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COMPOUNDS.

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COMPARISONS OF ORGANIC GROUP IVB LITHIUM COMPOUNDS

by

Frank Kehrer Cartledge

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INTRODUCTION

The chemistry of silylmetallic compounds has received considerable study in These Laboratories and elsewhere since the first preparations of stable silylmetallics in 1950 and 1951 (1). These reagents, like the well known organometallic species, have a wide range of synthetic possibilities. They are of fundamental interest in silicon chemistry, because they allow studies of the behavior of the silyl anion in solution; and, just as the study of organometallic compounds has laid the foundations of carbanion chemistry, silylmetallic reagents are being used to elucidate the properties of negatively charged silicon.

Germyl-, tin-, and leadmetallic species are no less interesting than their silicon analogs, but have received much less study. In particular, relatively little attention has been centered upon the variations in properties of metallic derivatives of silicon, germanium, tin, and lead. Therefore, the present work has sought to throw light upon the relative reactivities of these reagents.

The aspect of this work concerned with the analysis of organometallic compounds served as a starting point. The method to be described has been successfully applied to the analysis of solutions of silyl-, germyl-, and tinlithium compounds (2), and thus has afforded the possibility of making quantitative comparisons of the reactivities of the reagents.

Emphasis has been placed also upon extending synthetic possibilities, particularly with tinlithium reagents. Several new triorganotinlithium compounds have been prepared, and triphenyltinlithium has been used for the synthesis of a compound, tetrakis(triphenylstannyl)tin, which is representative of a hitherto uninvestigated series of branched chain polytin compounds.

HISTORICAL

Analysis of Organolithium Compounds

There has been much interest in recent years in analytical methods for solutions of organometallic compounds. The necessity for reliable methods when structural and mechanistic studies are being carried out is obvious, and such studies are becoming increasingly common in the literature. Analytical procedures for organomagnesium compounds have been recently evaluated (3-5).

In the case of organolithium compounds there have been several studies aimed at developing a simple, accurate procedure (6-16). It is well recognized that hydrolysis of an aliquot of an organolithium compound followed by titration with acid (6) leads to an analysis that is always high, because of the impossibility of excluding all traces of oxygen and moisture, which react with organolithium reagents to give other basic species. Thus, the simple acid titration is measuring the combined concentrations of the several basic components of the solution.

The most commonly used method of analysis for alkyllithium compounds has been a double titration in which benzyl chloride is used to destroy the organolithium compound (8). Acid titration after treatment of the solution with benzyl chloride measures basic species other than the organolithium compound. The difference between the total basic content and that after treatment with benzyl chloride thus corresponds to the organolithium content. The method is more convenient to carry out than other procedures proposed, but several drawbacks have become apparent. Quite low concentration values are obtained when the analysis is carried out on solutions of methyllithium and aryllithium compounds, and recent work has also indicated that the analysis is somewhat low for other alkyllithium compounds as well (11, 16, 17). The implication is that benzyl chloride does not react quantitatively with an organolithium compound to give nonbasic products.

It has been estimated (11, 17) that the benzyl chloride double titration method gives an analysis which is about 5% low for n-butyllithium in hydrocarbon solvents. The argument is based on the fact that lithium alkoxides have low solubility in hydrocarbons, so that almost the total basic content of the solution should be due to the organolithium compound. Consequently, a new method of analysis was developed which consisted of oxidative titration with vanadium pentoxide (11). The latter method showed that n-butyllithium contributed approximately 99% of the base released upon hydrolysis of the hydrocarbon solutions. However, the method is less convenient to carry out than the double titration because of the standard solutions that must be prepared, and apparently some experience is required before consistent results can be obtained (16). Also, some caution is required with the titration because of the very strong oxidative power of vanadium pentoxide, which may also oxidize unsaturated carbon compounds present.

Recently, still another independent method of analysis for n-butyllithium in hydrocarbon solvents has been proposed (16). The procedure employs thermometric titration with n-butanol, a reaction which produces lithium n-butoxide. The approach appears to be a sound one, since basic species other than the organolithium compound would not be expected to interfere. Solutions of n-butyllithium were analyzed both by thermometric and vanadium pentoxide titration, and the concentrations found were in essential agreement (16). The thermometric titration is rapid, but again there is a major drawback. The normal research laboratory, performing occasional analyses, will find it expensive and inconvenient to set up and maintain the required equipment.

Several variations of the double titration procedure have been proposed (9, 12 - 14), employing organic halides other than benzyl chloride, but these procedures have not been investigated as to reliability or generality. Titration with iodine has been investigated (10), but side reactions may be expected to affect the accuracy of the method, since iodine compounds formed during the titration can react with the excess of organometallic compound or with alkoxides.

Cleavage of Alkoxysilanes

A variety of reagents, both electrophilic and nucleophilic, bring about the cleavage of alkoxysilanes (18). In virtually all of the known cases cleavage of the silicon-oxygen bond occurs to the exclusion of scission of the carbon-oxygen bond, in spite of the fact that the Si-O bond energy is greater than that of the C-O bond (18). Indeed, the alkoxy group attached to silicon behaves as a pseudohalogen. Extensive use has been made of this fact for the synthesis of organosilicon compounds. The readily available tetramethoxy- and tetraethoxysilane may be reacted with organometallic reagents to obtain good yields of organosilanes. Experimental procedures for replacing one, two, or three alkoxy groups with an organic residue have been described in some detail (19,20).

Wurtz-Fittig condensations of alkoxysilanes with organic halides can be carried out using sodium in toluene (21):

$$Si(OC_2H_5)_4 + C_2H_5Br + Na \longrightarrow (C_2H_5)_xSi(OC_2H_5)_{4-x} \qquad (x = 1\text{-}3)$$

However, alkoxysilanes are less reactive than chlorosilanes in condensation reactions, so that the trimethylsilyl group may be used to protect an hydroxyl group during organometallic syntheses (22):

$$(CH_3)_3SiCl + HO(CH_2)_4Cl \longrightarrow (CH_3)_3SiO(CH_2)_4Cl$$

$$(CH_3)_3SiCl + (CH_3)_3SiO(CH_2)_4Cl + 2Na \longrightarrow (CH_3)_3SiO(CH_2)_4Si(CH_3)_3$$

$$(CH_3)_3SiO(CH_2)_4Si(CH_3)_3 + H_3O^+ \longrightarrow HO(CH_2)_4Si(CH_3)_3 + (CH_3)_3SiOH$$

Stable silylmetallic reagents may be obtained from the reaction of ethoxy- (23) or methoxytriphenylsilane (24) with sodium-potassium alloy in diethyl ether. Silylpotassium compounds are formed, apparently in good yield.

It is only rather recently that cleavage of the carbon-oxygen bond in alkoxysilanes has been observed. The reaction of n-butoxytrimethylsilane with phosphorus oxychloride proceeds in the normal manner (25):

$$(CH_3)_3SiOC_4H_9 + POCl_3 \longrightarrow (CH_3)_3SiCl + POCl_2(OC_4H_9)$$

However, when the reaction is carried out with (α-phenylethoxy)-trimethylsilane or (diphenylmethoxy)trimethylsilane, the products are those of carbon-oxygen bond cleavage (25):

$$(CH_3)_3SiOCH(CH_3)(C_6H_5) + POCl_3 \longrightarrow (CH_3)_3SiOPOCl_2 + (C_6H_5)(CH_3)CHCl$$

$$(CH_3)_3SiOCH(C_6H_5)_2 + POCl_3 \longrightarrow (CH_3)_3SiOPOCl_2 + (C_6H_5)_2CHCl$$

It appears then that alkoxides derived from relatively reactive alcohols undergo C-O bond scission with some facility.

A second factor which appears to favor abnormal cleavage is increasing electronegativity of groups attached to silicon. This fact is indicated by the following two reactions (26):

$$(CH_3)_3SiOCH(CH_3)(C_2H_5) + BCl_3 \longrightarrow (CH_3)_3SiCl + (C_2H_5)(CH_3)CHOBCl_2$$

$$Cl_3SiOCH(CH_3)(C_2H_5) + BCl_3 \longrightarrow (Cl_3SiO)_3B + (C_2H_5)(CH_3)CHCl$$

The redistribution of alkoxy groups attached to silicon under the influence of sodium ethoxide has been known for some time (27). Recently the reaction has been investigated further using methoxysilanes and sodium methoxide or alkali metals as catalysts (28). In all of the reactions run, dimethyl ether is formed in minor amounts. Presumably this product arises from C-O bond cleavage in the following manner:

$$CH_3O^- + CH_3OSiR_3 \longrightarrow CH_3OCH_3 + R_3SiO^-$$

When alkali metals are used at high temperatures, some reduction of the methoxysilanes took place. The mechanism proposed for the reaction involves C-O bond cleavage by the alkali metal (28):

$$CH_3OSiR_3 + 2\ Na \longrightarrow CH_3Na + R_3SiONa$$

$$CH_3Na + CH_3OSiR_3 \longrightarrow CH_3SiR_3 + CH_3ONa$$

The reduction could be effected when either methoxy or phenoxy groups were attached to silicon, but it was not facile compared to the redistribution reaction.

Reactions of silylmetallic compounds with alkoxysilanes have been carried out (29), but attack at silicon and not at carbon has been observed.

Relative Reactivities of Organic Group IVB Lithium Compounds

No strictly quantitative comparisons of the Group IVB lithium reagents have been made or attempted. Any attempt in this direction has been hampered until recently by the lack of a convenient method for the quantitative analysis of solutions of the compounds. Most often comparisons must be made by culling information from various sources, which allows only rough estimates at best.

The most definitive information available is that for metalation reactions. The proton transfer involved in metalation affords a measure of the basicity of the metalating agent, a property of rather fundamental significance. A study has been made (30) in which triphenylsilyl-, -germyl-, -tin-, and -leadlithium were reacted, all under the same conditions, with fluorene, the reaction mixtures carbonated, and yields of fluorene-9-carboxylic acid determined. The following order of decreasing metalating ability was found:

$$(C_6H_5)_3SiLi \approx (C_6H_5)_3GeLi > (C_6H_5)_3SnLi > (C_6H_5)_3PbLi$$

The concentrations of the solutions of metalating agents were not standardized, nor was the actual amount of reagent present known with precision. These inaccuracies could conceivably reverse the positions of triphenylsilyllithium and triphenylgermyllithium, since the two gave nearly the same yield of acid. However, triphenylsilyllithium was shown to metalate triphenylgermane (30), and this observation was taken to indicate the greater basicity of the silyllithium reagent. It should be noted, however, that a conclusive judgment is not warranted on this basis, since the metalation by triphenylsilyllithium is probably an irreversible reaction. The product, triphenylsilane, is not metalated even by n-butyllithium. The reaction which does occur is hydride displacement leading to n-butyltriphenylsilane (31).

Early investigations (32) showed a rather high metalating ability for triphenyltinlithium and triphenylleadlithium when the reagents were prepared from diphenyltin and diphenyllead, respectively, and phenyllithium in diethyl ether. It was proposed, however, that the actual metalating agent in these reactions was phenyllithium, and that preparation of the tin- and leadlithium reagents corresponded to the establishment of a readily reversible equilibrium:

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

The existence of such an equilibrium under these conditions has been questioned with regard to triphenyltinlithium (33), but it appears very likely to exist for triphenylleadlithium, since a solution of the latter reagent gives benzoic acid on carbonation (34). Thus, it seems unwise to compare the metalating power of triphenyltinlithium and triphenylleadlithium prepared from phenyllithium in diethyl ether with the same reagents prepared in tetrahydrofuran from triphenyltin or - lead chloride.

Some comparisons can be made in the area of nucleophilic displacement reactions. The interaction of the lithium reagents with organic halides is complicated by the possibility of halogen-metal interconversion. In general, alkyl chlorides react with triphenylsilyllithium to give good yields of the corresponding alkyltriphenylsilanes with little or no side products (29). Bromides and iodides normally give some halogen-metal interconversion with formation of hexaphenyldisilane (29). Triphenylgermyllithium does not appear to enter into halogen-metal interconversion as readily as the silyllithium, as indicated by the following comparison:

$$(C_6H_5)_3SiLi + \underline{n}\text{-}C_8H_{17}Br \rightarrow \underset{26.4\%}{(C_6H_5)_3SiC_8H_{17}\text{-}\underline{n}} + \underset{44.4\%}{(C_6H_5)_6Si_2} \quad (29, p.306)$$

$$(C_6H_5)_3GeLi + \underline{n}\text{-}C_8H_{17}Br \rightarrow \underset{70\%}{(C_6H_5)_3GeC_8H_{17}\text{-}\underline{n}} + \underset{0\%}{(C_6H_5)_6Ge_2} \quad (35)$$

Triphenyltinlithium (35-37) and triphenylleadlithium (36, 38) in tetrahydrofuran also appear to give coupling to the virtual exclusion of halogen-metal interconversion in reactions with organic halides. Several sources report reactions of organic halides with triphenyltinlithium (33, 39) and triphenylleadlithium (34, 40) prepared from phenyllithium in diethyl ether. Halogen-metal interconversion can occur in these systems (39), but again phenyllithium may be the active reagent. It would thus be possible to compare the nucleophilicity of the Group IVB lithium compounds in displacements on alkyl chlorides without serious interference from side reactions, but such a comparison is not available.

Ethylene oxide has been treated with triphenylsilyl-, -germyl-, and -tinlithium. This reaction, involving nucleophilic attack, affords the corresponding β-hydroxyethyl derivatives. Triphenylsilyllithium in tetrahydrofuran gave an 85.5% yield of alcohol (41), triphenylgermyllithium in ethylene glycol dimethyl ether a 71% yield (42), and triphenyltinlithium in diethyl ether a 44.8% yield (43). However, due to the difference in experimental conditions, the comparison may not be a valid indication of reactivities.

Triphenylsilyllithium has been proposed to be more reactive than phenyllithium, n-butyllithium, or benzyllithium in coupling reactions with chlorotriphenylsilane (44). The observation was made on the basis of competitive reactions of two of the lithium reagents with a quantity of chlorosilane insufficient to react with both.

When two moles of triphenylsilyllithium are added to one mole of hexaphenyldigermane, a quantitative yield of hexaphenyldisilane is obtained along with 70% of triphenylgermane (45). The formation of triphenylgermyllithium from a cleavage reaction with triphenylsilyllithium would at first glance indicate that the silyllithium is the more reactive of the two. However, all that may have been proved is that the silicon-silicon bond is a stronger one than the germanium-germanium bond. A variety of cleavage reactions of this type has been run, but their significance for determining relative reactivities is doubtful.

Another area in which some comparisons can be made is that of additions to double bonds. Triphenylsilyllithium adds to benzophenone to give a 50% yield of a rearranged product (46):

$$(C_6H_5)_3SiLi + (C_6H_5)_2CO \rightarrow (C_6H_5)_3SiOCH(C_6H_5)_2$$

On the other hand, triphenylgermyllithium adds to the same ketone to give a 37% yield of the normal carbinol product (47). Triphenyltinlithium has been reported not to add to benzophenone, benzalacetophenone, or stilbene (43). Again, triphenylsilyllithium adds to 1,1-diphenylethylene in 80% yield (29, p.322), while triphenylgermyllithium adds in only 14.8% yield (48). Both of the latter two reagents add to azoxybenzene to give N-substituted hydrazines, triphenylsilyllithium in 52.9% yield and triphenylgermyllithium in 51.4% yield (49). It thus appears that triphenylsilyllithium gives more facile additions to multiple bonds than triphenylgermyllithium, while triphenyltinlithium and triphenylleadlithium have not been observed to give addition reactions.

Organic Polytin Compounds

The chemistry of catenated organotin compounds began as early as 1852 with the report by Löwig (50) of the reaction of ethyl iodide with tin-sodium alloy. A product of this reaction, a diethyltin, has only very recently been characterized (51-53). A similar situation may be cited in the case of tetrakis (triphenylstannyl)tin, which was prepared as early as 1923 (54), but was not rigorously identified until the present study. This compound is the only discrete branched chain polytin in the literature at present. These two examples are not entirely representative of the state of the science in catenated tin chemistry, but they are indicative of the current active interest in the field and of the kind of fundamental questions which are only now being given answers.

The ditin compounds known outnumber the higher polytins. This is in part due undoubtedly to the greater difficulty of synthesizing some of the latter compounds. The pioneer in this area, C. A. Kraus, characterized the first tritin and pentatin derivatives in 1925 (55), but his work was not elaborated upon until recent years. The synthetic possibilities have now been broadened considerably by the characterization of cyclic polytin compounds, which may serve as precursors for many new derivatives. Any number of fundamental questions bearing upon the effects of chain length in catenated tin compounds may find answers in the near future.

A particularly active area of investigation is that concerned with the nature of "divalent" tin species, R_2Sn. It has now been well established that these compounds are in many cases polymers of the R_2Sn structure, and do not, in fact, contain tin species in the divalent state. Some diorganotin compounds, particularly those prepared from organolithium or organomagnesium reagents and stannous chloride, have been shown (52, 53, 56-58) to correspond to R_2Sn compounds only in gross composition, and to contain tin polymers with chain branching, so that R_3Sn- and $RSn\equiv$ moieties are present in the compounds. A review (53) of the nature of these compounds and the problems involved in their study has recently appeared, so that the present writing will in the main treat only those compounds which have been shown to be reasonably discrete species.

Methods of preparation

Almost every useful method for the synthesis of organopolytin compounds has involved organotin halides or hydrides as starting materials. The classic Wurtz synthesis employing a triorganotin halide and sodium in benzene, toluene or xylene has been used frequently for the preparation of ditin compounds (43, 59-63):

$$(\underline{p}\text{-ClC}_6H_4)_3SnBr + Na \xrightarrow{\text{xylene}} (\underline{p}\text{-ClC}_6H_4)_6Sn_2 \qquad 89.5\% \qquad (62)$$

Other solvents, such as diethyl ether (64), isoamyl ether (65, 66) or ethanol (59) have been successfully employed, or the reaction may be run using sodium powder and a liquid organotin halide without solvent (64). Another solvent which has been shown to have considerable versatility is liquid ammonia. A simple coupling may be accomplished with a triorganotin halide and lithium (67) or sodium (67-70) in liquid ammonia. But, more importantly, the reaction may be halted with the formation of a triorganotinsodium compound, which may be treated subsequently with a different triorganotin halide to obtain an unsymmetrical ditin (68, 69):

$$(CH_3)_3SnBr + Na \xrightarrow{\text{liq. }NH_3} (CH_3)_3SnNa \xrightarrow{(C_2H_5)_3SnI} (CH_3)_3SnSn(C_2H_5)_3 \qquad (68)$$

The versatility does not end here, however, for diorganotin dihalides may be reacted with sodium to produce polytinsodium compounds (55, 71, 72). Thus, Kraus has shown that proper choice of the ratio of sodium to dimethyltin dibromide leads to 1,2-disodiotetramethylditin or 1,3-disodiohexamethyltritin. Using this method a chain of five tin atoms has been obtained:

$$3(CH_3)_2SnBr_2 + 8\,Na \xrightarrow{\text{liq. }NH_3} Na\left[Sn(CH_3)_2\right]_3Na + 6\,NaBr$$

$$\xrightarrow{2\,(CH_3)_3SnBr} (CH_3)_3Sn\left[Sn(CH_3)_2\right]_3Sn(CH_3)_3 \qquad (55)$$

Using diorganotin dichlorides and sodium in xylene, α,ω-dichloropolytin compounds may be obtained in yields of up to 50% (73). One major product was obtained from each tin halide; dimethyltin dichloride produced a ditin; diethyl-, dipropyl-, and dibutyltin dichloride gave tetratin, tritin, and pentatin, respectively (73).

$$R_2SnCl_2 + Na \xrightarrow{\text{xylene}} Cl[R_2Sn]_nCl$$

$R = CH_3, \ n = 2$

$R = CH_3CH_2, \ n = 4$

$R = CH_3CH_2CH_2, \ n = 3$

$R = CH_3CH_2CH_2CH_2, \ n = 5$

A number of additional preparations involving alkali metals has been reported. The first preparation of a hexaorganoditin involved the addition of ethyl iodide to a tin-sodium alloy to produce what appears to be hexaethylditin, along with other products (50, 74). Tin-sodium alloy has also been reacted with organomercuric halides to produce a hexa-substituted ditin along with tetra-substituted tin (75). A phenoxy group attached to tin serves as a pseudohalogen in the reaction of trimethylphenoxytin with sodium in liquid ammonia, the product being hexamethylditin (71). Trimethyltin hydroxide also may be used in the coupling reaction to produce hexamethylditin (70, 76). Reaction of triphenyltin chloride with potassium graphite (KC_8) leads to hexaphenylditin (77). Triorganotinlithium reagents, obtained on treatment of stannous chloride (33, 43) or R_2Sn compounds (67) with an organolithium compound in diethyl ether or by direct reaction of R_3SnCl with lithium in tetrahydrofuran (36, 38, 78) disproportionate under a variety of conditions to produce the corresponding hexaorganoditin. Hydrolysis (36, 38, 43, 78) or carbonation (42, 37) of a tinlithium reagent leads to the ditin, as also does reaction of a triorganotinlithium or -sodium compound with organic halides which can undergo halogen-metal interconversion (36, 39, 79, 80):

$$3\ C_6H_5Li + SnCl_2 \xrightarrow{(C_2H_5)_2O} (C_6H_5)_3SnLi \xrightarrow[2)\ \ CO_2]{1)\ 2,6\text{-}(CH_3)_2C_6H_3I} \tag{39}$$

$$(C_6H_5)_6Sn_2 + (C_6H_5)_4Sn + 2,6\text{-}(CH_3)_2C_6H_3CO_2H$$

The lithium reagents may be used to make unsymmetrical ditin compounds (78) just as the sodium reagents while avoiding the use of liquid ammonia.

The reaction of an organolithium compound with stannous chloride often leads to polymeric diorganotin species of indefinite composition (53). In two cases relatively discrete compounds, eicosaethylcyclodecatin and hexadeca-n-butylcyclooctatin, appear to have been obtained (81). Treatment of stannous chloride with a Grignard reagent may lead directly to the hexaorganoditin (59, 63). A rather thorough investigation of the products of the interaction of stannous chloride with phenylmagnesium bromide in a 1:6 molar ratio showed the presence of three products: hexaphenylditin, tetraphenyltin, and the supposed tetrakis(triphenylstannyl)tin (54).

In a synthesis which is unique, octa-tert-butylcyclotetratin, has been obtained from di-tert-butyltin dichloride and tert-butylmagnesium chloride (82). The reaction does not lead to the normal product, tetra-tert-butyltin, probably for steric reasons.

Hexaphenylditin has also been obtained by electrolysis of a methanol solution of triphenyltin chloride, the product being produced at the cathode (83). Other triorganotin halides have been electrolyzed in aqueous isopropanol, but the ditin compounds thought to be produced were not isolated (84).

A variety of synthetic methods employs tin hydrides as the starting materials. The interaction of triethyltin hydride with diethylmercury leads to hexaethylditin, mercury, and ethane (85). Hexamethylditin has been obtained by treatment of dimethyltin dihydride with sodium in liquid ammonia, followed by addition of methyl iodide:

$$(CH_3)_2SnH_2 + Na \xrightarrow{\text{liq. } NH_3} Na(CH_3)_2SnSn(CH_3)_2Na \xrightarrow{CH_3I} (CH_3)_6Sn_2 \quad (86)$$

Simple pyrolysis of the same dihydride produces some hexamethylditin, but the reaction is complex and appears to be of little synthetic utility (87).

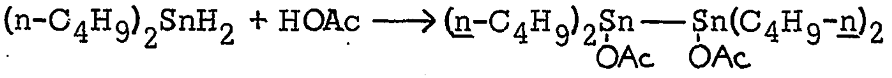
Reactions of triorganotin hydrides with amines lead to the corresponding ditin (88-92). It was originally thought that the reaction was a deamination, but more recent work indicates that the action of the amine is catalytic, no hydrocarbon or ammonia being formed (91, 92).

