesis than the ammoniation method of Chambers and Scherer[66]. Wittig, Meyer and Lange[5] successfully reduced triphenyltin bromide to form triphenyltin hydride (43%), but it was found that triphenyltin chloride apparently could not be reduced by lithium aluminum hydride, under corresponding conditions, as evidenced by almost quantitative recovery of the organotin chloride.

Wittig, Meyer and Lange[5] reported that triphenyltin-lithium was prepared by the addition of methyllithium to triphenyltin hydride in ether. The complex was indirectly identified by reaction with triphenyltin bromide to form hexa-

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[66] R. F. Chambers and P. C. Scherer, J. Am. Chem. Soc., 48, 1054 (1928).

phenylditin. It was learned in a private communication from

$$(C_6H_5)_3SnH + CH_3Li \longrightarrow (C_6H_5)_3SnLi + CH_4$$

Dr. Wittig that the gas which was evolved during the methyllithium addition was not analyzed, and that the reaction was not run in duplicate. It is known that silanes of the type R_3SiH (where R may be alkyl or aryl) react with organolithium compounds to form symmetrical and unsymmetrical silanes, and lithium hydride[67]. Triphenyltin hydride has been reacted with phenyllithium to form tetraphenyltin (90%) and lithium hydride[67]. Because of the apparent contradiction between these latter results and the report of Wittig and coworkers, triphenyltin hydride was reacted with methyllithium. It was found that no gas was evolved, and that the reaction apparently progressed as reported for silanes to form triphenylmethyltin (18%), tetraphenyltin (25%) and lithium hydride. Apparently disproportionation takes place, even under these mild conditions, to form the tetraphenyltin and its presence may, in part, account for the low yield of triphenylmethyltin by rendering the latter more difficult to purify.

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[67] H. Gilman and S. P. Massie, ibid., 68, 1128 (1946); R. N. Meals, ibid., 68, 1880 (1946); R. A. Benkeser and F. J. Riel, ibid., 73, 3472 (1951).

To check these findings the reaction was repeated and essentially the same results were obtained. An attempt to prepare triphenyltin-lithium by reaction of triphenyltin chloride with lithium metal in ether proved to be unsuccessful as evidenced by almost quantitative recovery of the chloride.

In the preparation of triphenyl-2,5-dimethylphenyltin and triphenyl-m-dimethylaminophenyltin from triphenyltin chloride and the appropriate organolithium compound, it was found that tetraphenyltin was formed as a by-product if the organolithium compound was added rapidly to an ethereal solution of the chloride. The tetraphenyltin is probably formed by disproportionation, even under these mild conditions. The formation of the tetraphenyltin could be prevented by slow addition of the organolithium compound to a cold ethereal solution of the chloride.

The reaction between triphenylbenzyltin and phenyllithium proved to be extremely interesting in that the benzyl group was preferentially cleaved by the organolithium compound. This result is an exact reversal of the reaction between triphenylbenzyltin and halogen acid, in which the phenyl group is preferentially removed[68]. This contradiction suggests that

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[68] G. A. Razuvaev and V. Fetyukova, J. Gen Chem. (U.S.S.R.), 21, 1010 (1951) [C.A., 46, 1479 (1952)].

a systematic investigation of the cleavage of alkyl and aryl groups from tin by basic agents, such as n-butyllithium[2] or phenyllithium[2], might prove to be of interest.

Another cleavage reaction which opens the way for further investigation is that between hexaphenylditin and phenyllithium, which resulted in the preparation of tetraphenyltin in very high yield. It would be of interest to explore this reaction using other organolithium compounds and other ditin compounds.

The preparation of azo tin compounds by reaction of triphenyl-p-dimethylaminophenyltin with p-substituted benzenediazonium chlorides in a buffered solution proved to be a rather unsatisfactory method. In fact, it is highly doubtful that the diazonium chlorides actually exist as such under the conditions of the reaction. It is more likely that the diazo compound is the diazonium acetate or hydroxide, which are of a lower energy level than the true salts[69].

The use of the easily isolated and purified p-substituted benzenediazonium fluoborates in the coupling reaction proved to be very interesting. When reacted with triphenyl-

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[69] K. H. Saunders, "The Aromatic Diazo-Compounds and Their Technical Applications", Edward Arnold, London, 1949, 2nd ed.

p-dimethylaminophenyltin these salts caused expulsion of the triphenylstannyl group with formation of p,p'-substituted azobenzene compounds. Isolated examples of the expulsion reaction have been reported[69], but no systematic investigation of the phenomenon has been made. The expulsion of the triphenylstannyl group in reactions with triphenyl-p-dimethylaminophenyltin suggests that it may provide an excellent method for the study of the relative reactivity of diazonium compounds toward the coupling reaction by the use of kinetic and quantitative measurements.