In an interesting extension of the above reactions, diorganotin dihydrides have been treated with amines to obtain cyclic polytin compounds (51, 52, 56, 93). In one reported case (52) a 94% yield of octadecaethylcyclononatin was obtained from diethyltin dihydride and a pyridine-diethyltin dichloride complex. It is apparently also possible to obtain straight-chain products with suitable reagents:

$$(C_6H_5)_2SnH_2 + CH_3OH \longrightarrow H[(C_6H_5)_2Sn]_6H \qquad (93)$$

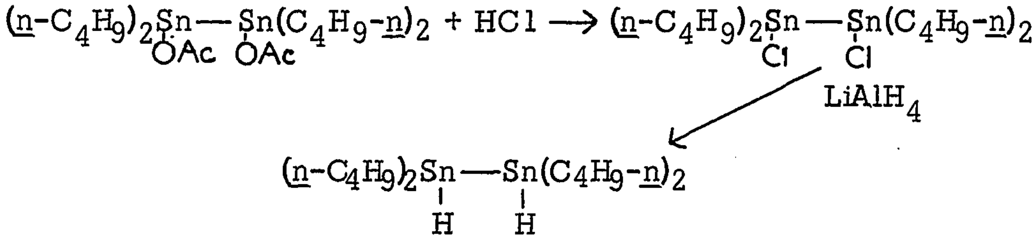
Reductions of ketones, sulfones and sulfoxides with triphenyltin hydride have been shown to give hexaphenylditin as the tin-containing product (89, 94). Aryl isocyanates or isothiocyanates also produce the same product from triphenyltin hydride (95).

A potentially quite useful synthetic method was recently reported by Sawyer and Kuivila (96-98), who treated diorganotin dihydrides with carboxylic acids to obtain functionally substituted ditin compounds. Thus, the reaction of dibutyltin dihydride with acetic acid leads to 1,1,2,2-tetra-n-butyl-1,2-diacetoxyditin in 65% yield:



$$(n\text{-}C_4H_9)_2SnH_2 + HOAc \longrightarrow (\underline{n}\text{-}C_4H_9)_2\underset{OAc}{Sn}-\underset{OAc}{Sn}(C_4H_9\text{-}\underline{n})_2$$

The acetoxy groups may be replaced by halogen through treatment with hydrogen chloride in diethyl ether, and the dihalide reduced with lithium aluminum hydride, all without scission of the tin-tin bond:



$$(\underline{n}\text{-}C_4H_9)_2\underset{OAc}{Sn}-\underset{OAc}{Sn}(C_4H_9\text{-}\underline{n})_2 + HCl \longrightarrow (\underline{n}\text{-}C_4H_9)_2\underset{Cl}{Sn}-\underset{Cl}{Sn}(C_4H_9\text{-}\underline{n})_2 \xrightarrow{LiAlH_4} (\underline{n}\text{-}C_4H_9)_2\underset{H}{Sn}-\underset{H}{Sn}(C_4H_9\text{-}\underline{n})_2 \qquad (99)$$

The same diacetoxyditin was prepared from the interaction of dibutyltin dihydride and dibutyltin diacetate (96, 97). In the same papers another method was found to be successful: namely, treatment of diphenyltin with benzoyl peroxide to produce 1,1,2,2-tetraphenyl-1,2-dibenzoyloxyditin in 81% yield (96, 97).

The cyclic polytin compounds have not as yet been used extensively for synthetic purposes, but indicative of what might be done is the reaction of octa-tert-butylcyclotetratin with iodine to prepare 1,4-diiodoocta-tert-butyltetratin (82).

Physical properties

The lower molecular weight hexaalkylditins are generally rather high boiling liquids, while the compounds containing aryl groups are solids. The hexaorganoditins are generally soluble in aromatic solvents, less so in chloroform or diethyl ether, and insoluble in ethanol.

The known polytins appear to be reasonably stable to heat. In an isolated example, hexamethylditin has been observed to decompose in boiling benzene (100). Normally temperatures above 250° are required, and several aryl and alkyl derivatives have been observed to deposit tin under these conditions (59, 81, 101-103). A method for decomposing hexaethyl- and hexaphenylditin at 1000°F in order to obtain a tin coating has been patented (101). The thermal decomposition of hexaethylditin at 275° may be represented as follows:

$$(C_2H_5)_6Sn_2 \longrightarrow (C_2H_5)_4Sn + Sn + 2\,C_2H_5\cdot \qquad (103)$$

It is likely that the first stage in the process is the conversion of the ditin to tetraethyltin and diethyltin, the latter producing tin and two ethyl radicals (103).

For a number of years, the ditins were thought to be considerably dissociated in solution into triorganotin radicals. Molecular weight determinations on several ditins corresponded to almost complete dissociation at low concentrations in benzene or ether solution (54, 68, 104). However, cryoscopic molecular weight determinations on hexamethylditin in benzene (69) and hexaphenylditin in camphor (54) indicated the dimeric structure. Magnetic susceptibility measurements on hexamethylditin and even hexa-o-tolylditin indicated no dissociation (100, 105). It seems quite unlikely that dissociation does, in fact, occur in solution. A tin-tin bond energy of 50 kcal./mole has been calculated for hexaethylditin on the basis of its heat of reaction with benzoyl peroxide (106).

Molar refractions for compounds containing a tin-tin bond have been calculated (107-109). The most recent work shows a tin-tin bond refraction of 10.683 (107).

The Raman spectrum of hexamethylditin has been determined and analyzed, with a tin-tin bond stretching force constant of $1.0 \pm 0.1 \times 10^5$ dynes/cm.

calculated (110). The value is smaller than that determined for the silicon-silicon and germanium-germanium bonds in the analogous methyl derivatives. The infrared spectra of hexaphenyl- (111, 112) and hexaethylditin (113, 114) appear in the literature, as well as hexaphenylditin in the 15 - 35μ region (115).

The nuclear magnetic resonance spectrum of hexamethylditin has been determined and compared with that for tetramethyltin (116). A decrease in diamagnetic shielding is observed in the ditin. The NMR spectrum of the same ditin has also been compared to those of octamethyltritin, dodecamethylcyclohexatin, and a dimethyltin polymer of uncertain composition (117). The values of the coupling constant, J_{Sn-CH_3}, were determined and related to the percent s character in the Sn-C bonds. The latter value becomes lower with increasing chain length; consequently, the percent s character in the Sn-Sn bond increases with chain length. The coupling constants are also linearly related to the observed Sn-C stretching frequencies in the infrared spectra of the compounds (117). Still another NMR study involving hexamethylditin and 1,1,1-trimethyl-2,2,2-triethylditin has found $J_{Sn^{119}-CH_3}$ to be anomalously low for the ditin compared to other methyltin derivatives (118, 119).

The ultraviolet spectrum of hexaphenylditin has been determined (120a), and it is proposed that there is intense interaction of phenyl groups on opposite tin atoms. The phenomenon, which occurs with analogous compounds of silicon, germanium, and lead, has been attributed in the case of silicon (120b) to an excitation involving the silicon-silicon bond. It is reasonable that the same explanation is applicable in the case of the tin-tin bond. Ultraviolet spectra of hexaethylditin (103) and octadecaethylcyclononatin (52) have been reported, but without extinction coefficients. The ultraviolet absorption of diethyltin (from pyrolysis of the ditin, degree of polymerization not known) is thought to occur at higher wavelength than hexaethylditin. These examples are consistent with the observations for polysilanes (120), but the data are as yet rather sketchy.

Chemical properties

Organopolytin compounds with reactive functional groups attached to tin have been prepared only recently, so that most of the known chemistry of the polytins involves scission of the tin-tin bond. Such cleavage occurs under a variety of oxidative conditions. Some alkyl-substituted ditins are oxidized even in air. Hexamethylditin (68) and hexaethylditin (104) are both unstable in the presence of air, while 1,1,1-trimethyl-2,2,2-triphenylditin is unaffected by air, (69); and hexaphenylditin in benzene solution withstands treatment with oxygen itself (43). The air oxidation of hexaethylditin in n-nonane is proposed to occur through the initial formation of the peroxide, $[(C_2H_5)_3SnO]_2$, which is subsequently converted to bis(triethyltin)oxide (113). The recently prepared 1,1,2,2-tetra-n-butyl-1,2-dihydroditin reacts with air to form dibutyltin oxide (99). 1,2-Diacetoxytetra-n-butylditin also decomposes slowly in air, while the analogous tetraphenyl compound is unaffected over 48 days (96, 97). The reaction of hexaethylditin with oxygen has been studied by Harada (72) and by Aleksandrov and coworkers (121, 122). The products obtained under the conditions of the latter workers are bis(triethyltin)oxide and diethyltin oxide, and a free radical chain mechanism is involved. Elemental sulfur has been shown to react with hexamethylditin in benzene to form bis(trimethyltin)sulfide (68).

Reaction with alcoholic silver nitrate has been used as a qualitative test for the ditin linkage, and a variety of compounds, including aryl derivatives, have been shown to deposit a silver mirror on treatment with the reagent (59, 62, 63, 76, 123). Potassium permanganate is also reduced readily (63, 124). Hexaphenylditin has been shown to react virtually quantitatively to produce triphenyltin hydroxide when subjected to the action of potassium permanganate in acetone solution (124).

A variety of other oxidizing agents, including dibenzoyl peroxide (106, 125, 126), acetyl benzoyl peroxide (125), di-tert-butyl peroxide (127), cyclohexyl percarbonate (125), lead tetraacetate (125), and nitrosoacetanilide (125, 128, 129) have been shown to cleave the tin-tin bond homolytically.

$$(C_2H_5)_6Sn_2 + Bz_2O_2 \xrightarrow{\text{benzene}} \underset{75.4\%}{(C_2H_5)_3SnOBz} + \underset{7.1\%}{(C_2H_5)_2Sn(OBz)_2} \quad (125)$$

$$(C_2H_5)_6Sn_2 + Bz_2O_2 \xrightarrow{CCl_4} (C_2H_5)_3SnCl + (C_2H_5)_2SnCl_2 \quad (126)$$

Although the reaction with benzoyl peroxide apparently results in some cleavage of ethyl groups from tin, it has been exploited for the structural investigation of some diorganotin polymers (57, 58, 85, 130). A polymer produced from hexaethylditin and aluminum chloride was treated with the peroxide to show that the tin chains contained considerable branching:

$$(C_2H_5)_2Sn + Bz_2O_2 \longrightarrow C_2H_5Sn(OBz)_3 + (C_2H_5)_2Sn(OBz)_2 + (C_2H_5)_3SnOBz + (C_2H_5)_4Sn + Sn \quad (57)$$

The most thoroughly examined reaction of the tin-tin bond is that with the halogens.

$$R_3Sn\text{-}SnR_3 + X_2 \longrightarrow 2\,R_3SnX$$

The reactions with bromine (56, 59, 62, 63, 81, 96, 97, 131, 132) and iodine (52, 54, 56, 61-63, 68, 74, 75, 93, 123, 124, 131) are believed to be quantitative, and have been employed for the analysis of ditin content. Reaction with chlorine in some cases results in cleavage of organic groups from tin as well as the expected tin-tin scission (123, 133).

$$(\underline{n}\text{-}C_4H_9)_6Sn_2 + Cl_2 \longrightarrow (\underline{n}\text{-}C_4H_9)_3SnCl + (\underline{n}\text{-}C_4H_9)_2SnCl_2 \qquad (133)$$

No ditin has been observed to be resistant to halogen cleavage. Even a compound such as hexakis(2-biphenylyl)ditin, which could be expected to exhibit considerable steric hindrance to reaction readily decolorizes bromine in carbon tetrachloride and iodine in benzene (63). The reaction has a number of potentialities for structural analysis. As an example, the compounds recently prepared by Neumann from diorganotin dihydrides and basic reagents were shown to have a cyclic structure by use of the reactions with chlorine, bromine or iodine (52, 56, 93). The compounds gave only diorganotin dihalides after halogen cleavage with no triorganotin halide or organotin trihalide being isolated:

$$(C_2H_5)_{18}Sn_9 + Cl_2 \longrightarrow (C_2H_5)_2SnCl_2 \qquad (52)$$

A dibutyltin polymer prepared from $\underline{n}$-butyllithium and stannous chloride likewise showed specific cleavage to dibutyltin dibromide on treatment with bromine (81).

Cleavage with formation of the halide is accomplished with a number of reagents other than the halogens. Treatment of hexamethylditin with concentrated hydrobromic acid leads to trimethyltin bromide (68). However, hexaethylditin has been found to react with four moles of hydrogen chloride to form diethyltin dichloride:

$$(C_2H_5)_6Sn_2 + 4\,HCl \longrightarrow 2\,(C_2H_5)_2SnCl_2 + 2\,C_2H_6 + H_2 \qquad (134)$$

Mercuric chloride has been used by several workers to obtain the triorganotin halide (63, 65, 66, 68, 135) and stannic chloride in greater than catalytic amounts is also effective:

$$(C_2H_5)_6Sn_2 + SnCl_4 \longrightarrow 4\,(C_2H_5)_3SnCl + Sn \qquad (134)$$

An interesting reaction that has been proposed (136) to have a free radical mechanism is the interaction of hexamethylditin and trifluoroiodomethane, catalyzed by ultraviolet light. The product isolated is trifluoromethyltrimethyltin (136, 137). The same reaction occurs under the influence of heat, but a cyclic mechanism is favored for this process (138). A variety of organic halides have been shown to react with hexaethylditin (135, 139, 140). Temperatures above 100° are usually required in order to bring about reaction in a reasonable length of time.

$$(C_2H_5)_6Sn_2 + C_6H_5CH_2Cl \xrightarrow[4\ hr.]{200^\circ} \underset{(73.4\%)}{(C_2H_5)_3SnCl} + \underset{(35.4\%)}{C_6H_5CH_2CH_2C_6H_5} \qquad (139)$$

Ultraviolet light also catalyzes the reaction of hexaethylditin with benzyl bromide (141):

$$(C_2H_5)_6Sn_2 + C_6H_5CH_2Br \xrightarrow{UV} (C_2H_5)_3SnBr\ (68.8\%) +$$
$$(C_2H_5)_2SnBr_2\ (7.7\%) + C_6H_5CH_2CH_2C_6H_5 \quad (59.5\%)$$

As has been indicated earlier, an organic halide such as carbon tetrachloride can react with a ditin to produce the triorganotin halide with the aid of a free radical initiator such as benzoyl peroxide (125, 126). Again with ultraviolet catalysis, hexamethylditin adds to tetrafluoroethylene to produce 1,2-bis(trimethylstannyl)tetrafluoroethane (142).

A number of Lewis acids have been shown to effect disproportionation of hexaorganoditin compounds. Treatment of hexaethylditin with aluminum chloride in catalytic amounts results in the formation of tetraethyltin, metallic tin, and a diethyltin polymer:

$$(C_2H_5)_6Sn_2 + AlCl_3 \xrightarrow{70-75^{\circ}} (C_2H_5)_4Sn + Sn + \left[(C_2H_5)_2Sn\right]_x \qquad (102)$$

The reaction does not occur with tetraethyltin even under more forcing conditions, so that it has been proposed as a qualitative test for the tin-tin linkage (127). The same type of process also occurs with aluminum bromide (130), stannous chloride (130), and zirconium (103), titanium (103), and tin (103, 130) tetrachlorides. Boron trifluoride, dimethylboron fluoride, and diborane have been shown to bring about the cleavage of hexamethylditin to form tetramethyltin (143).

As would be expected by analogy with other Group IVB elements, the tin-tin bond is susceptible to attack by nucleophilic reagents. Hexa-n-butyl and hexaphenylditin are cleaved by lithium aluminum hydride, but the reactions lead to a rather complex product mixture and are not very facile (144). Phenyllithium cleaves hexaphenylditin to give tetraphenyltin in 88.6% yield (39). Phenylmercuric chloride and diphenylmercury have been shown to produce a similar cleavage (65, 66).

$$(C_2H_5)_6Sn_2 + C_6H_5HgCl \xrightarrow{150^{\circ}} (C_2H_5)_3SnC_6H_5 + (C_2H_5)_3SnCl \qquad (65)$$

$$(C_2H_5)_6Sn_2 + (C_6H_5)_2Hg \xrightarrow{160^{\circ}} (C_2H_5)_3SnC_6H_5$$

Sodium amide in liquid ammonia is also effective:

$$(CH_3)_6Sn_2 + NaNH_2 \xrightarrow{\text{liq. } NH_3} (CH_3)_3SnNH_2 + (CH_3)_3SnNa \qquad (145)$$

On the other hand, the monosodium adduct of naphthalene leads to reduction of hexaphenylditin with formation of triphenyltinsodium (146). Alkali metals themselves also produce this reduction. The earliest system used was sodium in liquid ammonia (68, 70, 76) with which Kraus prepared trimethyltin sodium from hexamethylditin (68). Sodium-potassium alloy in ethylene glycol dimethyl ether also cleaves the same ditin (147). Most recently, lithium in tetrahydrofuran has been shown to cleave hexaphenylditin (36, 38) and hexa-n-butylditin (78). Also, hexaphenylditin may be cleaved by magnesium when ethyl bromide is used to initiate the reaction (147b). In an interesting variation, a catalytic amount of sodium in liquid ammonia causes the addition of vinylacetylene to hexaethylditin (148):

$$(C_2H_5)_6Sn_2 + HC{\equiv}C\text{-}CH{=}CH_2 + Na \xrightarrow{\text{liq. }NH_3} (C_2H_5)_3SnC{\equiv}C\text{-}CH{=}CH_2$$

The few reactions known (99) which proceed without breaking the tin-tin bond have been discussed in the section on methods of preparation.

EXPERIMENTAL

The reagents and solvents used in the following experiments were commercially available materials. Tetrahydrofuran was dried by refluxing over sodium wire, distillation into lithium aluminum hydride, and distillation from the hydride immediately before use. Dry diethyl ether and hydrocarbon solvents were obtained by storage of the solvents over sodium wire.

The organosilicon halides were purchased from Dow Corning Corporation, Midland, Michigan. Organotin halides were obtained from M & T Chemicals, Rahway, New Jersey; Columbia Organic Chemicals, Inc., Columbia, South Carolina; or Peninsular Chem Research, Inc., Gainesville, Florida. Chlorotriethylgermane and hexaphenyldigermane were obtained from Reaction Products, Inc., Painesville, Ohio.

Reactions were run in a three-necked flask of appropriate size with ground glass joints, fitted with a Trubore stirrer, a Friedrichs condenser, and an addition funnel. The condenser and addition funnel were connected to nitrogen inlets. All glassware was dried in an oven before use and purged while hot with dry, oxygen-free nitrogen.

Lithium metal was obtained commercially from Lithium Corporation of America and was wiped free of its protective coating and cut into small pieces into the nitrogen filled flask. Magnesium metal was

Grignard grade turnings obtained from Mallinkrodt Chemical Works.

n-Butyllithium (149), methyllithium (150), and phenyllithium (150, 151) were prepared in diethyl ether according to published directions. Likewise, previously described preparations of triphenylsilyllithium (152), methyldiphenylsilyllithium (152), dimethylphenylsilyllithium (152), triphenylgermyllithium (47, 49), triphenyltinlithium (36), and triphenylleadlithium (36) were employed, using tetrahydrofuran as solvent. When molarity is quoted for a solution of an organic Group IVB lithium compound, the value was obtained by double titration with allyl bromide (2). Color Test I (153) was used as a qualitative test for the metallic reagents. Silicon and tin analyses were carried out according to a published procedure (154). Likewise, a standard procedure (155) for the determination of chlorine attached to silicon or tin was employed.

Melting points were determined with a Mel-Temp apparatus or in an electrically heated oil bath. Infrared spectra were determined with a Perkin-Elmer, model 21, spectrophotometer, and ultraviolet spectra with a Beckman DK-2A spectrophotometer.

Analysis of Organolithium Compounds

Double titration procedure

A 3 ml. aliquot of the solution to be analyzed was withdrawn by pipette using a suction bulb and added to 10 ml. of diethyl ether. The solution was hydrolyzed with 10 ml. of distilled water and titrated with standard hydrochloric acid, using phenolphthalein as indicator, to give the total alkali present. A second 3 ml. aliquot was withdrawn and added to 10 ml. of diethyl ether, containing 1 ml. of the organic halide, under an atmosphere of nitrogen. The solution was swirled gently and allowed to stand for 2 min., after which it was hydrolyzed with distilled water and titrated immediately with standard acid, again using phenolphthalein as indicator.

In titrating the solution containing the organic halide the end point is easily overstepped, since the aqueous layer decolorizes before the ether layer. Vigorous shaking near the end point is recommended. In some cases there is the possibility of interference from hydrolysis of the halide, so that the titration should be carried out without delay.

Reaction with triphenyltin chloride

A diethyl ether solution of phenyllithium was added dropwise to a stirred solution of triphenyltin chloride in the minimum amount of tetrahydrofuran required for dissolution. An amount of triphenyltin chloride corresponding to a 25% excess over the theoretical phenyllithium content of the diethyl ether solution was employed. At the completion of the addition, more dry diethyl ether was added, and stirring was continued for 4 hours. The tetraphenyltin formed was filtered on a sintered glass funnel and washed twice with hot water and once with cold methanol. It was then dried in an oven and weighed. The product melted at 228-230° (mixed m.p.). The organic layer was evaporated, but no additional tetraphenyltin was obtained.

Reactions of organic halides with lithium ethoxide and phenoxide

Solutions of lithium ethoxide and phenoxide were prepared by addition of a diethyl ether solution of ethanol or phenol to finely cut lithium wire in diethyl ether under vigorous stirring. The resulting cloudy solutions were filtered under nitrogen through a sintered glass funnel. The solutions were titrated as in the procedure previously described, but using standard sulfuric acid. After the acid titration, a Volhard titration was carried out in the case of the lithium ethoxide reactions in order to measure the halide ion released.

Cleavage of Alkoxysilanes

Preparation of starting materials

2-Cyclohexen-1-yloxytriphenylsilane To a mixture of 9.81 g. (0.10 mole) of 2-cyclohexen-1-ol and 29.5 g. (0.10 mole) of chlorotriphenylsilane in 100 ml. of dry benzene was added dropwise 7.91 g. (0.10 mole) of pyridine, which had been dried by storage over barium oxide. An exothermic reaction occurred, accompanied by the evolution of a gas. The mixture was stirred overnight at ca. 40°, at the end of which time a solid (pyridinium chloride) was filtered off. The solvent was evaporated from the filtrate and the residue absorbed in petroleum ether (b.p. 60-70°) and chromatographed on alumina. Petroleum ether (b.p. 60-70°) eluted 20.5 g. (57.5%) of 2-cyclohexen-1-yloxytriphenylsilane, m.p. 61-63.5°. Recrystallization from petroleum ether (b.p. 28-38°) gave 51.2% of the pure product, m.p. 61.5-62.5°.

Anal. Calcd. for $C_{24}H_{24}OSi$: Si, 7.87. Found: Si, 7.71, 7.87.

Crotyloxytriphenylsilane A mixture of 14.4 g. (0.20 mole) of crotyl alcohol and 59.0 g. (0.20 mole) of chlorotriphenylsilane in 100 ml. of dry benzene was treated with 15.8 g. (0.20 mole) of pyridine as described in the previous experiment. Work-up as before was followed by chromatography on alumina. Petroleum ether (b.p. 60-70°) eluted 28.8 g. (44.2%) of a viscous oil which crystallized on cooling. The bulk of the solid was recrystallized from petroleum ether (b.p. 28-38°), aided by seeding with the impure material, to give 21.4 g. (33.0%) of crotyloxytriphenylsilane, m.p. 44-46°.

Anal. Calcd. for $C_{22}H_{22}OSi$: Si, 8.49. Found: Si, 8.56, 8.43.

The same preparative procedure was used for the following compounds which have been previously described: allyloxytriphenylsilane (156) (46.0% yield, m.p. and mixed m.p. 79-80°), (diphenylmethoxy) triphenylsilane (157) (36.9% yield, m.p. 84-85°). An attempted preparation of (triphenylmethoxy) triphenylsilane gave none of the desired product, undoubtedly due to a considerable steric hindrance to formation of the compound. Benzyloxytriphenylsilane was prepared from triphenylsilanol, benzyl alcohol, and a catalytic amount of hydrochloric acid at 150°, as described elsewhere (158). The yield of product, m.p. 84-85° (mixed m.p.), was 60%.

Cleavages with triphenylsilyllithium

Allyloxytriphenylsilane To 9.49 g. (0.030 mole) of allyloxytriphenylsilane in 50 ml. of tetrahydrofuran was added 108 ml. of 0.415 M triphenylsilyllithium (0.045 mole). The mixture was stirred overnight and hydrolyzed in dilute hydrochloric acid. Separation and filtration of the organic layer afforded 6.60 g. (42.2%) of hexaphenyldisilane, m.p. 365-370° (mixed m.p.). The solvent was distilled from the organic filtrate, and petroleum ether (b.p. 60-70°) was added to the residue, precipitating a gummy solid, from which no pure products were obtained upon attempted crystallization from benzene. The petroleum ether (b.p.

60-70°) solution was chromatographed on alumina. Elution with the same solvent afforded impure allyltriphenylsilane which was recrystallized from petroleum ether (b.p. 28-38°) to obtain the pure compound, 0.52 g. (5.8%), m.p. 87-88° (mixed m.p. 88.5-89.5°). Further elution afforded 1.03 g. of a solid, m.p. 147-149° cloudy, which showed siloxane and aliphatic carbon-hydrogen absorptions in its infrared spectrum. This material was not further fractionated.

Benzyloxytriphenylsilane To 11.0 g. (0.030 mole) of benzyloxytriphenylsilane in 75 ml. of tetrahydrofuran was added 110 ml. of 0.424 M triphenylsilyllithium (0.047 mole), and the resulting mixture was stirred overnight. Hydrolysis in dilute hydrochloric acid and filtration of the organic layer afforded 13.7 g. (88%) of hexaphenyldisilane, m.p. 364-368° (mixed m.p.). Work-up of the organic layer, followed by alumina chromatography gave 0.22 g. of solid, m.p. 196-200°, which showed strong siloxane absorption in its infrared spectrum.

Ethoxytriphenylsilane To a solution of 15.6 g. (0.051 mole) of ethoxytriphenylsilane in 50 ml. of tetrahydrofuran was added *ca.* 0.05 mole of triphenylsilyllithium in tetrahydrofuran. The reaction mixture was stirred overnight, then hydrolyzed in dilute hydrochloric acid. Filtration of the organic layer gave 24.0 g. (91%) of hexaphenyldisilane, m.p. 365-370°. Distillation of the solvent from the filtrate afforded only a small amount of gummy material, from which no pure products were obtained.

(Diphenylmethoxy)triphenylsilane To 13.3 g. (0.030 mole) of (diphenylmethoxy)triphenylsilane in 50 ml. of tetrahydrofuran was added *ca*. 0.05 mole of triphenylsilyllithium in tetrahydrofuran. After stirring overnight, the mixture was hydrolyzed in dilute hydrochloric acid. Filtration of the organic layer gave 5.54 g. (35.6%) of hexaphenyldisilane, m.p. 360-365° (mixed m.p.). The solvent was evaporated from the filtrate, and the residue was absorbed in petroleum ether (b.p. 60-70°) and chromatographed on alumina. Elution with the same solvent afforded first an oil which slowly crystallized to give 6.90 g. (63% based on triphenylsilyllithium) of triphenylsilane, m.p. 42-44° (mixed m.p.). Further elution gave a solid which was recrystallized from petroleum ether (b.p. 28-38°) to obtain 3.22 g. (24.3%) of (diphenylmethoxy)triphenylsilane, m.p. 83.5-84.5° (mixed m.p.). Additional oily solid, 2.5 g., was obtained from the chromatography, but it was not identified.

2-Cyclohexen-1-yloxytriphenylsilane To 3.56 g. (0.010 mole) of 2-cyclohexen-1-yloxytriphenylsilane in 40 ml. of tetrahydrofuran was added 22 ml. of 0.453 M triphenylsilyllithium (0.010 mole).

After stirring for 48 hours, Color Test I was still slightly positive, and the mixture was hydrolyzed in dilute hydrochloric acid. Filtration of the organic layer afforded 2.95 g. (57%) of hexaphenyldisilane, m.p. 367-370°. The filtrate was worked up as before and chromatographed on alumina. Petroleum ether (b.p. 60-70°) eluted a solid which melted at 155-165° after recrystallization from petroleum ether (b.p. 28-38°). Fractional crystallization from absolute ethanol gave two solids, m.p. 190-200° and m.p. 155-165°, which were not identified and a trace amount of 2-cyclohexen-1-yltriphenylsilane (156), m.p. 129-131° (mixed m.p.).

Cleavages with lithium

Benzyloxytriphenylsilane A solution of 7.31 g. (0.020 mole) of benzyloxytriphenylsilane in 60 ml. of tetrahydrofuran was added dropwise to 1.4 g. (0.20 g.-atom) of lithium in 20 ml. of tetrahydrofuran. Reaction began within 15 min., and the mixture turned orange, then black. At the end of the addition, Color Test I was positive. The mixture was stirred for an additional 1.5 hours, filtered through a glass wool plug, and added to a solution of 5.9 g. (0.020 mole) of chlorotriphenylsilane in 50 ml. of tetrahydrofuran. The mixture was hydrolyzed in dilute hydrochloric acid. Removal of the solvent from the organic layer, addition of petroleum ether (b.p. 60-70°), and filtration afforded 8.47 g. (76.7%) of triphenylsilanol, m.p. 144-146° (mixed m.p.). The filtrate was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave 0.4 g. (5.7%) of impure benzyltriphenylsilane, m.p. 86-89° (mixed m.p. 92-94°). The infrared spectrum of this product was superimposable with that of an authentic sample. Further elution with the same solvent gave 0.15 g. (1.4%) of hexaphenyldisiloxane, m.p. 225-227° (mixed m.p.). Elution with benzene afforded 2.15 g. of an oil which was not identified.

(Diphenylmethoxy)triphenylsilane To a mixture of 8.85 g. (0.020 mole) of (diphenylmethoxy)triphenylsilane and 1.4 g. (0.20 g.-atom) of lithium was added dropwise 100 ml. of tetrahydrofuran. Reaction began immediately with the appearance of a dark red color. When the addition was complete, Color Test I was positive. After 3 hours of stirring, double titration with allyl bromide showed the presence of 0.17 equivalent of lithium reagents (C-Li and/or Si-Li). The mixture was decanted through a glass wool plug and added to 11.8 g. (0.04 mole) of chlorotriphenylsilane in 50 ml. of tetrahydrofuran. The mixture was stirred overnight, then hydrolyzed in dilute hydrochloric acid. Addition of petroleum ether (b.p. 60-70°) to the residue after removing the solvent from the organic layer and filtration afforded a solid. Fractional crystallization from benzene and from absolute ethanol gave 3.6 g. (33.7%) of hexaphenyldisiloxane, m.p. 225-227° (mixed m.p. 227-230°), and 2.78 g. (35.0%) of (diphenylmethyl)triphenylsilane, m.p. 158-160° (mixed m.p.). From the ethanol solution was obtained

2.5 g. (27.6% based on chlorotriphenylsilane) of triphenylsilanol, m.p. 147-149° (mixed m.p. 151-153°). The petroleum ether solution above was chromatographed on alumina to obtain an additional 0.28 g. (3.3%) of (diphenylmethyl)triphenylsilane, m.p. 155-157° (mixed m.p. 156-158°).

<u>2-Cyclohexen-1-yloxytriphenylsilane</u> To 3.56 g. (0.010 mole) of 2-cyclohexen-1-yloxytriphenylsilane and 0.69 g. (0.10 g.-atom) of lithium was added over a period of 1.5 hours 50 ml. of tetrahydrofuran. The lithium became golden in color. Titration with allyl bromide showed 44% reaction. The mixture was filtered through glass wool and added to 5.9 g. (0.020 mole) of chlorotriphenylsilane in 50 ml. of tetrahydrofuran. Work-up as before afforded only hexaphenyldisiloxane, 1.69 g. (21.1%), m.p. 220-224° (mixed m.p. 228-230°), and triphenylsilanol, 1.59 g. (19.2%), m.p. 144-146° (mixed m.p. 146-148°), and solids which appeared from their melting point behavior to be mixtures of the two compounds.

<u>Crotyloxytriphenylsilane</u> To a mixture of 6.61 g. (0.020 mole) of crotyloxytriphenylsilane and 1.4 g. (0.20 g.-atom) of lithium was added 50 ml. of tetrahydrofuran. After stirring the mixture for 14 hours, double titration showed 61% reaction. The solution was decanted and added to 11.8 g. (0.040 mole) of chlorotriphenylsilane in 50 ml. of

tetrahydrofuran. Hydrolysis and the usual work-up afforded 0.13 g. (0.8%) of hexaphenyldisilane, m.p. 354-357° (mixed m.p.), 1.69 g. (10.5%) of hexaphenyldisiloxane, m.p. 230-233° (mixed m.p. 227-229°), and 4.10 g. (24.8%) of triphenylsilanol, m.p. 149-150° (mixed m.p. 149-151°).

Relative Reactivities of Group IVB Lithium Compounds

Reactions of triphenyltinlithium

With pyridine To 1.58 g. (0.020 mole) of pyridine was added 49 ml. of 0.408 M triphenyltinlithium (0.020 mole). The resulting solution was heated at reflux temperature for 3 hours, at the end of which time Color Test I was positive. The solution was hydrolyzed with dilute hydrochloric acid. The usual work-up of the organic layer afforded a solid residue, which was crystallized from benzene. The product, m.p. 195-200°, showed an infrared spectrum similar to that of hexaphenylditin and tetraphenyltin, and was evidently a mixture of the two compounds. The yield was 3.6 g. or about 50%. No further products were obtained.

With azobenzene To 3.28 g. (0.018 mole) of azobenzene in 50 ml. of tetrahydrofuran was added dropwise over 30 min. 55 ml. of 0.325 M triphenyltinlithium (0.018 mole). Color Test I was negative at the end of the addition. The mixture was stirred 30 min. longer, then hydrolyzed in saturated ammonium chloride. The organic layer was separated and concentrated, followed by filtration. The solid product obtained was recrystallized from a mixture of benzene and petroleum ether (b.p. 60-70°) to give 5.32 g. (84.4%) of hexaphenylditin, m.p. 236-238° (mixed m.p.). The remaining organic layer was evaporated, leaving an orange solid, which was recrystallized from methanol-water. The product was azobenzene, 2.30 g. (70.1%), m.p. 67-68° (mixed m.p.). Further concentration of the mother liquor afforded a light orange solid which melted at 76-85°. The infrared spectrum of this product indicated it to be a mixture of hexaphenylditin and azobenzene, and no absorption due to the N-H group was present.

With 4.4'-bis(dimethylamino)benzophenone To 3.76 g. (0.014 mole) of 4,4'-bis(dimethylamino)benzophenone in 60 ml. of tetrahydrofuran was added over a period of 20 min. 30 ml. of 0.470 M triphenyltinlithium (0.014 mole). The mixture was stirred for 18 hours, followed by hydrolysis in saturated ammonium chloride. Separation and concentration of the organic layer afforded 2.75 g. (72.6%) of the starting ketone, identified by mixed m.p. (167-168°) and superimposition of infrared spectra. Further work-up was not carried out.

With benzophenone To 2.74 g. (0.015 mole) of benzophenone in

25 ml. of tetrahydrofuran was added 30 ml. of 0.505 M triphenyltinlithium (0.015 mole) over 20 min. The reaction mixture rapidly turned bright blue and was stirred for 2 hours. Hydrolysis in saturated ammonium chloride and the usual work-up afforded hexaphenylditin. From the concentrated organic layer was isolated a solid, which was recrystallized from benzene-petroleum ether (b.p. 60-70°) to obtain 0.3 g. (12%) of benzopinacol, m.p. 184-187° (mixed m.p.).

In a separate experiment an electron spin resonance spectrum[1] was obtained on the blue reaction mixture. A quite strong signal was observed. The solution was too concentrated to allow hyperfine splitting to be seen, but presumably the radical was the ketyl of benzophenone.

Competitive reactions for n-butyl chloride

Infrared analysis of product mixtures Strong infrared absorption bands for phenyl groups attached to silicon, germanium, tin, and lead fall at 9.04, 9.19, 9.34, and 9.45μ, respectively, depending upon the element present. In the spectra of alkyltriphenyl derivatives of these elements, the bands are the only ones in this region of the spectrum.

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[1] The electron spin resonance spectrum was determined by Dr. Edward G. Janzen, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa.

Thus, in spectra of mixtures of two such compounds, e.g. n-butyltriphenylsilane and n-butyltriphenylgermane, two adjacent bands are seen. The areas of these bands may be defined without concern over vagaries of the base line by drawing a horizontal line through the point of minimum absorbance between the two bands. The areas thus enclosed are measured. Synthetic mixtures of n-butyltriphenylsilane and n-butyltriphenylgermane in weight ratios of 1:1, 2:1, and 3:1, respectively, were prepared, the spectra run, then the relative areas of the peaks at 9.04 and 9.19μ measured. The area ratios plotted against the weight ratios gave a straight line with a maximum deviation of 5%. For mixtures other than that above, only a 1:1 synthetic mixture was prepared, and the weight ratio in the product mixture was determined by a simple proportion.

Triphenylsilyllithium and triphenyltinlithium To 88 ml. of a 0.522 M solution of triphenylsilyllithium (0.046 mole) in tetrahydrofuran was added 90 ml. of 0.511 M triphenyltinlithium (0.046 mole) and the mixture cooled to -30° in a Dry Ice-acetone bath. n-Butyl chloride, 4.26 g. (0.046 mole) in 10 ml. of tetrahydrofuran, was added over a period of 15 seconds. Cooling was then discontinued, and the solution was stirred for 1.5 hours and carbonated by pouring onto a Dry Ice-diethyl ether slurry. The resulting mixture was extracted twice with cold 2% sodium hydroxide. The organic layer was dried over anhydrous sodium sulfate and the solvents evaporated. To the solid remaining, petroleum ether (b.p. 28-38°) was added. Filtration afforded hexaphenylditin, 3.0 g. (18.6%), which melted at 228-232° (mixed m.p. 232-235°) upon recrystallization from benzene. The petroleum ether filtrate was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave n-butyltriphenylsilane, which was recrystallized from the same solvent to obtain 8.8 g. (60.5%) of the product, m.p. 84-85° (mixed m.p.). Further elution of the column gave 1.5 g. of solid melting over the range of 64-74°. An infrared spectrum of this material in carbon disulfide showed the relative areas of the phenyl-silicon and phenyl-tin absorptions at 9.04 and 9.34μ, respectively, to be 6.2:1. A spectrum of a synthetic mixture of n-butyltriphenylsilane and n-butyltriphenyltin in 1:1 weight ratio gave the relative areas of the same bands as 3.8:1. A simple proportion gives a weight ratio of n-butyltriphenylsilane to n-butyltriphenyltin of 1.6:1 and yields of 0.9 g. of the former and 0.6 g. of the latter. The total yield of the two products was 67% of n-butyltriphenylsilane and 3.1% of n-butyltriphenyltin.

In a second run of the reaction under the same conditions of time and temperature, 89 ml. of 0.475 M triphenyltinlithium (0.042 mole) was combined with 75 ml. of 0.565 M triphenylsilyllithium (0.042 mole) and reacted with 3.92 g. (0.042 mole) of n-butyl chloride in 10 ml. of tetrahydrofuran. Product yields were 5.0 g. (36%) of n-butyltriphenylsilane and 0.2 g. (1.2%) of n-butyltriphenyltin.

Triphenylgermyllithium and triphenyltinlithium Under the same conditions as outlined above, 70 ml. of 0.549 M triphenylgermyllithium (0.038 mole) was added to 70 ml. of 0.549 M triphenyltinlithium (0.038 mole) followed by treatment with 3.56 g. (0.038 mole) of n-butyl chloride. Subsequent to the same work-up and alumina chromatography, 5.8 g. of n-butyltriphenylgermane, m.p. 80.5-81.5° (mixed m.p. 81.5-82.5°), was isolated. Additional solid, 3.7 g., m.p. 73-75°, was shown to contain 3.0 g. of n-butyltriphenylgermane and 0.7 g. of n-butyltriphenyltin by infrared analysis. Combined yields were 63% of germanium derivative and 4.5% of tin derivative.

The reaction was repeated using 85 ml. of 0.556 M triphenylgermyllithium (0.047 mole), 81 ml. of 0.588 M triphenyltinlithium (0.047 mole), and 4.39 g. (0.047 mole) of n-butyl chloride to obtain 9.5 g. (55.5%) of n-butyltriphenylgermane and 1.2 g. (6.2%) of n-butyltriphenyltin.

Triphenyltinlithium and triphenylleadlithium Triphenylleadlithium prepared from 19.0 g. (0.040 mole) of triphenyllead chloride was combined with triphenyltinlithium prepared from 15.4 g. (0.040 mole) of triphenyltin chloride (0.034 mole of triphenyltinlithium by double titration). To this mixture at -30° was added 3.18 g. (0.034 mole) of n-butyl chloride. The usual work-up followed by alumina chromatography gave 6.5 g. of product, m.p. 57-58°. Infrared analysis indicated 6.2 g. (45%) of n-butyltriphenyltin and 0.3 g. (2%) of n-butyltriphenyllead. Because of the small area of the phenyl-lead band in this spectrum, the analysis is undoubtedly less accurate than in the previous reactions.

Triphenylsilyllithium and triphenylgermyllithium To 57 ml. of 0.480 M triphenylsilyllithium (0.027 mole) and 61 ml. of 0.446 M triphenylgermyllithium (0.027 mole) at -15° (the solution became inhomogeneous at lower temperature) was added at one time 2.52 g. (0.027 mole) of n-butyl chloride in 10 ml. of tetrahydrofuran. After the usual work-up, the product was crystallized twice from petroleum ether (b.p. 60-70°) and once from methanol to obtain solid melting at 77-83°. Infrared analysis using the calibration curve described previously showed the presence of 3.7 g. (42.5%) of n-butyltriphenylsilane and 3.0 g. (31%) of n-butyltriphenylgermane.

Triphenylsilyllithium and methyldiphenylsilyllithium To 75 ml. of 0.596 M triphenylsilyllithium (0.045 mole) and 74 ml. of 0.602 M methyldiphenylsilyllithium (0.045 mole), cooled to -30°, was added 4.14 g. (0.045 mole) of n-butyl chloride in 10 ml. of tetrahydrofuran. After carbonation and the usual work-up, the solvent was removed from the neutral layer to leave an oily residue. Methanol was added, and after standing several hours, 3.65 g. (26.4%) of n-butyltriphenylsilane, m.p. 79-81°, was filtered off. The filtrate was concentrated to remove the majority of the solvent, and the remaining liquid was analyzed by vapor phase chromatography using trimethylsilyldiphenylsilane[1] as a standard, as described in the next section. The yield of n-butylmethyldiphenylsilane was determined to be 38%.

Methyldiphenylsilyllithium and dimethylphenylsilyllithium To a mixture of 79 ml. of 0.549 M methyldiphenylsilyllithium (0.043 mole) and 62 ml. of 0.694 M dimethylphenylsilyllithium (0.043 mole) at -30° was added 4.01 g. (0.043 mole) of n-butyl chloride in 10 ml. of tetrahydrofuran. The usual work-up and removal of the solvent by distillation left a liquid residue. The mixture was analyzed quantitatively by vapor phase chromatography using a column of Dow Corning Hi-vac grease on firebrick at 170°. The standard, which was added in known quantity to the product mixture, was trimethylsilyldiphenylsilane, which is eluted from the column between the two butyl derivatives. Each of the butyl compounds was combined in known quantity with the standard in order to determine a correction factor for the observed peak areas. These factors were close to unity, i.e. equimolar quantities of the standard and the butyl derivatives give peaks of almost the same area. Analysis of the product mixture above showed yields of 48.6% for n-

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[1] G. L. Schwebke, Iowa State University of Science and Technology, Ames, Iowa. Information on the preparation and properties of trimethylsilyldiphenylsilane. Private communication. 1963.

butylmethyldiphenylsilane and 45.5% for n-butyldimethylphenylsilane.

The reaction was repeated using 93 ml. of 0.705 M methyldiphenylsilyllithium (0.066 mole), 92 ml. of 0.715 M dimethylphenylsilyllithium (0.066 mole), and 6.09 g. (0.066 mole) of n-butyl chloride. The same work-up and analytical procedure showed yields of 53% for n-butylmethyldiphenylsilane and 51.5% for n-butyldimethylphenylsilane. There is an obvious error here, since the combined yields are greater than 100%, but the source of the error is not known. However, the relative yields of the products are in reasonably good agreement with those of the first run.

Competition of triphenylsilyllithium and triphenylgermyllithium for n-hexyl chloride

A mixture of 72 ml. of 0.649 M triphenylsilyllithium (0.046 mole) and 73 ml. of 0.636 M triphenylgermyllithium (0.046 mole) was cooled to -5°, and 5.60 g. (0.046 mole) of n-hexyl chloride in 10 ml. of tetrahydrofuran was added. Work-up in the usual manner, followed by alumina chromatography gave 9.3 g. of product melting over the range 70-76.5°. Infrared analysis using the same calibration curve as before showed 6.1 g. (38%) of n-hexyltriphenylsilane and 3.2 g. (18%) of n-hexyltriphenylgermane.

The reaction was repeated using 104 ml. of 0.444 M triphenylsilyllithium (0.045 mole), 106 ml. of 0.436 M triphenylgermyllithium (0.045 mole), and 5.42 g. (0.045 mole) of n-hexyl chloride. The yields of products were 6.9 g. (44%) of n-hexyltriphenylsilane and 3.1 g. (18%) of n-hexyltriphenylgermane.

Reaction of methyldiphenylsilyllithium with n-butyl chloride

To 68 ml. of 0.590 M methyldiphenylsilyllithium (0.040 mole) was added dropwise over a period of 45 min. 3.72 g. (0.040 mole) of n-butyl chloride in 25 ml. of tetrahydrofuran. Color Test I was negative at the end of the addition, and the solution was hydrolyzed in dilute hydrochloric acid. The tetrahydrofuran layer was removed, dried, and distilled to remove the solvent. The residue was distilled under reduced pressure to obtain 2.0 g. of forerun, b.p. 118-120°/0.5mm., n_D^{20} 1.5537, and 6.0 g. (59%) of n-butylmethyldiphenylsilane, b.p. 120-122°/0.5mm., n_D^{20} 1.5524.

Anal. Calcd. for $C_{17}H_{22}Si$: C, 80.27; H, 8.72. Found: C, 80.10, 79.94; H, 8.26, 8.36.

Reaction of dimethylphenylsilyllithium with n-butyl chloride

To 85 ml. of 0.575 M dimethylphenylsilyllithium (0.049 mole) was added dropwise 4.52 g. (0.049 mole) of n-butyl chloride in 50 ml. of tetrahydrofuran. The usual work-up followed by distillation at reduced pressure gave 0.4 g. of forerun, b.p. 113-116°/30 mm., n_D^{20} 1.4932; 1.0 g. (10.6%) of impure product, b.p. 116-

120°/30 mm., n_D^{20} 1.4924; and 3.7 g. (39.4%) of n-butyldimethylphenylsilane, b.p. 120-121°/30 mm., n_D^{20} 1.4921. Vapor phase chromatography showed low-boiling impurity in the second fraction, but none in the third fraction.

Anal. Calcd. for $C_{12}H_{20}Si$: C, 74.92; H, 10.48. Found: C, 74.48, 74.26; H, 10.36, 10.61.

Metalations of fluorene

By triphenylsilyllithium To a solution of 7.63 g. (0.046 mole) of fluorene in 60 ml. of tetrahydrofuran at room temperature was added at one time 80 ml. of 0.575 M triphenylsilyllithium (0.046 mole). The solution was stirred for 4 hours, then carbonated by pouring onto a Dry Ice-diethyl ether slurry. After allowing the mixture to warm to 0°, dilute hydrochloric acid was added, followed by several extractions with diethyl ether. The combined ether layers were extracted with 400 ml. of 5% sodium hydroxide in several portions. The basic extract was boiled to remove traces of tetrahydrofuran, then acidified with 10% hydrochloric acid. Filtration afforded solid product which was recrystallized from glacial acetic acid to obtain 9.28 g. (96.8%) of fluorene-9-carboxylic acid, m.p. 226-230°. In addition, 6.7 g. (62%) of triphenylsilane, m.p. 40-41°, and 0.2 g. (2.5%) of fluorene, m.p. 111-113° (mixed m.p.), were isolated on alumina chromatography of the neutral fraction of the reaction mixture.

General procedure for comparative reactions To 7.63 g. (0.046 mole) of fluorene in 380 ml. of tetrahydrofuran, cooled to 0° with a Dry Ice-acetone bath, was added at one time 77 ml. of 0.596 M triphenylsilyllithium (0.046 mole). The solution was stirred for 1.5 hours with the temperature maintained between 0° and 5°, then carbonated and worked up as previously described. Two recrystallizations of the crude product obtained upon acidification of the basic extract, again from glacial acetic acid, afforded 4.3 g. (44.5%) of fluorene-9-carboxylic acid, m.p. 229-232°.

The remainder of the reactions reported in Table 11 were carried out as described above, under the same conditions of time, temperature, and concentrations of reagents. Fluorene-9-carboxylic acid was considered of sufficient purity when it began to melt at 226° or above.