It was found that azo tin compounds could be prepared directly and in good yields by reacting triphenyl-m-dimethylaminophenyltin with p-substituted benzenediazonium fluoborates. The problem remaining is to synthesize azo tin compounds which are sufficiently water soluble to be tested clinically as anticarcenogenic agents. This might be done by reacting p-carboxybenzenediazonium fluoborate with triphenyl-m-hydroxyphenyltin or triphenyl-2,5-dihydroxyphenyltin, and then converting the resulting azo tin compounds to the di- and trisodium salts, respectively.

The structure of the dyes prepared by reacting triphenyl-m-dimethylaminophenyltin with p-substituted benzenediazonium fluoborates was determined by chemical methods. The key to the structure proof was the isolation of p-dimethylaminoacetanilide (35%). This compound could have been formed only if the azo group and dimethylamino group were *para* to each other in the original dye (barring molecular rearrangement). Therefore, in the trisubstituted benzene ring, the triphenylstannyl group has been assigned the 1 position; the dimethylamino group, the 3 position; and the *p*-substituted azophenyl group, the 6 position. Infrared studies on triphenyl-3-dimethylamino-6-(4'-nitrophenylazo)phenyltin were inconclusive and a definite orientation of the groups could not be assigned, but with triphenyl-3-dimethylamino-6-(4'-bromophenylazo)phenyltin 1,2,4-substitution was clearly indicated by the infrared spectrum. This latter finding supports the structure assigned as a result of the chemical degradation of triphenyl-3-dimethylamino-6-(4'-nitrophenylazo)phenyltin. Two of the dyes, triphenyl-3-dimethylamino-6-(4'-nitrophenylazo)phenyltin and triphenyl-3-dimethylamino-6-(4'-bromophenylazo)phenyltin, were tested by Dr. Dickey[70] for their substantivity as dyes. The former compound was tested with 12 different fabrics and a slight pink coloration was developed with each, but this coloration almost com-

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[70] Dr. J. B. Dickey of Tennessee Eastman Company, Division of Eastman Kodak Company, Kingsport, Tennessee.

pletely faded on exposure to light for 20 hours. The latter dye was tested with 6 fabrics and there was no coloration at all. In a letter discussing the results Dr. Dickey stated, "I would like to suggest that you switch from the triphenyl compound to the trimethyl or ethyl, for example as the color will be shifted to the blue and there will be a better chance for the resulting compounds to color cellulose acetate, nylon, dacron and the like."

SUMMARY

A thorough survey of the chemical literature beginning with January 1941 and ending with September 1952 has been made. The methods of preparation of organotin compounds used during this period have been reviewed, and a series of tables listing the various compounds mentioned in the literature has been made.

The preparation of triphenyltin-lithium from stannous chloride and phenyllithium in ether has been described. This complex is not part of an equilibrium system.

Triphenyltin-lithium possesses sufficient activity to successfully attack the oxirane ring but it does not add to carbon-carbon or carbon-oxygen double bonds. The complex has been reacted with alkyl and aryl halides to form unsymmetrical organotin compounds in fair yields. With _o_-substituted aryl iodides, triphenyltin-lithium enters into a halogen-metal interconversion reaction.

Complexes other than triphenyltin-lithium may be obtained by substituting other organolithium compounds for phenyllithium, and the preparation of symmetrical alkyl and aryl organotin compounds by this method appears to be quite

promising.

A series of organotin compounds has been prepared by reacting triphenyltin chloride with an appropriate Grignard reagent or organolithium compound. This method of preparation of unsymmetrical compounds appears to be superior to the reaction of triphenyltin-lithium with appropriate organic halides.

The preparation of azo tin compounds by reaction of triphenyl-p-dimethylaminophenyltin with p-substituted benzenediazonium chlorides in a buffered solution proved to be an unsatisfactory method. It was found that azo tin compounds could be prepared directly and in good yields by reacting triphenyl-m-dimethylaminophenyltin with p-substituted benzenediazonium fluoborates. Chemical degradation of one of these dyes showed that the azo group couples *para* to the dimethylamino group.

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