Preparations and Reactions of Organic Group IVB Lithium Compounds

Pentaphenyldisilanyllithium (159)

Preparation of reagent To 10.50 g. (0.0115 mole) of decaphenylcyclopentasilane (160) in 150 ml. of tetrahydrofuran was added 103 ml. of 0.675 M triphenylsilyllithium (0.070 mole), and the mixture was stirred at room temperature for 46 hours. A 25 ml. aliquot was removed by pipette and hydrolyzed in dilute hydrochloric acid. The organic layer was separated and filtered to obtain hexaphenyldisilane, 0.24 g., m.p. 360-364°. The filtrate was dried and the solvent evaporated, followed by alumina chromatography of the resulting solid. Petroleum ether (b.p. 60-70°) eluted traces of oil. Mixtures of petroleum ether (b.p. 60-70°) and benzene eluted pentaphenyldisilane, which was recrystallized from the same solvent system to obtain 0.76 g. (ca. 40%) of the product, m.p. 219-221° (mixed m.p.).

A second 25 ml. aliquot was removed from the reaction mixture after 94 hours. The same work-up afforded hexaphenyldisilane (0.27 g.) and pentaphenyldisilane (1.12 g., ca. 63%).

A repeated run of the reaction gave ca. 35% of pentaphenyldisilane after 48 hours and ca. 57% after 96 hours. Subsequent preparations of the reagent were stirred for 96 hours.

Reaction with *n*-butyl chloride To the silyllithium reagent prepared from 6.98 g. (0.0077 mole) of decaphenylcyclopentasilane in 75 ml. of tetrahydrofuran and 79 ml. of 0.533 M triphenylsilyllithium (0.042 mole) was added 3.90 g. (0.042 mole) of *n*-butyl chloride. Color Test I was negative at the end of the addition, and the mixture was hydrolyzed in dilute hydrochloric acid. Separation and filtration of the organic layer gave a solid, m.p. 300-320°, which was treated with benzene and filtered to obtain 0.75 g. of hexaphenyldisilane, m.p. 358-362° (mixed m.p.). Evaporation of the filtrate from the organic layer left a solid which was recrystallized from benzene-petroleum ether (b.p. 60-70°) mixture to obtain material melting at 224-227°. Two recrystallizations from ethyl acetate gave 5.4 g. (28%) of pure n-butylpentaphenyldisilane, m.p. 224-226°.

Anal. Calcd. for $C_{34}H_{34}Si_2$: C, 81.87; H, 6.87; Si, 11.26. Found: C, 82.09, 82.04; H, 6.54, 6.54; Si, 11.52, 11.62.

Dimethyl-p-tolylsilyllithium

Preparation of starting materials

Chlorodimethyl-p-tolylsilane The Grignard reagent prepared from 85.5 g. (0.50 g.-atom) of magnesium in 400 ml. of diethyl ether was added dropwise to 73 g. (0.47 mole) of dichlorodimethylsilane in 100 ml. of ether. The solution was stirred overnight, followed by replacement of the ether with dry petroleum ether (b.p. 60-70°). The resulting mixture was filtered through a sintered glass funnel under nitrogen pressure. The solvent was removed, followed by distillation at reduced pressure to obtain 41.5 g. (48.4%) of the product, b.p. 110.5-113°/20 mm., n_D^{20} 1.5130 [reported (161) b.p. 130-131°/40 mm., n_D^{25} 1.5055] . The infrared spectrum showed no absorptions due to Si-OH or Si-O-Si groups.

A second run of the reaction was made using twice the previous quantities of reagents. The yield of product was 98.1 g. (53.1%), b.p. 106-108°/20 mm., n_D^{20} 1.5132.

1,2-Di-p-tolyl-1,1,2,2-tetramethyldisilane

Chlorodimethyl-p-tolylsilane, 41.5 g. (0.225 mole); sodium, 11.5 g. (0.50 g.-atom); and xylene, 150 ml., were heated until the sodium melted, and the mixture stirred for 48 hours. The excess sodium was destroyed by slow addition of 95% aqueous ethanol, and the resulting mixture filtered. The solvent was removed from the filtrate by distillation at reduced pressure. The solid thus obtained was recrystallized from methanol to give 15 g. (45%) of 1,2-di-p-tolyl-1,1,2,2-tetramethyldisilane, m.p. 68-70°. Three recrystallizations from methanol raised the melting point to 70-72°.

Anal. Calcd. for $C_{18}H_{26}Si_2$: C, 72.42; H, 8.81. Found: C, 72.92, 72.90; H, 8.75, 8.90.

Preparation of reagent

From disilane (attempted) To a mixture of 8.95 g. (0.03 mole) of 1,2-di-p-tolyl-1,1,2,2-tetramethyldisilane and 1.5 g. (0.22 g.-atom) of lithium was added 5 ml. of tetrahydrofuran. Stirring of the mixture for 1.5 hours produced no apparent effect. Additional tetrahydrofuran (100 ml.) was introduced, and stirring was continued for 15 hours. Color Test I remained negative. The reaction mixture was hydrolyzed and worked up in the normal manner to recover 6.9 g. (77%) of the disilane, m.p. 69-71°.

In a second run the mixture of disilane, lithium, and a small volume of tetrahydrofuran, sufficient to make a paste, was stirred for 2 hours. Addition of small amounts of chlorotriphenylsilane and ethyl iodide had no apparent effect, but after stirring for 10 hours the reaction mixture turned brown. Tetrahydrofuran (60 ml.) was added, and stirring was continued for an additional 12 hours. Color Test I appeared slightly positive, and double titration showed a silyllithium content corresponding to a 3.8% yield of the reagent. Hydrolysis and the usual work-up afforded 31% of recovered disilane.

From chlorosilane To 4.2 g. (0.6 g.-atom) of lithium was added over a period of 1.5 hours a solution of 11.1 g. (0.06 mole) of chlorodimethyl-p-tolylsilane in 50 ml. of tetrahydrofuran. An exothermic reaction took place, and a brown color developed slowly. Titrations were made after stirring for 6, 24, and 30 hours, showing yields of 4.2, 41.2, and 42.5%, respectively. The solution gave a positive Color Test I.

In a second run, the maximum yield by titration was 33.6% after 25 hours.

Dimethyl-p-methoxyphenylsilyllithium

Chlorodimethyl-p-methoxyphenylsilane The Grignard reagent prepared from 93.5 g. (0.50 mole) of p-bromoanisole and 18.2 g.

(0.75 g.-atom) of magnesium in 400 ml. of ether was added dropwise to 107 g. (0.83 mole) of dichlorodimethylsilane in 150 ml. of ether. The mixture was stirred for 3 days, followed by replacement of the ether with petroleum ether (b.p. 60-70°). Filtration under nitrogen and removal of the solvent were followed by distillation under reduced pressure to give 22.4 g. (24%) of the product, b.p. 143-146°/25 mm., n_D^{20} 1.5219 [reported (162) b.p. 163-165°/50 mm., n_D^{20} 1.5528].

Anal. Calcd. for $C_9H_{13}ClOSi$: Cl, 17.7%. Found: Cl, 17.5, 17.3%.

Preparation of reagent (attempted) To 1.73 g. (0.25 g.-atom) of lithium was added over a period of 1.5 hours a solution of 10.0 g. (0.050 mole) of chlorodimethyl-p-methoxyphenylsilane. An exothermic reaction occurred, and the mixture soon became red-brown. After stirring for 17 hours, Color Test I was slightly positive, and the solution was titrated. The total basic content corresponded to a yield of 102%, but silyllithium content was only 0.4%. Stirring was continued for 41 hours, when the color test was positive, and the yield of silyllithium was 2.1%.

Dimethyl-p-phenoxyphenylsilyllithium

Chlorodimethyl-p-phenoxyphenylsilane The Grignard reagent prepared from 249.1 g. (1.0 mole) of p-bromodiphenyl ether and 36.5 g. (1.5 g.-atoms) of magnesium in 550 ml. of ether was added to

193 g. (1.5 moles) of dichlorodimethylsilane in 250 ml. of ether. Color Test I was negative at the end of the addition. Work-up as before and distillation at reduced pressure afforded 156.8 g. (66.5%) of product, b.p. 140-160°/1.6 mm. This material was redistilled to give the pure product, b.p. 170-171°/3.2 mm., n_D^{20} 1.5668 [reported (162) b.p. 204-210°/40 mm., n_D^{20} 1.5722].

Preparation of reagent (attempted) To 0.6 g. (0.085 g.-atom) of lithium was added dropwise a solution of 10.5 g. (0.040 mole) of chlorodimethyl-*p*-phenoxyphenylsilane in 50 ml. of tetrahydrofuran. An exothermic reaction occurred with the formation of a dark red color. After 1.5 hours of stirring, titration showed 112% yield of base and 4.0% yield of silyllithium.

In a repeated run, stirring was continued for 3 hours, when the yield of silyllithium compound was 2.4% by titration.

p-Biphenylyldimethylsilyllithium

p-Biphenylylchlorodimethylsilane The Grignard reagent prepared from 233 g. (1.0 mole) of *p*-bromobiphenyl and 36.5 g. (1.5 g.-atoms) of magnesium in 600 ml. of ether was added dropwise to 193 g. (1.5 moles) of dichlorodimethylsilane in 200 ml. of ether. After stirring overnight Color Test I was negative, and the reaction mixture was worked up in the usual manner. Distillation at reduced pressure afforded the product, b.p. 147-167°/3.0-2.4 mm. The material tended to solidify in the side arm of the condenser, which was kept free by heating with an infrared lamp. The product was redistilled to obtain pure p-biphenylylchlorodimethylsilane, b.p. 164-167°/ 2.5 mm.

Anal. Calcd. for $C_{14}H_{15}ClSi$: Cl, 13.7%. Found: Cl, 13.7, 13.4%. A yield of product was not determined, since a portion of the Grignard reagent was lost through an insecure stopcock on the addition funnel.

Preparation of reagent (attempted) To 0.6 g. (0.085 g.-atom) of lithium was added over a period of 3 hours a solution of 10.36 g. (0.040 mole) of p-biphenylylchlorodimethylsilane in 190 ml. of tetrahydrofuran. A dark green color developed rapidly, and the reaction mixture became rather viscous. The solution gave a positive Color Test I. After stirring for an hour after the end of the addition, titration showed a 134% yield of base and 103% of organolithium, The solution was added to n-butyl chloride to form a mixture of products which were not identified.

Triethylgermyllithium (attempted)

To 0.7 g. (0.1 g.-atom) of lithium was added 2.4 g. (0.012 mole) of chlorotriethylgermane in a few ml. of tetrahydrofuran.

Stirring produced an exothermic reaction, and the mixture became cloudy. A second 2.4 g. (0.012 mole) portion of chlorotriethylgermane in 50 ml. of tetrahydrofuran was added over a period of 20 min. At the end of the addition the solution gave a negative Color Test I. Hydrolysis of an aliquot of the solution released no base. The reaction mixture was hydrolyzed in dilute hydrochloric acid and worked up in the usual manner. Removal of the solvent from the organic layer was followed by distillation to obtain 2.2 g. (55%) of hexaethyldigermane, b.p. 97-98°/0.9 mm., n_D^{20} 1.4948 [reported (163) b.p. 61-62°/0.007 mm., n_D^{20} 1.4960] .

Variations in the manner of addition of the chlorotriethylgermane to the lithium did not alter the course of the reaction. None of the attempts gave a positive Color Test I or a basic solution on hydrolysis.

Tri-n-butyltinlithium

Preparation of reagent To 0.7 g. (0.1 g.-atom) of lithium was added 6.51 g. (0.02 mole) of tri-n-butyltin chloride in 1-2 ml. of tetrahydrofuran. Stirring was begun, and an immediate exothermic reaction was noted. Tetrahydrofuran (40 ml.) was then added at one time and stirring continued for 45 min. The solution had a light yellow color, gave a positive Color Test I, and showed a 65.9% yield of tinlithium reagent on titration. Variations in the method of addition of tri-*n*-butyltin chloride did not appreciably affect the yield of reagent.

Stability in tetrahydrofuran Aliquots of the tetrahydrofuran solution of tri-*n*-butyltinlithium were titrated at intervals. The solution was allowed to stand at room temperature over the period in which titrations were made. The results appear in Figure 2.

Reaction with *n*-butyl chloride To 1.69 g. (0.018 mole) of *n*-butyl chloride was added over a period of 45 min. 76 ml. of 0.239 M tri-*n*-butyltinlithium (0.018 mole). At the end of the addition, Color Test I was negative. The reaction mixture was stirred overnight, followed by hydrolysis in saturated ammonium chloride solution. Separation and drying of the organic layer were followed by distillation of the solvent. The residue was distilled at reduced pressure to obtain the crude product, b.p. 105-122°/1.2 mm. Redistillation afforded 2.6 g. (41%) of pure tetra-*n*-butyltin, b.p. 117-119°/0.8 mm., n_D^{20} 1.4751 [reported (164) b.p. 127°/1.7 mm., n_D^{20} 1.4729]. The infrared spectrum was identical to that of a known sample (164).

Reaction with iodobenzene To 4.1 g. (0.021 mole) of iodobenzene in 30 ml. of tetrahydrofuran was added 78 ml. of 0.271 M tri-*n*-butyltinlithium over a period of 1 hour. The resulting brown solution gave a negative Color Test I and was stirred for an additional 18 hours.

Hydrolysis in saturated ammonium chloride was followed by the usual work-up and distillation of the solvent. The residue was distilled at reduced pressure to obtain crude phenyltri-n-butyltin, b.p. 120-147°/0.6 mm. Redistillation afforded 1.3 g. (22%) of the pure product, b.p. 123-124°/0.5 mm., n_D^{20} 1.5210 [reported (164) b.p. 139°/0.6 mm., n_D^{20} 1.5155] . The infrared spectrum was identical with that of a known sample (164).

Reaction with trimethyl phosphate To 2.5 g. (0.018 mole) of trimethyl phosphate in 10 ml. of tetrahydrofuran was added over a period of 1 hour 77 ml. of 0.232 M tri-n-butyltinlithium (0.018 mole). The reaction was exothermic, and Color Test I was negative at the end of the addition. After stirring for an additional hour, the mixture was hydrolyzed in saturated ammonium chloride and worked up in the usual manner. After distillation of the solvent, methyltri-n-butyltin, 2.0 g. (36%), was obtained, b.p. 108-111°/4 mm., n_D^{20} 1.4731, d_{20}^{20} 1.0908 [reported (165) b.p. 122-124°/11 mm., d_{20}^{20} 1.0901].

Reaction with hexaphenyldisilane (attempted) To 10.25 g. (0.020 mole) of hexaphenyldisilane suspended in 30 ml. of tetrahydrofuran was added 96 ml. of 0.206 M tri-n-butyltinlithium (0.020 mole) over a period of 30 min. After stirring for 66 hours there was no evidence of reaction. Hydrolysis in saturated ammonium chloride was followed by filtration to obtain 10.25 g. (100%) of unreacted hexaphenyldisilane, m.p. 362-365°.

Methyldiphenyltinlithium

Preparation of methyltriphenyltin

From triphenyltin chloride and methyllithium (attempted) To 139 g. (0.36 mole) of triphenyltin chloride in 450 ml. of ether was added a solution of methyllithium prepared from 63.9 g. (0.45 mole) of methyl iodide and 6.94 g. (1.0 g.-atom) of lithium in 600 ml. of ether (0.30 mole of methyllithium by allyl bromide double titration). After stirring for 48 hours, Color Test I was still positive, and 7.7 g. (0.02 mole) of additional triphenyltin chloride in 100 ml. of ether was added. After another 2 hours, the color test was negative. The reaction mixture was hydrolyzed in dilute hydrochloric acid and the ether layer separated and filtered to obtain solid product, m.p. 222-228°. The material was recrystallized from benzene to obtain 83.2 g. (72.3% yield based on available phenyl groups) of tetraphenyltin, m.p. 227-230° (mixture m.p.).

From triphenyltinlithium and trimethyl phosphate To 36.5 g. (0.26 mole) of trimethyl phosphate in 100 ml. of tetrahydrofuran was added dropwise 510 ml. of 0.465 M triphenyltinlithium (0.24 mole). At the end of the addition stirring was continued for 2 hours, followed by hydrolysis with dilute hydrochloric acid. The normal work-up and evaporation of the organic layer afforded the crude product. Treatment with methanol and filtration gave 3.3 g. (3.6%) of hexaphenylditin, m.p. 225-230° (mixed m.p. 230-233°). Concentration of the filtrate afforded, after recrystallization of the product from methanol, 69.0 g. (73.1%) of methyltriphenyltin, m.p. 60-62° (mixed m.p.).

Methyldiphenyltin chloride

From methyltriphenyltin and hydrogen chloride A solution of 6.70 g. (0.018 mole) of methyltriphenyltin in 100 ml. of chloroform was heated to reflux temperature. Approximately 415 ml. (0.018 mole) of anhydrous hydrogen chloride, metered by a calibrated manometer, was bubbled into the solution over a period of 3 min. The reaction mixture was stirred for 30 min., decanted, and the solvent evaporated. From the resulting oil a solid, m.p. 95-98°, crystallized on standing overnight. Recrystallization from dry petroleum ether (b.p. 60-70°) afforded 1.4 g. (19.3%) of triphenyltin chloride, m.p. 101-103° (mixed m.p.). The remaining oil was distilled at reduced pressure to obtain the crude product, b.p. 143-150°/0.5 mm., n_D^{20} 1.6124. Two redistillations afforded pure methyldiphenyltin chloride, b.p. 125-128°/0.2 mm., n_D^{20} 1.6139.

Anal. Calcd. for $C_{13}H_{13}ClSn$: C, 48.28; H, 4.05; Cl, 11.0, Found: C, 48.59, 48.55; H, 4.16, 4.20; Cl, 11.2, 11.0.

From methyltriphenyltin and chlorine Into a solution of 50.0 g. (0.14 mole) of methyltriphenyltin in 500 ml. of dry petroleum ether (b.p. 60-70°) cooled to -25° with a Dry Ice-acetone bath was bubbled approximately 3500 ml. (0.16 mole) of chlorine over a period of 12 min. The mixture was allowed to warm to room temperature under stirring, and the solvent was evaporated. The resulting oil was distilled three times at reduced pressure to obtain 10.6 g. (24.0%) of methyldiphenyltin chloride, b.p. 128-132°/0.25 mm., n_D^{20} 1.6140. The residue from the first distillation solidified and was recrystallized from dry petroleum ether (b.p. 60-70°) to obtain 3.6 g. (6.8%) of impure triphenyltin chloride, m.p. 85-90° (mixed m.p. 92-95°).

From methyltriphenyltin and iodine followed by hydrolysis and treatment with hydrochloric acid To a solution of 72.8 g. (0.20 mole) of methyltriphenyltin in 350 ml. of chloroform heated to reflux temperature was added dropwise a solution of 50.5 g. (0.20 mole) of iodine in 1 l. of chloroform. The purple iodine color was discharged rapidly at first, then more slowly, until 1 hour was required to lose the color at the end of the addition. The solvent was evaporated and the resulting oil taken up in diethyl ether. The ether solution was extracted three times with 20% sodium hydroxide, once with distilled water, and three times with 10% hydrochloric acid. The ether layer was then dried over anhydrous sodium sulfate and the solvent evaporated to leave an oil which was distilled at reduced pressure to obtain impure methyldiphenyltin chloride, b.p. 137-150°/0.5 mm., n_D^{20} 1.6130. Redistillation afforded 29.4 g. (44.2%) of the pure product, b.p. 129-130°/ 0.15 mm., n_D^{20} 1.6140. From the residue of the first distillation was obtained a solid which was recrystallized from dry petroleum ether to give 2.4 g. (3.1%) of triphenyltin chloride, m.p. 101-103° (mixed m.p. 103-105°).

Preparation of reagent To 7.9 g. (0.024 mole) of methyldiphenyltin chloride and 0.52 g. (0.075 g.-atom) of finely cut lithium wire was added a small amount of tetrahydrofuran. Stirring was commenced, and an immediate exothermic reaction took place. Tetrahydrofuran (50 ml.) was added, and the mixture rapidly became green-brown in color. After stirring for 3 hours titration showed a 93.7% yield of the tinlithium reagent. The solution gave a positive Color Test I.

Stability in tetrahydrofuran Aliquots of a tetrahydrofuran solution of methyldiphenyltinlithium were titrated at intervals. The solution was allowed to stand at room temperature over the period in which titrations were made. The results appear in Figure 2.

Reaction with trimethyl phosphate To 3.42 g. (0.024 mole) of trimethyl phosphate in 50 ml. of tetrahydrofuran was added over a period of 1 hour 52 ml. of 0.409 M methyldiphenyltinlithium (0.021 mole).

The mixture was allowed to stir for an additional 1.5 hours, then hydrolyzed in dilute hydrochloric acid. Removal of the solvent from the organic layer left an oil which was distilled at reduced pressure to obtain crude dimethyldiphenyltin, b.p. 94-106°/0.15 mm. Redistillation afforded the pure product, 3.1 g. (41.9%), b.p. 93-96°/ 0.15 mm., n_D^{20} 1.5900. The infrared spectrum of the product was identical with that of the material prepared from diphenyltin dichloride and methylmagnesium iodide.

Dimethylphenyltinlithium

Preparation of starting materials

Dimethyldiphenyltin The Grignard reagent prepared from 39.8 g. (0.28 mole) of methyl iodide and 9.2 g. (0.38 g.-atom) of magnesium in 300 ml. of diethyl ether was added dropwise to 48.0 g. (0.14 mole) of diphenyltin dichloride in 300 ml. of diethyl ether. The mixture was stirred overnight, at the end of which time Color Test I was negative. Hydrolysis was effected with dilute hydrochloric acid, followed by the usual work-up. Evaporation of the solvent from the organic layer left a brown oil which was distilled at reduced pressure to obtain 36.2 g. (85.6%) of dimethyldiphenyltin, b.p. 97-99°/0.2 mm., n_D^{20} 1.5910, d_{20}^{20} 1.3650.

Anal. Calcd. for $C_{14}H_{16}Sn$: C, 55.50; H, 5.32; MR_D 74.98 (109).

Found: C, 54.89, 55.04; H, 5.36, 5.47; MR_D 75.01.

A second run of the reaction afforded dimethyldiphenyltin in 76.3% yield after two distillations of the product, b.p. 99-100°/0.25 mm., n^{20}_{D} 1.5909.

Dimethylphenyltin chloride To a solution of 50.0 g. (0.165 mole) of dimethyldiphenyltin in 900 ml. of chloroform heated to reflux temperature was added 41.9 g. (0.165 mole) of iodine in small portions. At the end of the addition the mixture was maintained at reflux temperature for 3 hours, then allowed to cool under stirring overnight. The solvent was distilled under nitrogen, then the residue distilled at reduced pressure to obtain 53.8 g. (92.5%) of a product assumed to be dimethylphenyltin iodide, b.p. 79-83°/0.25 mm., n^{20}_{D} 1.6271. This material was dissolved in 150 ml. of diethyl ether, extracted three times with 20% sodium hydroxide, once with water, and three times with 10% hydrochloric acid. The ether layer was then dried over anhydrous sodium sulfate and the solvent distilled. The residue was distilled at reduced pressure to obtain 28.9 g. (67.2% based on dimethyldiphenyltin) of dimethylphenyltin chloride, b.p. 91-92°/0.9 mm., n^{20}_{D} 1.5761.

Anal. Calcd. for $C_8H_{11}ClSn$: Cl, 13.6. Found: Cl, 13.8, 13.6.

When the reaction mixture was worked up without distilling the dimethylphenyltin iodide before converting it to the chloride, a more complex mixture of products was obtained. Five distillations were required to purify the product in this case.

Preparation of reagent To 6.54 g. (0.025 mole) of dimethylphenyltin chloride and 0.52 g. (0.075 g.-atom) of finely cut lithium wire was added a small amount of tetrahydrofuran. Stirring was begun, and an exothermic reaction ensued. Tetrahydrofuran (50 ml.) was added and the mixture stirred for 3 hours. At the end of this time Color Test I was positive, and titration showed a 77.9% yield of the tinlithium reagent.

Branched Chain Polytin Compounds

Preparations of tetrakis(triphenylstannyl)tin

From triphenyltinlithium and stannous chloride followed by triphenyltin chloride A solution of 3.66 g. (0.019 mole) of stannous chloride was cooled to ca. 0° with an ice-water bath, and 118 ml. of 0.479 M triphenyltinlithium (0.057 mole) was added over a period of 3 hours. The reaction mixture became yellow rapidly, then darkened to brown. At the end of the addition the mixture was stirred for 18 hours. The solution appeared homogeneous and gave a negative Color Test I. It was decanted and added dropwise to a solution of 7.05 g. (0.019 mole) of triphenyltin chloride in 100 ml. of tetrahydrofuran. The resulting brown solution was stirred for 20 hours, then hydrolyzed in saturated ammonium chloride. The organic layer was separated and filtered to obtain a white solid, m.p. 310-330° decomp. Recrystallization from benzene gave 15.7 g. (55%) of tetrakis(triphenylstannyl)tin, m.p. 315-330° decomp. Subsequent recrystallizations from benzene, chloroform or a carbon disulfide-acetone mixture did not raise the melting point.

Anal. Calcd. for $C_{72}H_{60}Sn$: C, 56.94; H, 3.98; Sn, 39.08; mol. wt. 1519. Found: C, 57.71, 57.91; H, 4.14, 4.16; Sn, 38.93, 39.21; mol. wt. (vapor pressure osmometer) 1498.

Evaporation of the tetrahydrofuran filtrate afforded a solid which was recrystallized from benzene-petroleum ether (b.p. 60-70°) to obtain 4.6 g. (17.5%) of hexaphenylditin, m.p. 229-232° (mixed m.p. 230-234°). Concentration of the mother liquor gave a material, m.p. 280-300° decomp., which appeared to be a mixture of the two products already described. The mixture was not fractionated.

Two subsequent runs of the reaction under the same conditions afforded tetrakis(triphenylstannyl)tin in yields of 69.4% and 47.5%. The infrared spectrum of the compound is identical to that of hexaphenylditin, while the ultraviolet spectrum ($\lambda_{max}^{cyclohexane}$ 275.5, 247 mμ) is distinctly different from that of the ditin (120a).

<u>From phenylmagnesium bromide and stannous chloride</u> The Grignard reagent prepared from 75.0 g. (0.48 mole) of bromobenzene and 12.2 g. (0.50 g.-atom) of magnesium in 400 ml. of diethyl ether was decanted through a glass wool plug into a reaction flask and

cooled to ca. 0° with an ice-water bath. Finely powdered stannous chloride, 15.0 g. (0.079 mole), was added, and the solution turned red in color as the stannous chloride slowly dissolved. The mixture was allowed to warm to room temperature and stirred for 1 hour, then heated to reflux temperature and stirred for 4.5 hours. Hydrolysis was effected in cold water. The organic layer was separated and filtered to obtain a brown, amorphous material which was boiled with benzene and filtered to give a brown solid that did not melt below 400°. The benzene solution was concentrated to obtain 2.7 g. (9.6%, based on stannous chloride) of impure hexaphenylditin, m.p. 225-230° (mixed m.p. 226-231°). The original organic layer was evaporated to obtain a solid which was fractionally crystallized from benzene to obtain impure hexaphenylditin, m.p. 223-230° (mixed m.p. 228-232°), 2.6 g. (9.2%), and a solid melting at 190-210°. The latter material was fractionally crystallized from benzene to give 0.9 g. (3.2%) of additional impure hexaphenylditin, m.p. 218-225° (mixed m.p. 224-229°) and 0.5 g. (2.1%) of tetrakis(triphenylstannyl)tin, m.p. 310-330° (mixed m.p.). Recrystallization from benzene-petroleum ether (b.p. 60-70°) raised the melting point to 315-330°. The ultraviolet spectrum and x-ray powder diffraction pattern of this compound were identical with those of the previously prepared tetrakis(triphenylstannyl)tin.

From phenyllithium and stannous chloride (attempted) A diethyl ether solution (420 ml.) of 0.41 mole of phenyllithium was cooled to ca. 0° in an ice-water bath, and 13.0 g. (0.068 mole) of stannous chloride was added. The reaction mixture became gray in color within a few minutes. It was allowed to warm to room temperature and stirred for 1 hour, followed by 4 hours at reflux temperature. Hydrolysis was effected in saturated ammonium chloride, and the organic layer was separated. The water layer, which contained gray solid, apparently elemental tin, was extracted with diethyl ether and with benzene. The combined organic layers were filtered to obtain 9.1 g. (31.3% based on stannous chloride) of tetraphenyltin, m.p. 228-231° (mixed m.p.). Evaporation of the filtrate gave a slightly yellow solid which was recrystallized from benzene to yield 4.6 g. (16%) of additional tetraphenyltin, m.p. 227-230° (mixed m.p.).

From triphenyltinlithium and stannic chloride Triphenyltinlithium was prepared from phenyllithium (0.30 mole in 330 ml. of diethyl ether) and stannous chloride [19.0 g. (0.10 mole) in 150 ml. of diethyl ether] according to published directions (33). The solution was added dropwise to 6.5 g. (0.025 mole) of stannic chloride in 100 ml. of diethyl ether. The resulting mixture was stirred overnight, then hydrolyzed in saturated ammonium chloride. The organic layer was separated and filtered to give a yellow solid. This material was treated with boiling benzene, and the resulting mixture filtered to obtain a brown solid which did not melt below 400°. The substance was not identified. The benzene filtrate was evaporated to obtain a solid, m.p. 220-250°. Fractional crystallization of the solid from chloroform gave 3.9 g. (9.7%) of tetrakis(triphenylstannyl)tin, m.p. 305-325° decomp., and material melting at 220-230°. The former was recrystallized from benzene-petroleum ether (b.p. 60-70°) to obtain the pure compound, m.p. 315-330° decomp., which was identical with previous samples in ultraviolet spectrum and x-ray diffraction pattern. Work-up of the organic layer afforded 3.25 g. of tetraphenyltin, m.p. 225-227° (mixed m.p.).

From triphenyltin chloride, stannic chloride, and lithium Solutions of 23.1 g. (0.060 mole) of triphenyltin chloride in 300 ml. of tetrahydrofuran and 3.91 g. (0.015 mole) of stannic chloride in 30 ml. of benzene were added simultaneously over a period of 1.5 hours to 0.83 g. (0.12 g.-atom) of finely cut lithium wire in 100 ml. of tetrahydrofuran. After approximately half of the addition had been completed, the lithium became shiny, and heat was evolved. The mixture turned pale green in color and was stirred overnight, followed by hydrolysis in saturated ammonium chloride. Filtration of the organic layer gave a solid which was crystallized from benzene-petroleum ether (b.p. 60-70°) to obtain 4.7 g. (20.6%) of tetrakis(triphenylstannyl)tin, m.p.

305-325° decomp. Recrystallization from the same solvent mixture afforded the pure material, m.p. 315-330° decomp., with ultraviolet spectrum and x-ray diffraction pattern identical to those of previous samples. Work-up of the organic layer gave 8.6 g. (41%) of hexaphenylditin, m.p. 230-234° (mixed m.p. 232-234°).

From bis(triphenyltin)magnesium and stannous chloride followed by triphenyltin chloride Bis(triphenyltin)magnesium was prepared from 23.1 g. (0.06 mole) of triphenyltin chloride and 2.19 g. (0.09 g.-atom) of magnesium in 150 ml. of tetrahydrofuran according to published directions (147b). Acid titration showed the presence of 0.051 equivalents of the reagent. The solution was added dropwise to a solution of 3.31 g. (0.017 mole) of stannous chloride in 100 ml. of tetrahydrofuran cooled to ca. 0° with an ice-water bath. The mixture was stirred overnight, then decanted and added to a solution of 6.55 g. (0.017 mole) of triphenyltin chloride in 100 ml. of tetrahydrofuran. This mixture was stirred overnight, then hydrolyzed in saturated ammonium chloride. Filtration of the organic layer and crystallization of the resulting solid from benzene gave a material melting at 225-300° decomp. Recrystallizations from benzene-petroleum ether (b.p. 60-70°) mixture and from chloroform afforded 0.8 g. (3.1%) of tetrakis-(triphenylstannyl)tin, m.p. 310-330°, identified by ultraviolet spectrum and x-ray diffraction pattern. Work-up of the organic layer gave 3.0

g. (11%) of hexaphenylditin, m.p. 225-232° (mixed m.p. 228-233°).

Reactions of tetrakis(triphenylstannyl)tin

With iodine (1:1 molar ratio) To a solution of 15.18 g. (0.01 mole) of tetrakis(triphenylstannyl)tin in 100 ml. of refluxing chloroform was added over a period of two hours a solution of 2.54 g. (0.01 mole) of iodine in 100 ml. of chloroform. The iodine color was discharged rapidly throughout the addition, but the reaction mixture developed a yellow color. The solution was allowed to cool by standing overnight, followed by evaporation of the solvent. The residue was treated with hot benzene-petroleum ether (b.p. 60-70°) and filtered to obtain a solid, m.p. 300-330° decomp. Concentration of the filtrate gave further solid melting at 280-310° decomp. The two fractions were combined and recrystallized twice from the same solvent mixture to obtain 7.4 g. (49%) of the starting tetrakis compound, m.p. 305-325° decomp. (mixed m.p.). The ultraviolet spectrum of this product was identical with that of tetrakis(triphenylstannyl)tin.

Further concentration of the original benzene-petroleum ether (b.p. 60-70°) filtrate afforded a light yellow solid, m.p. 114-118°. Recrystallization of this material from dry petroleum ether (b.p. 60-70°) gave 3.9 g. (82%) of triphenyltin iodide, m.p. 118-121° (mixed m.p.). It is believed that the yellow color of the reaction mixture and the solid products was due to the presence of small quantities of stannic iodide, a red-orange solid in the pure state. None of this product was isolated, however.

With iodine (1:4 molar ratio) To a solution of 15.18 g. (0.01 mole) of tetrakis(triphenylstannyl)tin in 100 ml. of refluxing chloroform was added over a period of 4 hours a solution of 10.16 g. (0.04 mole) of iodine in 300 ml. of chloroform. Decolorization of the iodine solution was rapid at first, but was noticeably slower toward the end of the addition. The mixture was allowed to stand for 20 hours, followed by evaporation of the solvent. The resulting solid was crystallized from dry benzene-petroleum ether (b.p. 60-70°) mixture to obtain orange solid, m.p. 100-115°. This material was digested with dry petroleum ether (b.p. 60-70°) and filtered to give 11.5 g. (60.3%) of triphenyltin iodide, m.p. 120-122° (mixed m.p.). Evaporation of the mother liquor, followed by fractional crystallization from petroleum ether (b.p. 28-38°) and from absolute ethanol gave an additional 4.2 g. (22.1%) of triphenyltin iodide, m.p. 119-122° (mixed m.p.). The remaining solid was a red-orange material which could not be further purified by crystallization. The material is believed to consist of a mixture of stannic iodide with some additional triphenyltin iodide.

With excess sym-tetrachloroethane A mixture of 15.18 g. (0.01

mole) of tetrakis(triphenylstannyl)tin and 50 ml. of sym-tetrachloroethane was heated to 140° by means of an oil bath and stirred for 18 hours. The reaction mixture was heterogeneous throughout this treatment, and brown solid was slowly deposited on the wall of the reaction flask. The mixture was allowed to cool, then filtered through a sintered glass funnel under nitrogen atmosphere. The solid obtained was a brown material which was insoluble in boiling benzene and which did not melt below 400°. It was not identified. The solvent was distilled from the filtrate and the residue crystallized from dry benzene-petroleum ether (b.p. 60-70°) to obtain solid, m.p. 185-205°. Recrystallization from the same solvent mixture afforded 0.6 g. of tetraphenyltin, m.p. 225-229° (mixed m.p.). From the original mother liquor there was obtained additional solid, m.p. 99-102°. Recrystallization of this material from dry petroleum ether (b.p. 60-70°) afforded 8.5 g. (55% based upon complete reaction of tetrakis(triphenylstannyl)tin) of triphenyltin chloride, m.p. 101-104° (mixed m.p. 102-105°).

With sym-tetrachloroethane (1:1 molar ratio, attempted) A mixture of 15.18 g. (0.01 mole) of tetrakis(triphenylstannyl)tin and 1.68 g. (0.01 mole) of sym-tetrachloroethane in 100 ml. of xylene was heated at gentle reflux for 48 hours. The mixture was heterogeneous, and no evidence of reaction was observed. The mixture was allowed to cool, then filtered to obtain 13.9 g. (91.6%) of the starting material, m.p. 315-330° decomp. (mixed m.p.). Distillation of the solvent, followed by crystallization of the residue from benzene-petroleum ether (b.p. 60-70°) afforded an additional 0.4 g. (2.6%) of tetrakis(triphenylstannyl)tin, m.p. 310-325° decomp. (mixed m.p.).

The reaction was repeated using only 15 ml. of xylene solvent and refluxing for 48 hours. Tetrakis(triphenylstannyl)tin was recovered in 94% yield.

With excess 1,2-dibromoethane A mixture of 15.18 g. (0.01 mole) of tetrakis(triphenylstannyl)tin and 50 ml. (approximately 0.6 mole) of freshly distilled 1,2-dibromoethane was stirred for 16 hours at 130°. The mixture did not become homogeneous, and slowly turned brown. The reaction mixture was allowed to cool and then filtered. The brown solid obtained was recrystallized twice from benzene-petroleum ether (b.p. 60-70°)to obtain 1.0 g. (6.8%) of starting material, m.p. 305-325° decomp. (mixed m.p.). The filtrate from the reaction mixture was distilled to remove 1,2-dibromoethane. The solid residue was recrystallized twice from dry benzene to obtain 10.2 g. (63.7% based on unrecovered tetrakis compound) of triphenyltin bromide, m.p. 117-119° (mixed m.p.).

With triphenyltinlithium (1:4 molar ratio) To a solution of 15.18

g. (0.01 mole) of tetrakis(triphenylstannyl)tin in 100 ml. of tetrahydrofuran was added dropwise 77 ml. of 0.520 M triphenyltinlithium (0.04 mole). During the addition the reaction mixture turned yellow, then brown. After stirring for 48 hours, hydrolysis was effected with saturated ammonium chloride. Separation and filtration of the organic layer gave a solid product. Two recrystallizations from benzene-petroleum ether (b.p. 60-70°) gave 6.7 g. (44%) of recovered tetrakis(triphenylstannyl)tin, m.p. 310-325° decomp. (mixed m.p.). Evaporation of the solvent from the organic filtrate afforded a solid which was recrystallized twice from benzene to obtain 16.2 g. (74% based on the total amount of triphenyltinlithium and unrecovered starting material) of hexaphenylditin, m.p. 230-234° (mixed m.p.).

With methyllithium (1:1 molar ratio) To a solution of 15.18 g. (0.01 mole) of tetrakis(triphenylstannyl)tin in 100 ml. of tetrahydrofuran was added 13 ml. of a 0.760 M diethyl ether solution of methyllithium (0.01 mole). The reaction mixture became light yellow in color, and Color Test I was negative after 45 min. of stirring. Hydrolysis with saturated ammonium chloride followed by filtration of the organic layer afforded a white solid which was recrystallized from benzene-petroleum ether (b.p. 60-70°) to obtain 8.4 g. (55%) of tetrakis(triphenylstannyl)tin, m.p. 310-325° decomp. (mixed m.p.). Evaporation of the organic filtrate gave a solid which was recrystallized from benzene to afford 0.8 g. of tetraphenyltin, m.p. 222-226° (mixed m.p. 224-226°). Concentration of the mother liquor gave additional solid, m.p. 190-200°, which appeared to be a mixture of tetraphenyltin and hexaphenylditin. The mixture was not separated.

Reactions of hexaphenylditin

With alcoholic potassium hydroxide (attempted) A mixture of 3.5 g. (0.005 mole) of hexaphenylditin and 50 ml. of a solution of 1% potassium hydroxide in 95% aqueous ethanol was stirred for 18 hours at reflux temperature. The reaction mixture was allowed to cool and filtered to obtain 3.2 g. (91.5%) of hexaphenylditin, m.p. 232-235° (mixed m.p. 233-236°).

With moist piperidine To 3.5 g. (0.005 mole) of hexaphenylditin was added 100 ml. of moist piperidine (10% by volume water). Heating produced a homogeneous solution which was stirred overnight. After cooling, the solution was added to 200 ml. of distilled water. Filtration afforded a solid which was fractionally crystallized from benzene-petroleum ether (b.p. 60-70°). The first fraction was a solid which was recrystallized from benzene to obtain 1.1 g. (32%) of hexaphenylditin, m.p. 230-235° (mixed m.p. 231-235°). The second fraction was 1.0 g. (28%) of bis(triphenyltin)oxide, m.p.

116-120° (mixed m.p.).

With excess sym-tetrachloroethane A mixture of 7.0 g. (0.01 mole of hexaphenylditin and 50 ml. of *sym*-tetrachloroethane was heated for 16 hours at gentle reflux. The mixture was allowed to cool, and brown solid was filtered off. The solid did not melt below 400° and was not identified. The filtrate was distilled and the residue fractionally crystallized from benzene-petroleum ether (b.p. 60-70°). The first fraction was a solid, m.p. 180-188°, which was not identified, but was presumably impure hexaphenylditin. The second fraction was impure triphenyltin chloride which was recrystallized from dry petroleum ether (b.p. 60-70°) to obtain 3.25 g. (42%) of the pure product, m.p. 100-102° (mixed m.p. 101-103°).

Reactions of tris(triphenylstannyl)tinlithium

With trimethyl phosphate A solution of tris(triphenylstannyl)-tinlithium, prepared from 104 ml. of 0.520 M triphenyltinlithium (0.054 mole) and 3.41 g. (0.018 mole) of stannous chloride in 100 ml. of tetrahydrofuran, was added dropwise to 2.52 g. (0.018 mole) of trimethyl phosphate in 100 ml. of tetrahydrofuran. The brown reaction mixture was stirred for 24 hours, then hydrolyzed in saturated ammonium chloride. Work-up of the organic layer in the usual manner afforded a white solid which was fractionally crystallized from benzene to obtain 8.3 g. (39.5%) of hexaphenylditin, m.p. 230-234° (mixed m.p. 232-235°), and solid melting in the range, 165-180°. Recrystallization of the latter material from chloroform gave 3.2 g. (15% as methyltris(triphenylstannyl)tin) of white solid, m.p. 180-183°. Three recrystallizations from benzene-petroleum ether (b.p. 60-70°) did not change the melting point. It was noted that a brown sediment began to be deposited from solutions of this material on standing for several hours.

Anal. Calcd. for $C_{55}H_{48}Sn_4$: Sn, 40.11; mol. wt. 1184. Found: Sn, 39.59, 38.77; mol. wt. (vapor pressure osmometer) 944.

A second run of the reaction was made, and a similar material was isolated. Recrystallization from ethyl acetate-methanol raised the melting point to 183-185°. A mixture melting point with the solid from the first run was not depressed. A molecular weight determination (vapor pressure osmometer) gave a value of 1002 (calcd. 1184). It seems likely that the product is the desired methyltris(triphenylstannyl)tin, but a pure sample has not as yet been obtained.

With methyl iodide A reaction exactly analogous to that above was run, except that derivatization was carried out with methyl iodide instead of trimethyl phosphate. Hexaphenylditin (32.7%) was obtained along with 4.8% of the same product as above, m.p. 181-184° (mixed m.p.). Again, further purification of the latter product could not be effected.

With chlorotriphenylgermane A solution of tris(triphenylstannyl)-tinlithium, prepared from 84 ml. of 0.613 M triphenyltinlithium (0.051 mole) and 3.24 g. (0.017 mole) of stannous chloride in 100 ml. of tetrahydrofuran, was added dropwise to 5.76 g. (0.017 mole) of chlorotriphenylgermane in 100 ml. of tetrahydrofuran. The reaction mixture was stirred for 45 hours, then hydrolyzed in saturated ammonium chloride. Separation and filtration of the organic layer gave white solid, m.p. 315-330° decomp. This material was recrystallized twice from benzene-petroleum ether (b.p. 60-70°) to give 4.4 g. (18%) of the product with the same melting point. The melting point was not depressed when mixed with tetrakis(triphenylstannyl)tin; however, an infrared spectrum of the product (carbon disulfide) showed an absorption at 9.24μ characteristic of the germanium-phenyl linkage in addition to the tin-phenyl absorption at 9.36μ. The x-ray powder diffraction pattern of the product was distinctly different from that of tetrakis(triphenylstannyl)tin and did not appear to be the pattern to be expected for a mixture of the tetrakis compound with another product containing germanium-phenyl linkages. The product is probably tris(triphenylstannyl)triphenylgermyltin.

Anal. Calcd. for $C_{72}H_{60}GeSn_4$: Ge + Sn, 37.17; mol. wt. 1473.

Found: Ge + Sn, 35.58, 35.99; mol. wt. (vapor pressure osmometer), 1503.

With chlorotriphenylsilane Tris(triphenylstannyl)tinlithium (0.019 mole) was prepared as described above and added to 5.60 g. (0.019 mole) of chlorotriphenylsilane in 75 ml. of tetrahydrofuran. The reaction mixture was stirred overnight, then hydrolyzed in saturated ammonium chloride. Separation and filtration of the organic layer afforded a solid which was crystallized from benzene to obtain a product, m.p. 310-330° decomp. Recrystallization from benzene-petroleum ether (b.p. 60-70°) gave 13.0 g. (57%) of tetrakis(triphenylstannyl)tin, m.p. 315-330° (mixed m.p.). The infrared spectrum of the product showed no evidence of silicon-phenyl absorptions, and the ultraviolet spectrum was identical to that of the previously prepared tetrakis(triphenylstannyl)tin.

With tri-n-butyltin chloride Tris(triphenylstannyl)tinlithium (0.019 mole) was prepared as described above and added to 6.18 g. (0.019 mole) of tri-n-butyltin chloride in 75 ml. of tetrahydrofuran. The mixture was stirred overnight, then worked up as described above. The only product obtained was tetrakis(triphenylstannyl)tin, 15.3 g. (67.2%), which was identified by mixture melting point, infrared and ultraviolet spectra.

With saturated aqueous ammonium chloride Tris(triphenylstannyl)tinlithium (0.019 mole) prepared as described above was hydrolyzed in saturated ammonium chloride. Work-up as previously described gave 7.6 g. (34.1%) of tetrakis(triphenylstannyl)tin, identified by mixture melting point, ultraviolet spectrum, and x-ray powder pattern. In addition, 3.1 g. (14.5%) of hexaphenylditin, m.p. 230-234° (mixed m.p. 232-235°), was obtained from the work-up of the organic layer.

DISCUSSION

Analysis of Organolithium Compounds

In the investigation a variety of organic halides was substituted for benzyl chloride in the standard double titration procedure for organolithium compounds. Nineteen allyl halides, polyhaloalkanes, and substituted benzyl halides were tested as possible reagents for titrations of alkyl- and aryllithium compounds. Many of the halides were those used in a previous study of the reactivity of octaphenylcyclotetrasilane with a large number of organic halogen compounds[1]. The halides are listed below in the order of increasing reactivity with phenyllithium, as judged from titration values obtained with them: p-methylbenzyl chloride, benzyl chloride, allyl chloride, p-bromobenzyl chloride, sym-tetrabromoethane, diphenylmethyl chloride, methyl iodide, o-chlorobenzyl chloride, benzyl bromide, o-methylbenzyl bromide, sym-tetrachloroethane, chloroform, o-bromobenzyl bromide, allyl bromide, allyl iodide, pentachloroethane, 1,2-dibromoethane, carbon tetrachloride, 1,1,2-tribromoethane, and α,α,α-trichlorotoluene. The order given here is only approximate for some of the halides, which were used a few times and not investigated further. The halides giving

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[1] J. M. Kraemer and H. Gilman, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Information on the reactions of octaphenylcyclotetrasilane with organic halides. Private communication. 1960.

the highest titration values were examined more thoroughly, with the exception of allyl iodide, which offers no advantages over other more readily available and more stable halides.

Attention was centered first on phenyllithium and methyllithium as compounds which give obviously low results with benzyl chloride. A number of halides gave higher results than benzyl chloride, and almost all the halides gave good precision when several titrations were made of a single preparation of organolithium compound, as is shown in Table 1. In the titrations of phenyllithium, a gravimetric method of analysis was used as a check on accuracy. The reaction used was that with triphenyltin chloride, which produces tetraphenyltin, a compound virtually insoluble in diethyl ether. It is felt that the reaction is as nearly quantitative as could be obtained for a gravimetric analysis of organolithium compounds, as no side products could be isolated. Furthermore, the tetraphenyltin has a high melting point (230°), making drying of the sample quite convenient. In Table 2 the results of the triphenyltin chloride analysis are compared with double titration values using several organic halides. The halides giving the closest agreement with the yield of derivative are 1,2-dibromoethane and carbon tetrachloride. 1,1,2-Tribromoethane gives slightly higher values, and α, α, α-trichlorotoluene is considerably higher.

Table 1. Analyses of one preparation of methyllithium in diethyl ether using the double titration procedure with several different organic halides

Halide	Molarity	Deviation, %	Yield, %
None	0.880		84.5
$C_6H_5CCl_3$	0.844, 0.845	0.1	81.1
$BrCH_2CHBr_2$	0.820, 0.813	0.8	78.4
$Br_2CHCHBr_2$	0.801, 0.800	0.1	76.8
$BrCH_2CH_2Br$	0.793, 0.785	1.0	75.8
$CH_2 = CHCH_2Br$	0.759, 0.755	0.5	72.8
$CHCl_3$	0.740, 0.744	0.5	71.3

Table 2. Analyses of three preparations of phenyllithium in diethyl ether by double titration with several halides and by gravimetric determination of the tetraphenyltin formed on reaction with triphenyltin chloride

Halide	Molarity		
	Run 1	Run 2	Run 3
None	0.980	1.07	0.942
$C_6H_5CCl_3$	0.945	1.02	0.861
$BrCH_2CHBr_2$	0.926	0.972	0.801
CCl_4	0.909	0.966	0.800
$BrCH_2CH_2Br$	0.907	0.962	0.785
Cl_3CCHCl_2	0.872	0.924	---
$CH_2 = CHCH_2Br$	0.835	0.870	0.686
$(C_6H_5)_3SnCl$	0.905	0.961	0.797

The most probable reason for obtaining a titration value higher than the actual concentration is reaction of the organic halide with lithium alkoxide. Reactions of the halides with lithium ethoxide and phenoxide were therefore carried out. The results are given in Tables 3, 4, and 5. It is immediately clear that α,α,α-trichlorotoluene must be suspected of giving unreliable titration values due to considerable reaction with both lithium ethoxide and phenoxide. With 1,1,2-tribromoethane there is an appreciable reaction with lithium ethoxide. Probably the 10% reaction observed in this case would not substantially alter the titration values for fresh preparations of organolithium compounds in which the concentration of alkoxide is low. However, 1,1,2-tribromoethane should certainly be used with caution where alkoxide concentration is suspected of being high. With allyl bromide, 1,2-dibromoethane, and carbon tetrachloride the interference should not be appreciable. It has been suggested (14) that there is no reaction between allyl bromide and lithium ethoxide under the conditions of the double titration, but the present results do indicate a slight reaction.

Thus, in the phenyllithium titrations in Table 2, the values with α,α,α-trichlorotoluene are undoubtedly too high. However, it is difficult to choose among 1,1,2-tribromoethane, carbon tetrachloride, and 1,2-dibromoethane. Carbon tetrachloride has not been used regularly, because it is more difficult to obtain consistent results with that halide.

Table 3. Reactions of organic halides with lithium ethoxide in diethyl ether

	Halide	Molarity	% Reaction	
			H_2SO_4	$AgNO_3$
Run 1	None	0.140		
	$BrCH_2CH_2Br$	0.136	2.8	2.4
	$BrCH_2CHBr_2$	0.125	10.7	7.9
	$C_6H_5CCl_3$	0.106	24.2	31
Run 2	None	0.429		
	CCl_4	0.426	0.7	--[a]
	$BrCH_2CH_2Br$	0.422	1.7	--[a]

[a] There was no visible cloudiness on addition of aqueous silver nitrate.

Table 4. Reactions of allyl bromide with lithium ethoxide in diethyl ether

	Lithium ethoxide (ml.)	Allyl bromide (ml.)	Molarity	% Reaction
Run 1	2	0	0.097	
	2	1	0.095	2.1
	2	1	0.095	2.1
Run 2	2	0	0.169	
	2	1	0.166	1.8
	3	1	0.166	1.8

Table 5. Reactions of organic halides with lithium phenoxide in diethyl ether

Halide	Molarity	% Reaction
None	0.144	
CCl_4	0.144	0[a]
$BrCH_2CH_2Br$	0.142	1.4[a]
$BrCH_2CHBr_2$	0.143	0.7[a]
$C_6H_5CCl_3$	0.114	21

[a] There was no visible cloudiness on addition of aqueous silver nitrate.

Its reaction with organolithium compounds is extremely vigorous, resulting in spattering the solution on the sides of the vessel, and the resulting solution is orange in color, making a phenolphthalein end point more difficult to see. Also, both carbon tetrachloride and chloroform give low values when titrating methyllithium (see Table 1 for a comparison of chloroform with other halides). 1,1,2-Tribromoethane has been used regularly in this Laboratory for the analysis of fresh preparations of phenyl- and methyllithium, because the triphenyltin chloride treatment involves the isolation and purification of a derivative, and might be expected to give a slightly low analysis. However, 1,2-dibromoethane certainly gives a satisfactory analysis for normal work and is more readily available and in the experience of the author is more stable when opened to the air at regular intervals than is 1,1,2-tribromoethane. Indeed, the dibromoethane has been previously proposed (9) as a titrating agent for phenyllithium, although the reliability of the analysis was not investigated at that time.

The titrations of methyllithium have not been similarly checked by an alternate method of analysis. However, the range of titration values obtained with various halides is quite similar to that with phenyllithium (compare Tables 1 and 2), and the author feels that the statements above concerning the latter reagent apply also for methyllithium.

Titrations of n-butyllithium were investigated in some detail, particularly with allyl bromide, which had been previously proposed as a titrating agent for alkyllithium compounds (13,14). It is extremely difficult to assess the accuracy of analyses of alkyllithium compounds. This is indicated by the fact that one author (166) has recently indicated that he considers the benzyl chloride double titration quite reliable. However, with care taken in the preparation of an organolithium compound in a hydrocarbon solvent, it should be possible to make the organolithium compound virtually the sole contributor to the basic content of the solution. This criterion has been taken as the best means for determining the accuracy of titrations of n-butyllithium. Table 6 shows typical titrations of the reagent with allyl bromide, benzyl chloride, and 1,2-dibromoethane, the results being expressed as the percentage of the total basic content of the solution which is due to n-butyllithium. The first three runs are for preparations in diethyl ether, and it may be noted that the allyl bromide values are consistently 5% above those with benzyl chloride. This difference corresponds to the error previously estimated (11, 17) for the benzyl chloride method. The last three runs are for preparations in hexane solution, using rigorous conditions to exclude air and moisture (see footnote to the table). The high percentage found with allyl bromide titrations is taken to indicate that the n-butyllithium in the solutions is more completely consumed by allyl bromide than by benzyl chloride.

It has been noted that the analytical procedure involving thermometric titration with n-butanol gives concentrations for n-butyllithium

Table 6. Titrations of n-butyllithium

Preparation	Percentage of total base due to C-Li		
	$C_6H_5CH_2Cl$	$CH_2=CHCH_2Br$	$BrCH_2CH_2Br$
BuLi in Et_2O[a]	88.1	93.6	
BuLi in Et_2O[a]	90.1	95.1	
BuLi in Et_2O[a]	76.3	81.2	
BuLi in Hexane[b]	94.7	98.6	
BuLi in Hexane[c]	97.1	99.2	
BuLi in Hexane[c]	97.0	99.2	99.1

[a] Solution was prepared and analyzed under nitrogen atmosphere as described in the experimental section.

[b] Solution was prepared under an argon atmosphere in a beverage bottle using lithium-vaseline dispersion, and introducing hexane and n-butyl chloride with a syringe through a Buna N liner. The analysis was carried out in a nitrogen-purged bottle with reagents being transferred by syringe.

[c] The solution was a clear commercial preparation analyzed as above. The author wishes to express his appreciation to Dr. K. C. Eberly, The Firestone Tire and Rubber Company, Akron, Ohio, for carrying out the preparation and analyses of the n-butyllithium in hexane.

which are in essential agreement with those obtained by the vanadium pentoxide method and higher than is obtained by double titration with benzyl chloride (16). The thermometric titration values quoted (16) for fresh preparations of n-butyllithium in hydrocarbons show that approximately 99% of the basic content of the solutions is due to organolithium compound, in good agreement with the results quoted in Table 6 for double titrations with allyl bromide and 1,2-dibromoethane. It has also been shown recently[1] that analyses of the same preparation of n-butyllithium by the thermometric method and by double titration with allyl bromide and 1,2-dibromoethane give values in essential agreement.

Table 7 compares titrations of n-butyllithium in diethyl ether with allyl bromide and 1,2-dibromoethane. Values with the latter reagent are consistently slightly higher than those with allyl bromide, but the author feels that the two reagents may be used interchangeably without significant sacrifice of accuracy.

The use of 1,2-dibromoethane for the analysis of cyclopropyllithium has been reported recently (167). In that case nuclear magnetic resonance spectroscopy was used in a rough check of the accuracy of the titration, with the conclusion that the analysis was satisfactory.

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[1] W. L. Everson, Shell Development Company, Emeryville, California. Information on titrations of n-butyllithium. Private communication. 1964.

Table 7. Titration of n-butyllithium in diethyl ether

	Molarity		% Deviation
	$CH_2=CHCH_2Br$	$BrCH_2CH_2Br$	
Run 1	0.913	0.922	1.0
Run 2	0.741	0.749	1.1
Run 3	0.648	0.665	2.6

It should be noted that this investigation has not been extended to preparations of organolithium compounds in tetrahydrofuran. The titrating agents described in this work, with the exception of allyl bromide, give unacceptably high results in titrations of silyl-, germyl-, and tinlithium compounds in tetrahydrofuran (2). The opinion was expressed (2) that there is finely divided or dissolved lithium metal in the above solutions causing the high titration values. Until the question is investigated further, the use of allyl bromide is suggested for titrations of organolithium compounds in tetrahydrofuran.

In conclusion, the normal research laboratory which desires occasional analyses of a variety of organolithium compounds, will find it most convenient to use 1,2-dibromoethane for double titrations. This reagent gives reliable results for both alkyl- and aryllithium compounds in diethyl ether and for alkyllithium reagents in hydrocarbons. The dibromoethane retains its efficacy for several months at least, when being used at frequent intervals, so that redistillation is not often required. When R_3MLi (M = Si, Ge, Sn) compounds are being analyzed, allyl bromide should be employed (2), and its use may be extended to the titration of alkyllithium compounds as well. Accuracy will be less satisfactory when allyl bromide is used with aryllithium compounds or methyllithium. These latter reagents may be titrated satisfactorily with 1,2-dibromoethane, but accuracy is probably slightly better with the more expensive 1,1,2-tribromoethane.

Cleavage of Alkoxysilanes

In a recent study in this Laboratory (156) it was found that reactions of alkoxysilanes derived from allylic alcohols with metals or silylmetallic reagents were anomalous, in that cleavage of the carbon-oxygen bond was competitive with cleavage of the silicon-oxygen bond. Reaction of allyloxytriphenylsilane with triphenylsilyllithium afforded hexaphenyldisilane in 62% yield along with allyltriphenylsilane in 1.5% yield. The present work has shown that allyloxytriphenylsilane is not an isolated example, but that other alkoxysilanes derived from allylic and benzylic alcohols behave in an analogous manner. The results obtained in the present work are shown in Tables 8 and 9.

Distinct differences may be noted between the allyloxysilanes and the benzyloxysilanes. In reactions with triphenylsilyllithium the former give small yields of product derived from C-O bond cleavage, while the latter give none. As would be expected, ethoxytriphenylsilane gave a high yield of hexaphenyldisilane and no ethyltriphenylsilane. In direct contrast to these results, cleavage with lithium, followed by treatment with chlorotriphenylsilane, gave much more C-O bond cleavage with the benzyloxysilanes. Indeed, with (diphenylmethoxy)triphenylsilane 38.3% of (diphenylmethyl)triphenylsilane was obtained and no hexaphenyldisilane. It is certainly not surprising that the two cleavage reactions afford different results, since the mechanisms of cleavage must of necessity be different.

Table 8. Cleavage of alkoxysilanes with triphenylsilyllithium

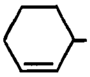
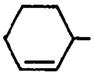
$ROSi(C_6H_5)_3$Compound	Yield of products, %	
R=	$RSi(C_6H_5)_3$	$(C_6H_5)_6Si_2$
$C_6H_5CH_2$-	0	88
$(C_6H_5)_2CH$-	0	32.6
CH_3CH_2-	0	91
$CH_2 = CHCH_2$-	5.8	44.2
	trace	57

Table 9. Cleavage of alkoxysilanes with lithium followed by treatment with chlorotriphenylsilane

$ROSi(C_6H_5)_3$Compound	Yield of products, %	
R=	$RSi(C_6H_5)_3$	$(C_6H_5)_6Si_2$
$C_6H_5CH_2$-	5.7	6
$(C_6H_5)_2CH$-	38.3	0
$CH_3CH = CHCH_2$-	0	1
	0	0

In general, however, the observations tend to confirm the previous postulate (25) that the carbon-oxygen bond is more susceptible to cleavage in alkoxysilanes derived from reactive alcohols. Obviously a number of factors, including relative strengths of the C-O bond and Si-O bond and stabilities of the anions obtained on cleavage, will be important in determining the mode of reaction.

Relative Reactivities of Organic Group IVB Lithium Compounds

As a means for determining relative reactivities, the reaction of the Group IVB lithium compounds with n-butyl chloride was chosen. In the case of triphenylsilyllithium, the interaction has been reported (168) to give 75% of n-butyltriphenylsilane with no hexaphenyldisilane. It is then not to be expected that the germanium, tin, and lead reagents will give any halogen-metal interconversion. Competitive reactions were run in which two lithium reagents and n-butyl chloride were combined in 1:1:1 molar ratio. The reaction mixtures were carbonated in order to convert the excess lithium reagents into products which could be easily separated from the butyl derivatives.

The results of the experiments are given in Table 10. It may be seen that the order of reactivity toward n-butyl chloride parallels the basicities of the anions as determined from metalation studies (30). That is, for the triphenyl derivatives, the order of decreasing reactivity is:

$(C_6H_5)_3SiLi > (C_6H_5)_3GeLi >> (C_6H_5)_3SnLi >> (C_6H_5)_3PbLi$.

The comparison of the silyl- and germyllithium compounds was a point of particular concern for several reasons. First, because the electronegativity and size of the two elements are very nearly the same, and second because a clear distinction could not be made between the two lithium reagents on the basis of the fluorene metalations (30).

In the present study, the greater reactivity of triphenylsilyllithium seems to be on firm ground. Competitive reactions were carried out between triphenylsilyllithium and triphenylgermyllithium for both n-butyl chloride and n-hexyl chloride with much the same results. Also, both reagents were allowed to compete with triphenyltinlithium for n-butyl chloride. Higher yields of the butyltin derivative were obtained in the competition with triphenylgermyllithium than with triphenylsilyllithium.

It is perhaps surprising that the order of reactivity of the Group IVB lithium compounds does correspond so well with the basicities of the anions. Details of the mechanism of the reactions are not known. Indeed, it cannot be said whether the mechanism is the same for all the reagents, although that would seem to be a reasonable assumption. It has been suggested (169) that the reaction mechanism of phenyllithium with n-butyl chloride may approach that of the S_N2 type. That conclusion does not seem to be indicated in the present reactions, since one might have expected to see a greater disparity between nucleophilicity and basicity.

Table 10. Competitive reactions for n-butyl chloride

$(C_6H_5)_3MLi$ Reagents		$(C_6H_5)_3MC_4H_{9}$-n Derivatives and yields, %
Si	Ge	Si (42.5), Ge (31)
Si	Sn	Si (67), Sn (3.1)
Si	Sn	Si (36), Sn (1.2)
Ge	Sn	Ge (63), Sn (4.5)
Ge	Sn	Ge (55.5), Sn (6.2)
Sn	Pb	Sn (45), Pb (2)

Factors determining nucleophilic reactivities have been discussed recently (170), and it was noted that for displacements on primary alkyl chlorides, polarizability of the nucleophile is normally more important than basicity in determining nucleophilicity. However, one of the important advantages of polarizability appears to be the removal of non-bonding electrons on the nucleophile from the area of interaction between the nucleophile and the substrate, reducing the repulsions which would result when the reactants approach one another (170). Since the reagents in the present study lack such non-bonding electrons, the effect of polarizability may be reduced.

An alternate explanation for the present observations would be that considerable positive charge is built up on the carbon atom under attack in the transition state. This could be caused by initial coordination of lithium with the chlorine of n-butyl chloride, followed subsequently by attack of the anion on carbon.

A quite surprising result was obtained with the methylated silyllithium reagents. One would expect that the replacement of a phenyl group in triphenylsilyllithium with a methyl group would result in a more reactive species due to decreased stabilization of the silyl anion. This seems to be the case when comparing triphenylsilyllithium with methyldiphenylsilyllithium, as indicated by the competitive reaction. However, in the competition between methyldiphenylsilyllithium and dimethylphenylsilyllithium, slightly more product is obtained from the former than from the latter. What causes this departure from expectations is not at present known, but the reaction with n-butyl chloride does not seem to be an isolated case. As will be noted later, the same disparity is apparent in metalation of fluorene and in reaction with tetrahydrofuran. Unfortunately, the reagent, trimethylsilyllithium, is not available (29) to complete the series.

The product mixtures obtained from the reaction of the methylated silyllithium reagents with n-butyl chloride can be analyzed conveniently and rapidly by vapor phase chromatography. For this reason the preparation of reagents of the type, $(XC_6H_4)(CH_3)_2SiLi$, was attempted. It was hoped that the effects of substituents on the benzene ring would throw light upon the factors determining the reactivities of the silyllithium reagents. The study did not prove to be feasible, however, due to the fact that useful reagents could not be prepared. A methoxy group in the para position is apparently attacked by the silyllithium reagent as rapidly as the latter is formed. It had been reported previously (171) that triphenylsilyllithium cleaves anisole to give methyltriphenylsilane, but the reaction is not a facile one. Evidently, however, cleavage is rapid enough to prevent the formation of appreciable concentrations of dimethyl(p-methoxyphenyl)silyllithium. Cleavage of the ether linkage apparently occurred also during the attempted formation of dimethyl(p-phenoxyphenyl)silyllithium. When a phenyl group is placed in the para position a biphenylyl system is formed. Biphenyl itself is reduced by lithium with the formation of a dilithio compound (172). Such a reduction apparently takes place when p-biphenylyldimethylchlorosilane is reacted with lithium in tetrahydrofuran. The green, viscous solution formed is characteristic of the dilithio compound obtained from biphenyl (172), and double titration showed a yield of lithium derivative greater than 100% based on reaction of only the Si-Cl bond.

The only reagent in this series that could be obtained was dimethyl-p-tolylsilyllithium. The yield of this compound was relatively low, however, possibly due to impurity in the starting chlorosilane. The project was not pursued further.

An extension of the study (30) of the metalation of fluorene by Group IVB lithium compounds was made, including a wider variety of silyllithium reagents. It was expected that methyldiphenylsilyllithium and dimethylphenylsilyllithium would be more reactive than triphenylsilyllithium, so that the reactions were run under milder conditions than those previously used (30). It was discovered in the first experiment that the metalation of fluorene by triphenylsilyllithium is a somewhat more facile reaction than had been indicated in the earlier study. Carbonation of the reaction mixture after 4 hours at room temperature gave a 97% yield of fluorene-9-carboxylic acid; whereas, the previously reported 18 hour reaction period had given a 69% yield of acid (30). Even milder conditions were employed for the comparative studies given in Table 11, and triphenylgermyllithium was included with the hope of differentiating its metalating ability from that of triphenylsilyllithium.

The results indicate the following series of decreasing reactivity: $(CH_3)(C_6H_5)_2SiLi \geqq (CH_3)_2(C_6H_5)SiLi > (C_6H_5)_3GeLi > (C_6H_5)_3SiLi \approx (C_6H_5)_3SiSi(C_6H_5)_2Li$. The order of methyldiphenylsilyllithium and dimethylphenylsilyllithium is the same as that observed in the competitive reactions for n-butyl chloride and is not that which would be expected from a consideration of the electronic effects of methyl and phenyl groups. The greater reactivity of triphenylgermyllithium over that of triphenylsilyllithium, seen in the present reactions, is not evident in other comparisons of the reagents. In fact, the opposite order is observed in the competitive reactions and in the rate of cleavage of tetrahydrofuran.

Difficulty was encountered in reproducing the yield of acid from metalations with pentaphenyldisilanyllithium. Definitive results were not expected, since the reagent is prepared (159) by cleavage of decaphenylcyclopentasilane (160) with an excess of triphenylsilyllithium. A 75-79% yield of pentaphenyldisilane was obtained (159) upon hydrolysis of the reaction mixture. In several attempts to repeat the preparation, the best yield of pentaphenyldisilane obtained upon

Table 11. Metalations of fluorene

Metalating agent	Yield of fluorene-9-carboxylic acid, % Run 1	Run 2	Average
$(CH_3)(C_6H_5)_2SiLi$	65.2	57.4	61.3
$(CH_3)_2(C_6H_5)SiLi$	61.6	54.7	58.1
$(C_6H_5)_3GeLi$	46.1	53.2	49.6
$(C_6H_5)_3SiLi$	44.5	37.7	41.1
$(C_6H_5)_3SiSi(C_6H_5)_2Li$[a]	44.6	39.8	42.2

[a] A third run with this reagent gave a yield of 20.3%. This value was not included in the average.

hydrolysis was 63%. It is likely that the solutions used for metalation of fluorene contained more than one silyllithium species. However, the yield of fluorene-9-carboxylic acid was not appreciably different from that obtained with triphenylsilyllithium. One might expect that d-orbitals on the silicon atom adjacent to the anion would participate in stabilization of the anion:

$$(C_6H_5)_3Si - \overset{\ominus}{Si}(C_6H_5)_2 \longleftrightarrow (C_6H_5)_3\overset{\ominus}{Si} = Si(C_6H_5)_2$$

Such an effect, which should decrease the reactivity of the silyllithium reagent, was not evident in the present reactions.

The Group IVB lithium compounds were compared with respect to stability in tetrahydrofuran solution. The reaction of triphenylsilyllithium with tetrahydrofuran has been investigated, and the product, formed in good yield, is 4-(triphenylsilyl)butan-1-ol (173). The stabilities of triphenyl-, methyldiphenyl-, and dimethylphenylsilyllithium in tetrahydrofuran have been measured (174) by analyzing for silyllithium content at various time intervals. The method of analysis employed consisted of decomposition of the silyllithium reagent with _n_-butyl bromide followed by determination of bromide ion by Volhard titration (174). The stabilities of triphenylgermyllithium and triphenyltinlithium have been measured[1] using the method of double titration with allyl bromide (2). These data, along with those obtained for methyldiphenyltinlithium and tri-n-butyltinlithium in the present work, were given a kinetic treatment to determine the rates of reaction with tetrahydrofuran.

In Figures 1 and 2 the logarithm of molarity is plotted against time. It will be noted that the decompositions follow pseudo first order kinetics only through the first part of the reaction. In all cases the rate is accelerated, possibly by a catalytic effect of one of the reaction products, until the deviation from first order kinetics is quite extreme. In Table 12 the first order constants for the reaction are given. The rate constants were determined using the initial linear portions of the curves in Figures 1 and 2.

Among the silyllithium reagents it will be noted that the rate of decomposition of methyldiphenylsilyllithium is greater than that of dimethylphenylsilyllithium, in agreement with the relative reactivities observed in chloride displacement from n-butyl chloride and in metalation of fluorene. Among the tinlithium reagents one observes the expected increase in rate on substituting alkyl groups for aryl groups on the tin atom.

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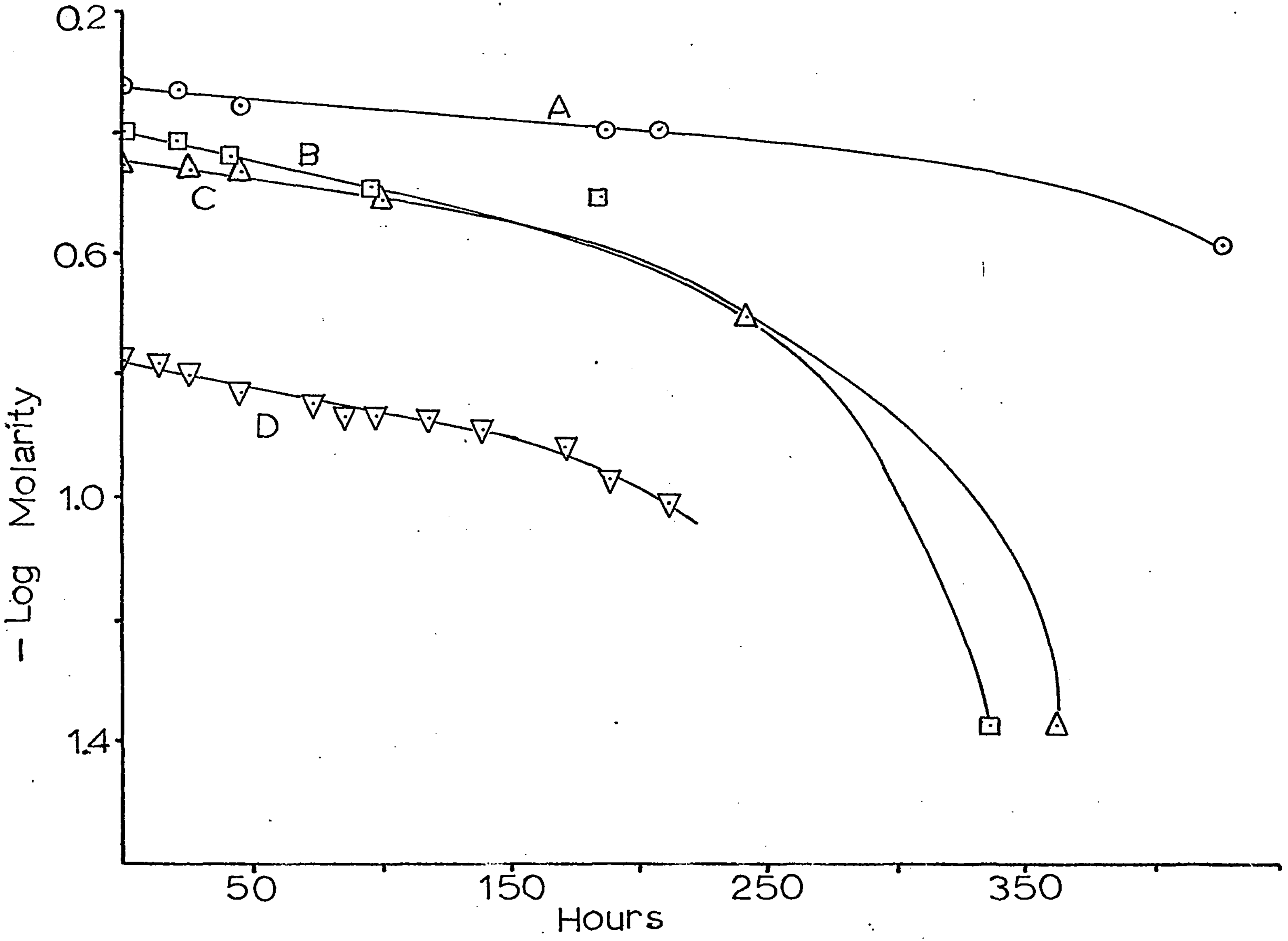
[1] S.-Y. Sim, Iowa State University of Science and Technology, Ames, Iowa. Information on the stabilities of triphenylgermyllithium and triphenyltinlithium in tetrahydrofuran. Private communication. 1963.

Table 12. Reactions of Group IVB lithium compounds with tetrahydrofuran

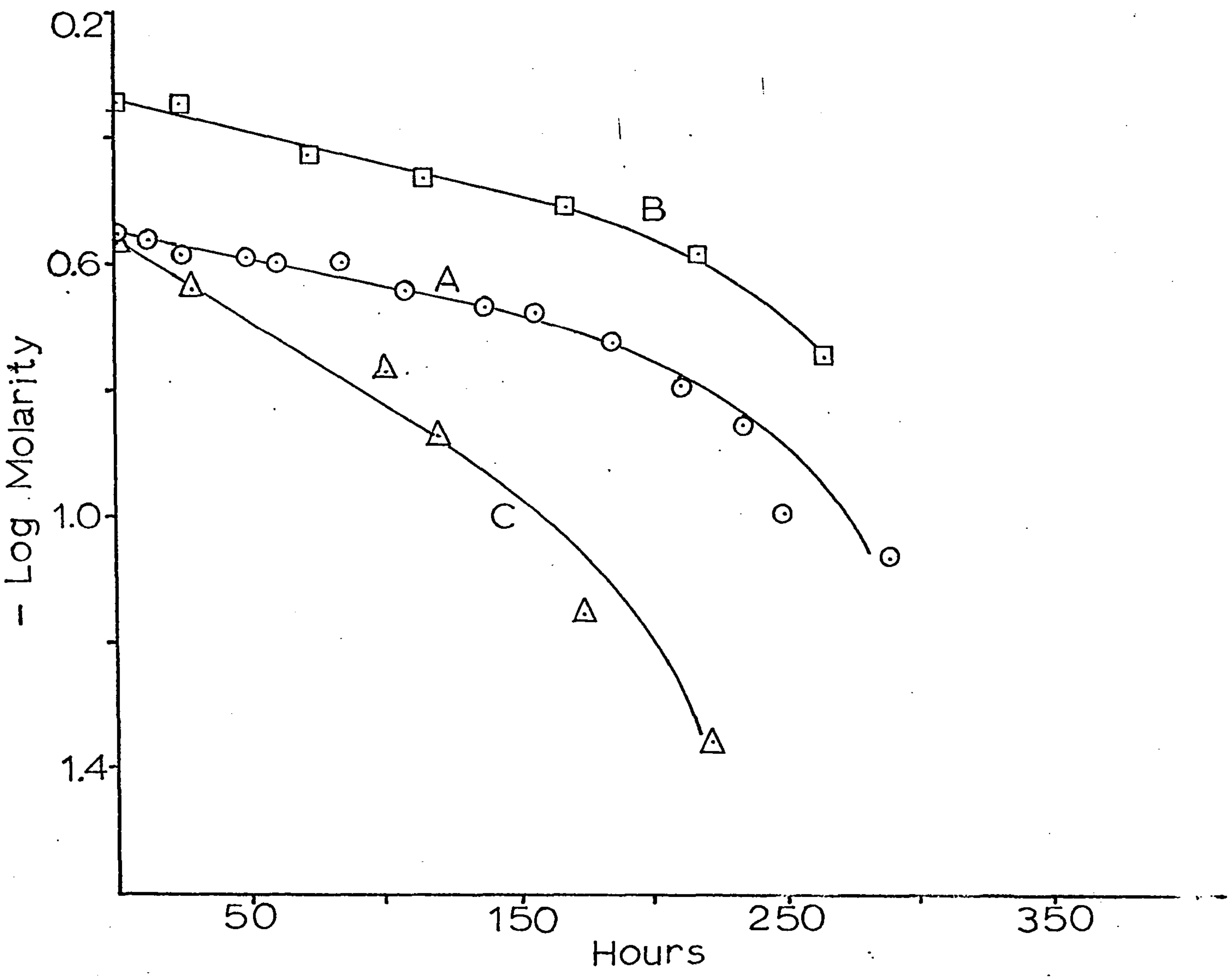
Reagent	$k_1 \times 10^3$ hours^{-1}
$(C_6H_5)_3SiLi$	0.84
$(C_6H_5)_2(CH_3)SiLi$	2.1
$(C_6H_5)(CH_3)_2SiLi$	1.4
$(C_6H_5)_3GeLi$	1.8
$(C_6H_5)_3SnLi$	1.8
$(C_6H_5)_2(CH_3)SnLi$	2.3
$(\underline{n}\text{-}C_4H_9)_3SnLi$	5.9

Figure 1. - Log molarity vs. time for triphenylsilyllithium (A), methyldiphenylsilyllithium (B), dimethylphenylsilyllithium (C), and triphenylgermyllithium (D) at room temperature in tetrahydrofuran



– Log Molarity
0.2
0.6
1.0
1.4
50
150
250
350
Hours
A
B
C
D

Figure 2. - Log molarity vs. time for triphenyltinlithium (A), methyldiphenyltinlithium (B), and tri-_n_-butyltinlithium at room temperature in tetrahydrofuran


- Log Molarity
0.2
0.6
1.0
1.4
Hours
50
150
250
350
A
B
C

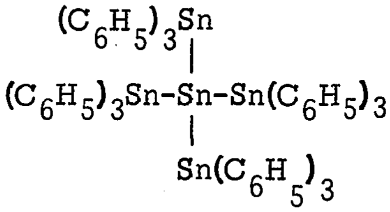
A rather interesting result, however, is that triphenylgermyllithium and triphenyltinlithium react faster than triphenylsilyllithium. Unfortunately, it is not known whether the reactions have the same mechanism, or even whether the cleavage reactions lead to the same type of products. Undoubtedly all of the reagents will be coordinated with the ether linkage in tetrahydrofuran solution. The rate of reaction will be influenced by the extent of coordination and the strength of the coordinate bond. However, the manner in which these factors exert their influence is not as yet clear.

Branched Chain Polytin Compounds

In 1923 Böeseken (54) reported that a minor product from the reaction of phenylmagnesium bromide with stannous chloride (6:1 molar ratio) was a compound with the empirical formula, $(C_6H_5)_{12}Sn_5$. He could not distinguish among the three possible structures (I), (II), and (III) for this derivative, but he thought the tetrakis configuration (II) was the

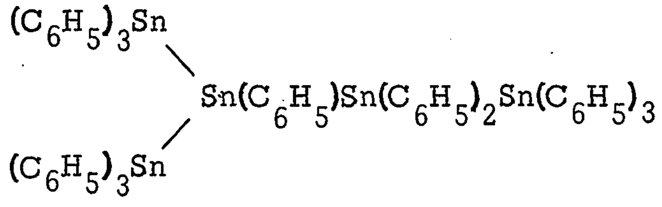
$(C_6H_5)_3Sn\left[(C_6H_5)_2Sn\right]_3Sn(C_6H_5)_3$

I



$$(C_6H_5)_3Sn-\overset{\overset{\displaystyle (C_6H_5)_3Sn}{|}}{\underset{\underset{\displaystyle Sn(C_6H_5)_3}{|}}{Sn}}-Sn(C_6H_5)_3$$

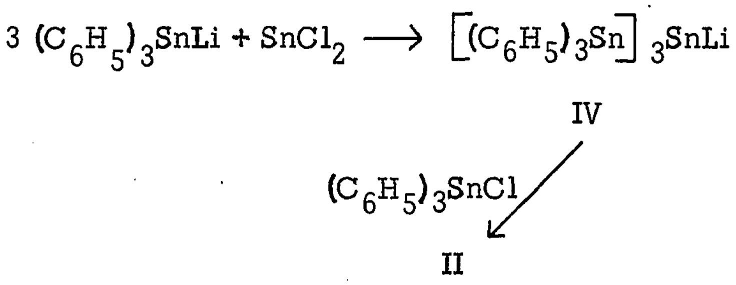
II



III

most likely structure. He reasoned that the latter structure should be the most stable of the three isomers, and, indeed, the compound which he isolated was one of the most thermally stable organotin compounds known, decomposing at 280°. One might also argue that the reaction conditions under which the compound was formed afford evidence for the tetrakis structure. If the pentatin had the straight chain structure (I), one might expect to find tritin or tetratin homologs in the reaction mixture. In contrast, the tetrakis structure is unique and could easily be formed in the absence of lower or higher homologs. In fact, the only two additional products obtained from the reaction were hexaphenylditin and tetraphenyltin.

Böeseken's compound is the only one in the literature which is assumed to contain a branched polytin chain. In view of the modification of properties which chain branching would be expected to cause in polytin compounds, an investigation of possible methods for preparing branched chain polytin compounds was undertaken. As an alternate synthetic method for tetrakis(triphenylstannyl)tin, the scheme below was carried out. It has been previously reported (175)



$$\begin{tikzcd} 3\,(C_6H_5)_3SnLi + SnCl_2 \arrow[r] & \underset{IV}{\left[(C_6H_5)_3Sn\right]_3SnLi} \arrow[dl, "(C_6H_5)_3SnCl"'] \\ \text{II} & \end{tikzcd}$$

that the reaction of triphenylgermyllithium with germanium diiodide in a 3:1 molar ratio affords tris(triphenylgermyl)germane subsequent to hydrolysis. Presumably the intermediate in the reaction is tris(triphenylgermyl)germyllithium. By analogy, the reaction of triphenyltinlithium with stannous chloride would be expected to produce tris(triphenylstannyl)tinlithium, which could be treated with triphenyltin chloride to form tetrakis(triphenylstannyl)tin. When the reaction was run, there was obtained in 70% yield a compound which began to turn brown at approximately 280° and melted with tin deposition at 315-330°. A tin analysis and molecular weight determination (vapor pressure osmometer) indicated that the empirical formula was $(C_6H_5)_{12}Sn_5$. The infrared spectrum of the compound (in carbon disulfide) was indistinguishable from that of hexaphenylditin, showing only absorptions associated with the phenyl moiety. The ultraviolet spectrum ($\lambda_{max}^{cyclohexane}$ 275.5, 247 mμ) was distinctly different from that of hexaphenylditin, which shows only a single maximum at 247.5 mμ (120a). The product could be recrystallized from benzene, chloroform, or a carbon disulfide-acetone mixture without changing the melting point range. The solubility properties are in agreement with those for Böeseken's compound. It seemed likely that the two were the same; thus, Böeseken's preparation was repeated, and a compound melting at 315-330° decomp. was obtained in 2% yield (based on stannous chloride). The two compounds were shown to be identical by the superimposition of x-ray powder patterns.

The compound was prepared by three additional procedures, each of which started with a $(C_6H_5)_3Sn$-containing compound. The x-ray

$$4\ (C_6H_5)_3SnLi + SnCl_4 \longrightarrow \text{II (9.7\%)} + (C_6H_5)_6Sn_2$$

$$4\ (C_6H_5)_3SnCl + 8\ Li + SnCl_4 \rightarrow \text{II (20.6\%)} + (C_6H_5)_6Sn_2$$

$$2\ SnCl_2 \xrightarrow[\text{2) 2 } (C_6H_5)_3SnCl]{\text{1) 3 } [(C_6H_5)_3Sn]_2Mg} \text{II (3.1\%)} + (C_6H_5)_6Sn_2$$

powder patterns of the compounds from the several syntheses were identical, and all showed the same ultraviolet spectrum. When phenyllithium was substituted for phenylmagnesium bromide in the reaction with stannous chloride, tetraphenyltin was the only product isolated.

Quite recently another study of compounds of the type, $(C_6H_5)_3M_4M$, has been reported (176). Derivatives were prepared in which M corresponded to Pb and Sn, the latter product being obtained from triphenyltinlithium and stannic chloride as well as by Böeseken's method. A detailed structural examination of the tin compound has not, however, been reported. A related tetrakis compound, tris(triphenylgermyl)triphenylstannylsilane, was prepared some time ago (177) but was not investigated in any detail structurally or chemically.

The methods of preparation offer strong evidence that the compound has the tetrakis configuration (II) and not the isomeric structures (I) or (III). Further, crystals from carbon disulfide-acetone were suitable for an x-ray single crystal study[1]. This analysis has given the unit cell dimensions. From considerations of the pseudosymmetry observed and the packing of the molecules in the unit cell, it is concluded that the tetrakis structure (II) is the most probable one[1].

Chemical evidence for the structure has likewise been obtained. The most significant result was afforded by reaction of the compound with four moles of iodine. Triphenyltin iodide was obtained in 82.4% yield along with a product which was thought to be stannic iodide. There was no evidence for the formation of diphenyltin diiodide or phenyltin triiodide. Likewise, reaction with an excess of refluxing 1,2-dibromoethane afforded 63.7% of triphenyltin bromide (based on unrecovered tetrakis compound) and no evidence for other tin bromides. Refluxing sym-tetrachloroethane reacted with tetrakis(triphenylstannyl)tin to give a 55% yield of triphenyltin chloride along with a small amount of tetraphenyltin and an unidentified,

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[1] A. W. Schleuter, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Information on an x-ray single crystal study of tetrakis(triphenylstannyl)tin. Private communication. 1964.

probably polymeric, material.

The tetrakis compound is also susceptible to nucleophilic cleavage, and with triphenyltinlithium attack can occur at the lateral position. When the reaction was run in a 4:1 molar ratio, 44% of tetrakis(triphenylstannyl)tin was recovered unchanged. The only other product isolated was hexaphenylditin. The latter product can arise from hydrolysis of triphenyltinlithium as well as from reaction with the tetrakis compound. The yield of hexaphenylditin based upon unrecovered starting material and the total amount of triphenyltinlithium employed was 74%. It should be noted that in the present reaction attack at the central tin atom should lead to no net reaction, so that all that can be seen is attack at the lateral position.

The reactions above offer reasonably good evidence that the structural assignment is correct. Attention was next centered upon the possibility of cleaving only one tin-tin bond in the tetrakis compound with the hope of obtaining a functionally substituted tris(triphenylstannyl)tin compound. Attempts to accomplish this limited cleavage have as yet been unsuccessful.

Reaction of tetrakis(triphenylstannyl)tin with one mole of iodine afforded an 81.9% yield of triphenyltin iodide; however, the only other product isolated was unreacted tetrakis compound in a 57% yield.

When tetrakis(triphenylstannyl)tin was treated with one mole of sym-tetrachloroethane in refluxing xylene, no reaction was observed, and the tetrakis compound was recovered in 94.2% yield. In like manner the nucleophilic reagent, methyllithium, gave only tetraphenyltin in addition to recovered starting material.

The conclusion which is drawn from these reactions is that the primary cleavage products formed are more reactive than the tetrakis compound itself. This is perhaps not surprising when one considers the steric hindrance to attack that must be present in the tetrakis structure. One might look upon the molecule as containing a sphere of phenyl groups surrounding the vulnerable tin-tin bonds. Investigations of the chemistry of the related compound, tetrakis(trimethylsilyl)silane (178) have indicated that the same effect is probably operating in that compound also[1].

An alternate method for forming derivatives of the tris(triphenylstannyl)tin structure was apparently available through reactions of tris(triphenylstannyl)tinlithium (IV), the intermediate presumed to be present in the preparation of tetrakis(triphenylstannyl)tin starting from triphenyltinlithium and stannous chloride. The tinlithium intermediate need not necessarily be present in the preparation to account for the

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[1] C. L. Smith, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Information on the chemistry of tetrakis(trimethylsilyl)silane. Private communication. 1964.

formation of the tetrakis compound, since the product could arise from a disproportionation reaction. Indeed, perhaps the most important method for the formation of hexaorganodilead compounds is the reaction of lead dihalides with organometallic compounds (179).

In order to test for the presence of tris(triphenylstannyl)tinlithium, chlorotriphenylgermane was substituted for triphenyltin chloride in the last step of the reaction. A product was obtained with a melting

$$3(C_6H_5)_3SnLi + SnCl_2 \longrightarrow \mathrm{IV} \xrightarrow{(C_6H_5)_3GeCl}$$

$$\left[(C_6H_5)_3Sn\right]_3SnGe(C_6H_5)_3$$

V

point and solubility properties quite similar to those of tetrakis(triphenylstannyl)tin. However, the infrared spectrum of the material showed the presence of germanium-phenyl absorptions, and the x-ray powder pattern was distinctly different from that of tetrakis(triphenylstannyl)tin. A molecular weight determination was quite satisfactory for the structure, tris(triphenylstannyl)triphenylgermyltin, but a combined analysis for germanium and tin was low. It might be mentioned that it is difficult to determine the purity of the samples of materials that melt with decomposition over a range of temperature, so that impurities may be the cause of the poor analysis in the case of the latter compound. It is believed that the product is the germanium derivative (V).

Reactions of the tinlithium intermediate (IV) with trimethyl phosphate or methyl iodide gave in low yield a product which is probably methyltris(triphenylstannyl)tin. However, the compound appeared to be relatively unstable in solution and could not be sufficiently purified to obtain an identification.

In contrast to the cases above, reaction of the supposed tris(triphenylstannyl)tinlithium with chlorotriphenylsilane or tri-_n_-butyltin chloride afforded only tetrakis(triphenylstannyl)tin. In like manner, hydrolysis with saturated aqueous ammonium chloride gave the tetrakis compound, but in lower yield than was obtained after derivatization with triphenyltin chloride. The desired product from the latter reaction was tris(triphenylstannyl)tin hydride. The related compounds, tris(triphenylsilyl)silane (180), tris(triphenylgermyl)silane (1a), and tris(triphenylgermyl)germane (175) are known and are quite stable, but the more polar Sn-H bond may cause the tin hydride to be unstable.

It is believed that tris(triphenylstannyl)tinlithium is formed on reaction of triphenyltinlithium with stannous chloride, but there are limits to the synthetic possibilities of the reagent, at least under the conditions employed in the present studies.

In connection with the investigations above, some reactions were carried out with hexaphenylditin before applying them to the tetrakis compound. The ditin was found to be inert to a refluxing solution of 1% potassium hydroxide in 95% aqueous ethanol. The insolubility of the compound is probably important in determining its reactivity in the aqueous ethanolic medium. Hexaphenylditin did react with hot moist piperidine, affording a 28% yield of bis(triphenyltin)oxide along with some recovered starting material. The compound was also cleaved by refluxing sym-tetrachloroethane to give a 42% yield of triphenyltin chloride.

Suggestions for Further Research

As the present investigations have demonstrated, there are definite limitations to the structural modifications that can be made in the organic Group IVB lithium reagents. However, the modifications that can be made have not been fully exploited. In particular, alkyldiphenyl- and dialkylphenylgermyllithium reagents should be readily preparable and stable. A study of the relative reactivities of these germyllithium compounds would be of interest in view of the apparently anomalous reactivities of the alkylated silyllithium compounds. Extensions of the present studies with tinlithium reagents should be made. The availability of trialkyltinlithium compounds makes possible a study of the reactivities of the entire series of reagents from fully arylated to fully alkylated. This study has only been begun in the present work.

In view of the results obtained in the measurements of stabilities of Group IVB lithium compounds in tetrahydrofuran, it would be valuable to determine the specific mode of decomposition of each reagent. As has been indicated earlier, it is not known whether germyl- and tinlithium reagents give the same type of cleavage product that silyllithium compounds do. Determination of the mode of decomposition and the allied question of the actual character of the reagents in solution would give insight into the influence of solvents on the reactivities of the reagents.

The present investigations have opened the area of branched chain polytin compounds. The effects of chain length and chain branching on the chemical and physical properties of polytin compounds are at present inadequately known. The preparation of a series of compounds of the general formula, Sn_nR_{2n+2}, and an investigation of their properties would afford much valuable information. Only in the permethylated series is a substantial number of compounds known, and often even the physical constants of the compounds are not available in the literature.

The preparation of polytin compounds with reactive functional groups attached to tin would be particularly useful for synthetic purposes and for the determination of reactivities. Some preparative methods are now available for this purpose. One possibility which has not been well exploited is the cleavage of cyclic polytin compounds to produce α, ω -difunctional polystannanes.

The tetrakis compounds, $(R_3Sn)_4Sn$, have not as yet shown themselves to be amenable to chemical transformations leading to other branched chain derivatives. The cleavage of one tin-tin bond in these compounds would lead to derivatives of the type, $(R_3Sn)_3SnX$, ideal species with which to determine the effects of chain branching on the reactivities of functional polytin compounds. Efforts should be made to prepare tetrakis compounds with organic substituents other than the phenyl group with the aim of further investigating the possibility of cleaving one tin-tin bond in the derivatives.

SUMMARY

A convenient and accurate method for the analysis of organolithium compounds has been developed. The method is a modification of the standard double titration procedure (8), using organic halides other than benzyl chloride. The halide of most general applicability is 1,2-dibromoethane, which gives reliable analyses for solutions of both alkyl- and aryllithium compounds in diethyl ether or alkyllithium reagents in hydrocarbons. Allyl bromide also gives good results when used in titrations of alkyllithium compounds, other than methyllithium, in the two solvents. The accuracy obtained in titrations with the above reagents is confirmed by the results of alternate methods of analysis which are less convenient to carry out than the relatively simple double titration. A more expensive reagent, 1,1,2-tribromoethane, may give slightly greater accuracy than the dibromoethane in titrations of fresh preparations of methyl- and phenyllithium, but general use of the tribromoethane is not recommended due to its greater tendency to react with lithium alkoxides.

Relative reactivities of organic Group IVB lithium compounds have been measured in three types of reactions. Competitive reactions were carried out in which two of the lithium reagents and _n_-butyl chloride were combined in a 1:1:1 molar ratio. Determination of the composition of the product mixtures showed the following order

of decreasing reactivity: $(CH_3)(C_6H_5)_2SiLi \approx (CH_3)_2(C_6H_5)SiLi >$ $(C_6H_5)_3SiLi > (C_6H_5)_3GeLi \gg (C_6H_5)_3SnLi \gg (C_6H_5)_3PbLi$. The observed order indicates that the basicity of the anions is the most important factor in determining the nucleophilicity of the reagents.

A study of the relative metalating abilities of the reagents was carried out by allowing the compounds to metalate fluorene under identical reaction conditions. The reaction mixtures were carbonated, and the yields of fluroene-9-carboxylic acid were determined. This series of reactions indicated the following order of decreasing reactivity: $(CH_3)(C_6H_5)_2SiLi \geqq (CH_3)_2(C_6H_5)SiLi > (C_6H_5)_3GeLi >$ $(C_6H_5)_3SiLi \approx (C_6H_5)_3SiSi(C_6H_5)_2Li$. This order is the same as that observed in the competitive reactions with the exception of the positions of triphenylgermyllithium and triphenylsilyllithium. An explanation of the discrepancy is not at present known.

Thirdly, rates of decomposition of the reagents in tetrahydrofuran solution were measured by titration of the reagents at intervals of time. Rate constants for the pseudo first order reactions were determined, and the following order of decreasing rates was observed: $(\underline{n}\text{-}C_4H_9)_3SnLi \gg (CH_3)(C_6H_5)_2SnLi > (CH_3)(C_6H_5)_2SiLi >$ $(C_6H_5)_3SnLi \approx (C_6H_5)_3GeLi > (CH_3)_2(C_6H_5)SiLi \gg (C_6H_5)_3SiLi$. This order indicates that reactivity toward tetrahydrofuran increases on going from silicon to tin, in contrast to the observations above.

However, among the silyllithium reagents, the order is much the same as that observed previously. Unfortunately, the reaction pathways are not known for all the reagents, so that a reasonable explanation for the observed order of reactivity cannot be offered.

Triphenyltinlithium, in contrast to triphenylsilyllithium, was found not to enter into addition reactions with pyridine, azobenzene, benzophenone, or 4,4'-bis(dimethylamino)benzophenone. With benzophenone, a one electron reduction occurs leading to benzophenone ketyl and hexaphenylditin.

The compound, tetrakis(triphenylstannyl)tin, was prepared from the reaction of three equivalents of triphenyltinlithium with stannous chloride, followed by treatement with triphenyltin chloride. The compound was shown to be identical with a product of the reaction of phenylmagnesium bromide with stannous chloride, a reaction previously run by Böeseken in 1923 (54). The product was also obtained from the reaction of triphenyltinlithium with stannic chloride; from triphenyltin chloride, stannic chloride, and lithium; and from bis(triphenyltin)magnesium and stannous chloride followed by triphenyltin chloride. Chemical and physical evidence for the structure of the compound is presented.

LITERATURE CITED

1a. J. G. Milligan and C. A. Kraus, J. Am. Chem. Soc., 72, 5297 (1950).

1b. R. A. Benkeser and R. G. Severson, J. Am. Chem. Soc., 73, 1424 (1951).

1c. H. Gilman and T. C. Wu, J. Am. Chem. Soc., 73, 4031 (1951).

2. H. Gilman, F. K. Cartledge, and S.-Y. Sim, J. Organometal. Chem., 1, 8 (1963).

3. R. D'Hollander and M. Anteunis, Bull. soc. chim. Belges, 72, 77 (1963); C. Blomberg, A. D. Vreugdenhil, and P. Vink, Rec. trav. chim., 83, 662 (1964).

4. S. Hayes. Études physico-chimique sur les phénomènes d'association au sein des solutions organo-magnésiennes. D.Sc. thesis. Paris, France, University of Paris. 1963. Ann. chim. Series 13, 8, 545 (1963).

5. Yu. N. Baryshnikov and A. A. Kvasov, Zh. Anal. Khim., 19, 117 (1964). Original available but not translated; abstracted in Chem. Abstr., 60, 13886 (1964).

6. H. Gilman, P. D. Wilkinson, W. P. Fishel and C. H. Meyers, J. Am. Chem. Soc., 45, 150 (1923).

7. K. Ziegler, F. Crössmann, H. Kleiner and O. Schäfer, Ann. Chem. Liebigs, 473, 31 (1929).

8. H. Gilman and A. H. Haubein, J. Am. Chem. Soc., 66, 1515 (1944).

9. G. Wittig and G. Harborth, Ber. deut. chem. Ges., 77, 315 (1944).

10. A. F. Clifford and R. R. Olsen, Anal. Chem., 32, 544 (1960).

11. P. F. Collins, C. W. Kamienski, D. L. Esmay and R. B. Ellestad, Anal. Chem., 33, 468 (1961).

12. S. J. Cristol and R. S. Bly, Jr., J. Am. Chem. Soc., 83, 4027 (1961).

13. D. E. Applequist and A. H. Peterson, J. Am. Chem. Soc., 83, 862 (1961).

14. D. E. Applequist and D. F. O'Brien, J. Am. Chem. Soc., 85, 743 (1963).

15. D. Bernstein, Z. anal. Chem., 182, 321 (1961).

16. W. L. Everson, Anal. Chem., 36, 854 (1964).

17. C. W. Kamienski and D. L. Esmay, J. Org. Chem., 25, 115 (1960).

18. C. Eaborn. Organosilicon compounds. London, England, Butterworths Scientific Publications, Ltd. 1960.

19. E. Larsson, Kg. Fysiograf. Sällskap. i Lund, Hand., 63, No. 12 (1952).

20. M. G. Voronkov and A. Ya. Yakubovskaya, Zh. Obshch. Khim., 25, 1124 (1955). English translation in J. Gen. Chem. U.S.S.R., 25, 1079 (1955).

21. C. Bondy and K. Reiser. British Patent 573, 906. 1945. Abstracted in Chem. Abstr., 43, 5033 (1949).

22. J. L. Speier, J. Am. Chem. Soc., 74, 1003 (1952).

23. H. Gilman and T. C. Wu, J. Am. Chem. Soc., 73, 4031 (1951).

24. R. A. Benkeser, H. Landesman and D. J. Foster, J. Am. Chem. Soc., 74, 648 (1952).

25. J. Fertig, W. Gerrard and H. Herbst, J. Chem. Soc., 1957, 1488.

26. M. J. Frazer, W. Gerrard and J. A. Strickson, J. Chem. Soc., 1960, 4701.

27. D. L. Bailey and A. N. Pines, Ind. Eng. Chem., 46, 2363 (1954).

28. J. W. Ryan, J. Am. Chem. Soc., 84, 4730 (1962).

29. H. Gilman and H. J. S. Winkler. Organosilylmetallic chemistry. In H. Zeiss, ed. Organometallic chemistry. pp. 270-345. New York, New York, Reinhold Publishing Corporation. 1960.

30. H. Gilman, O. L. Marrs, W. J. Trepka and J. W. Diehl, J. Org. Chem., 27, 1260 (1962).

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

32. J. D'Ans, H. Zimmer, E. Endrulat and K. Lübke, Naturwissenschaften, 39, 450 (1952); H. Zimmer, Angew. Chem., 64, 620 (1952).

33. H. Gilman and S. D. Rosenberg, J. Am. Chem. Soc., 74, 531 (1952).

34. H. Gilman, L. Summers and R. W. Leeper, J. Org. Chem., 17, 630 (1952).

35. H. Gilman and R. D. Gorsich, J. Am. Chem. Soc., 80, 3243 (1958).

36. H. Gilman, O. L. Marrs and S.-Y. Sim, J. Org. Chem., 27, 4232 (1962).

37. C. Tamborski, F. E. Ford, W. L. Lehn, G. J. Moore and E. J. Soloski, J. Org. Chem., 27, 619 (1962).

38. C. Tamborski, F. E. Ford and E. J. Soloski, J. Org. Chem., 28, 181 (1963).

39. H. Gilman and S. D. Rosenberg, J. Org. Chem., 18, 680 (1953).

40. H. Gilman and L. Summers, J. Am. Chem. Soc., 74, 5924 (1952).

41. H. Gilman, D. Aoki and D. Wittenberg, J. Am. Chem. Soc., 81, 1107 (1959).

42. C. W. Gerow. The preparation and cleavage of some organogermanium compounds. Unpublished Ph.D. thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1956.

43. H. Gilman and S. D. Rosenberg, J. Org. Chem., 18, 1554 (1953).

44. H. Gilman, W. J. Trepka and D. Wittenberg, J. Am. Chem. Soc., 84, 383 (1962).

45. G. D. Lichtenwalter. Organosilylmetallic compounds and derivatives. Unpublished Ph.D. thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1958.

46. H. Gilman and G. D. Lichtenwalter, *J. Am. Chem. Soc.*, *80*, 2680 (1958).

47. H. Gilman and C. W. Gerow, *J. Am. Chem. Soc.*, *77*, 5740 (1955).

48. H. Gilman and C. W. Gerow, *J. Am. Chem. Soc.*, *79*, 342 (1957).

49. M. V. George, P. B. Talukdar, C. W. Gerow and H. Gilman, *J. Am. Chem. Soc.*, *82*, 4562 (1960).

50. C. Löwig, *Ann. Chem. Liebigs*, *84*, 308 (1852).

51. W. P. Neumann, *Angew. Chem.*, *75*, 679 (1963).

52. W. P. Neumann and J. Pedain, *Ann. Chem. Liebigs*, *672*, 34 (1964).

53. W. P. Neumann, *Angew. Chem. International Edition*, *2*, 165 (1963).

54. J. Boëseken and J. J. Rutgers, *Rec. trav. chim.*, *42*, 1017 (1923).

55. C. A. Kraus and W. N. Greer, *J. Am. Chem. Soc.*, *47*, 2568 (1925).

56. W. P. Neumann, *Angew. Chem.*, *74*, 122 (1962).

57. G. A. Razuvaev, N. S. Vyazankin and O. A. Shchepetkova, *Tetrahedron*, *18*, 667 (1962).

58. G. A. Razuvaev, O. A. Shchepetkova and N. S. Vyazankin, *Zh. Obshch. Khim.*, *31*, 1401 (1961). English translation in *J. Gen. Chem. U.S.S.R.*, *31*, 1297 (1961).

59. E. Krause and R. Becker, *Ber. deut. chem. Ges.*, *53*, 173 (1920).

60. E. Krause and R. Pohland, *Ber. deut. chem. Ges.*, *57*, 532 (1924).

61. K. K. Law, *J. Chem. Soc.*, *1926*, 3243.

62. E. Krause and K. Weinberg, *Ber. deut. chem. Ges.*, *62*, 2235 (1929).

63. G. Bähr and R. Gelius, Chem. Ber., 91, 825 (1958).

64. G. Grüttner, Ber. deut. chem. Ges., 50, 1808 (1917).

65. K. A. Kozeschkow, A. N. Nesmejanow and W. P. Puserewa, Ber. deut. chem. Ges., 69, 1639 (1936).

66. A. N. Nesmeyanov, K. A. Kocheshkov and V. P. Puzyreva, Zh. Obshch. Khim., 7, 118 (1937). Original available but not translated; abstracted in Chem. Abstr., 31, 4290 (1937).

67. G. Wittig, F. J. Meyer and G. Lange, Ann. Chem. Liebigs, 571, 167 (1951).

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

69. C. A. Kraus and R. H. Bullard, J. Am. Chem. Soc., 48, 2131 (1926).

70. T. Harada, Sci. Papers Inst. Phys. Chem. Research (Tokyo), 35, 290 (1939).

71. C. A. Kraus and A. M. Neal, J. Am. Chem. Soc., 51, 2403 (1929).

72. T. Harada, Bull. Chem. Soc. Japan, 15, 481 (1940).

73. S. M. Zhivukhin, E. D. Dudikova and A. M. Kotov, Zh. Obshch. Khim., 33, 3274 (1963). Original available but not translated; abstracted in Chem. Abstr., 60, 4169 (1964).

74. A. Cahours, Ann. Chem. Liebigs, 114, 227 (1860).

75. M. M. Nad and K. A. Kocheshkov, Zh. Obshch. Khim., 8, 42 (1938). Original available but not translated; abstracted in Chem. Abstr., 32, 5387 (1938).

76. T. Harada, Bull. Chem. Soc. Japan, 4, 266 (1929).

77. F. Glockling and D. Kingston, Chem. Ind. (London), 1961, 1037.

78. C. Tamborski, F. E. Ford and E. J. Soloski, J. Org. Chem., 28, 237 (1963).

79. C. A. Kraus and A. M. Neal, *J. Am. Chem. Soc.*, *52*, 4426 (1930).

80. C. A. Kraus and H. Eatough, *J. Am. Chem. Soc.*, *55*, 5014 (1933).

81. N. N. Zemlyanskii, E. M. Panov and K. A. Kocheshkov, *Dokl. Akad. Nauk S.S.S.R.*, *146*, 1335 (1962). English translation in *Proc. Acad. Sci. U.S.S.R.*, *146*, 924 (1962).

82. W. V. Farrar and H. A. Skinner, *J. Organometal. Chem.*, *1*, 434 (1964).

83. L. Riccoboni, *Atti ist. Veneto sci.*, *96*, II, 183 (1937). Original available but not translated; abstracted in *Chem. Abstr.*, *33*, 7207 (1939).

84. G. Costa, *Gazz. chim. ital.*, *80*, 42 (1950). Original available but not translated; abstracted in *Chem. Abstr.*, *44*, 9826 (1950).

85. N. S. Vyazankin, G. A. Razuvaev and S. P. Korneva, *Zh. Obshch. Khim.*, *33*, 1041 (1963). English translation in *J. Gen. Chem. U.S.S.R.*, *33*, 1029 (1963).

86. S. F. A. Kettle, *J. Chem. Soc.*, *1959*, 2936.

87. H. C. Clark, S. G. Furnival and J. T. Kwon, *Can. J. Chem.*, *41*, 2889 (1963).

88. G. J. M. van der Kerk, J. G. Noltes and J. G. A. Luijten, *J. Appl. Chem. (London)*, *7*, 356 (1957).

89. J. G. Noltes and G. J. M. van der Kerk, *Chem. Ind. (London)*, *1959*, 294.

90. E. J. Kupchik and R. E. Connolly, *J. Org. Chem.*, *26*, 4747 (1961).

91. A. Stern and E. I. Becker, *J. Org. Chem.*, *27*, 4052 (1962).

92. G. J. M. van der Kerk, J. G. Noltes and J. G. A. Luijten, *Rec. trav. chim.*, *81*, 853 (1962).

93. W. P. Neumann and K. König, Angew. Chem., 74, 215 (1962).

94. H. G. Kuivila and O. F. Beumel, Jr., J. Am. Chem. Soc., 83, 1246 (1961).

95. D. H. Lorenz and E. I. Becker, J. Org. Chem., 28, 1707 (1963).

96. A. K. Sawyer and H. G. Kuivila, J. Am. Chem. Soc., 82, 5958 (1960).

97. A. K. Sawyer and H. G. Kuivila, J. Org. Chem., 27, 610 (1962).

98. A. K. Sawyer and H. G. Kuivila, J. Org. Chem., 27, 837 (1962).

99. A. K. Sawyer and H. G. Kuivila, J. Am. Chem. Soc., 85, 1010 (1963).

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

101. H. J. Homer and O. Cummins. U. S. Patent 2,916,400. 1959. Abstracted in Chem. Abstr., 54, 5420 (1960).

102. G. A. Razuvaev, N. S. Vyazankin, Yu. I. Dergunov and O. S. D'yachkovskaya, Dokl. Akad. Nauk S.S.S.R., 132, 364 (1960). English translation in Proc. Acad. Sci. U.S.S.R., 132, 521 (1960).

103. G. A. Razuvaev, N. S. Vyazankin, Yu. I. Dergunov and N. N. Vyshinskii, Zh. Obshch. Khim., 31, 1712 (1961). English translation in J. Gen. Chem. U.S.S.R., 31, 1598 (1961).

104. L. Rügheimer, Ann. Chem. Liebigs, 364, 51 (1909).

105. H. Morris and P. W. Selwood, J. Am. Chem. Soc., 63, 2509 (1941).

106. I. B. Rabinovich, V. I. Tel'noi, P. N. Nikolaev and G. A. Razuvaev, Dokl. Akad. Nauk S.S.S.R., 138, 852 (1961). English translation in Proc. Acad. Sci. U.S.S.R., 138, 545 (1961).

107. R. Sayre, J. Chem. Eng. Data, 6, 560 (1961).

108. R. West and E. G. Rochow, J. Am. Chem. Soc., 74, 2490 (1952).

109. A. I. Vogel, W. T. Cresswell and J. Leicester, J. Phys. Chem., 58, 174 (1954).

110. M. P. Brown, E. Cartmell and G. W. A. Fowles, J. Chem. Soc., 1960, 506.

111. M. C. Henry and J. G. Noltes, J. Am. Chem. Soc., 82, 555 (1960).

112. R. C. Poller, J. Inorg. Nucl. Chem., 24, 593 (1962).

113. Yu. A. Aleksandrov and N. N. Vyshinskii, Tr. po Khim. i Khim. Tekhnol., 4, 656 (1962). Original not available; abstracted in Chem. Abstr., 58, 3453 (1963).

114. N. N. Vyshinskii and N. K. Rudnevskii, Optika i Spektroskopiya, 10, 797 (1961). English translation in Optics and Spectroscopy, 10, 421 (1961).

115. L. A. Harrah, M. T. Ryan and C. Tamborski, Spectrochim. Acta, 18, 21 (1962).

116. M. P. Brown and D. E. Webster, J. Phys. Chem., 64, 698 (1960).

117. T. L. Brown and G. L. Morgan, Inorg. Chem., 2, 736 (1963).

118. H. C. Clark, J. T. Kwon, L. W. Reeves and E. J. Wells, Inorg. Chem., 3, 907 (1964).

119. H. C. Clark, J. T. Kwon, L. W. Reeves and E. J. Wells, Can. J. Chem., 42, 941 (1964).

120a. D. N. Hague and R. H. Prince, Proc. Chem. Soc., 1962, 300.

120b. H. Gilman, W. H. Atwell and G. L. Schwebke, Chem. Ind. (London), 1964, 1063.

121. Yu. A. Aleksandrov, B. A. Radbil and V. A. Shushunov, Tr. po Khim. i Khim. Tekhnol., 3, 381 (1960). Original not available; abstracted in Chem. Abstr., 55, 27023 (1961).

122. Yu. A. Aleksandrov, T. G. Brilkina and V. A. Shushunov, Tr. po Khim. i Khim. Tekhnol., 4, 3(1961). Original not available; abstracted in Chem. Abstr., 56, 492 (1962).

123. A. Ladenburg, Ber. deut. chem. Ges., 3, 353 (1870).

124. G. Bähr, Z. anorg. allgem. Chem., 256, 107 (1948).

125. G. A. Razuvaev, N. S. Vyazankin and O. A. Shchepetkova, Zh. Obshch. Khim., 30, 2498 (1960). English translation in J. Gen. Chem. U.S.S.R., 30, 2483 (1960).

126. G. A. Razuvaev, Yu. I. Dergunov and N. S. Vyazankin, Dokl. Akad. Nauk S.S.S.R., 145, 347 (1962). English translation in Proc. Acad. Sci. U.S.S.R., 145, 611 (1962).

127. N. S. Vyazankin, G. A. Razuvaev and O. A. Kruglaya, Izv. Akad. Nauk S.S.S.R., Otd. Khim. Nauk, 1962, 2008. English translation in Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci., 1962, 1919.

128. G. A. Razuvaev and E. I.Fedotova, Zh. Obshch. Khim., 21, 1118 (1951). English translation in J. Gen. Chem. U.S.S.R., 21, 1219 (1951).

129. N. S. Vyazankin and O. A. Shchepetkova, Zh. Obshch. Khim., 30, 3417 (1960). English translation in J. Gen. Chem. U.S.S.R., 30, 3384 (1960).

130. G. A. Razuvaev, N. S. Vyazankin and O. A. Shchepetkova, Zh. Obshch. Khim., 31, 3762 (1961). English translation in J. Gen. Chem. U.S.S.R., 31, 3515 (1961).

131. J. B. Pedley, H. A. Skinner and C. L. Chernik, Trans. Faraday Soc., 53, 1612 (1957).

132. G. Tagliavini and G. Plazzogna, Ric. Sci. Rend. Sec. A2, 1962, 356. Original available but not translated; abstracted in Chem. Abstr., 58, 5042 (1963).

133. G. J. M. van der Kerk and J. G. A. Luijten, J. Appl. Chem. (London), 4, 301 (1954).

134. A. Ladenburg, Ber. deut. chem. Ges., 3, 647 (1870).

135. A. Ladenburg, Ber. deut. chem. Ges., 4, 19 (1871).

136. R. D. Chambers, H. C. Clark and C. J. Willis, Chem. Ind. (London), 1960, 76.

137. H. D. Kaesz, J. R. Phillips and F. G. A. Stone, J. Am. Chem. Soc., 82, 6228 (1960).

138. H. C. Clark and C. J. Willis, J. Am. Chem. Soc., 82, 1888 (1960).

139. G. A. Razuvaev, N. S. Vyazankin, Yu. I. Dergunov and N. M. Pinchuk, Zhur. Vsesoyuz. Khim. Obshchestva im D. I. Mendeleeva, 5, 707 (1960). Original not available; abstracted in Chem. Abstr., 55, 13299 (1961).

140. G. A. Razuvaev, N. S. Vyazankin and Yu. I. Dergunov, Zh. Obshch. Khim., 30, 1310 (1960). English translation in J. Gen. Chem. U.S.S.R., 30, 1339 (1960).

141. G. A. Razuvaev, N. S. Vyazankin, E. N. Gladyshev and I. A. Borodavko, Zh. Obshch. Khim., 32, 2154 (1962). English translation in J. Gen. Chem. U.S.S.R., 32, 2123 (1962).

142. M. A. A. Beg and H. C. Clark, Chem. Ind. (London), 1962, 140.

143. A. B. Burg and J. R. Spielman, J. Am. Chem. Soc., 83, 2667 (1961).

144. G. A. Baum and W. J. Considine, J. Org. Chem., 29, 1267 (1964).

145. C. A. Kraus and A. M. Neal, J. Am. Chem. Soc., 52, 695 (1930).

146. D. Blake, G. E. Coates and J. M. Tate, J. Chem. Soc., 1961, 618.

147a. M. P. Brown and G. W. A. Fowles, J. Chem. Soc., 1958, 2811.

147b. C. Tamborski and E. J. Soloski, J. Am. Chem. Soc., 83, 3734 (1961).

148. V. S. Zavgorodnii and A. A. Petrov, Zh. Obshch. Khim., 33, 2791 (1963). Original available but not translated; abstracted in Chem. Abstr., 59, 15297 (1963).

149. H. Gilman, J. A. Beel, C. G. Brannen, M. H. Bullock, G. E. Dunn, and L. S. Miller, J. Am. Chem. Soc., 71, 1499 (1949).

150. H. Gilman, E. A. Zoellner and W. M. Selby, J. Am. Chem. Soc., 55, 1252 (1933).

151. H. Gilman, E. A. Zoellner and W. M. Selby, J. Am. Chem. Soc., 54, 1957 (1932).

152. H. Gilman and G. D. Lichtenwalter, J. Am. Chem. Soc., 80, 608 (1958).

153. H. Gilman and F. Schulze, J. Am. Chem. Soc., 47, 2002 (1925).

154. H. Gilman, B. Hofferth, H. W. Melvin and G. E. Dunn, J. Am. Chem. Soc., 72, 5767 (1950).

155. D. Seyferth and E. G. Rochow, J. Org. Chem., 20, 250 (1955).

156. D. J. Peterson. Trapping of organometallic and organometalloidal radicals. Unpublished Ph.D. thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1962.

157. H. Gilman and T. C. Wu, J. Am. Chem. Soc., 75, 2935 (1953).

158. B. J. Gaj. Reactions of triphenylsilyllithium with compounds containing group VB elements. Unpublished Ph.D. thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1960.

159. A. W. P. Jarvie and H. Gilman, J. Org. Chem., 26, 1999 (1961).

160. H. Gilman and G. L. Schwebke, J. Am. Chem. Soc., 85, 1016 (1963).

161. D. W. Lewis and G. C. Gainer, J. Am. Chem. Soc., 74, 2931 (1952).

162. V. S. Chugunov, Izv. Akad. Nauk. S.S.S.R., Otd. Khim. Nauk, 1959, 1341. English translation in Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci., 1959, 1294.

163. H. Gilman, M. B. Hughes and C. W. Gerow, J. Org. Chem., 24, 352 (1959).

164. H. Gilman and S. D. Rosenberg, J. Am. Chem. Soc., 75, 2507 (1953).

165. M. Lesbre and R. Buisson, Bull. soc. chim. France, 1957, 1204.

166. K. C. Eberly, J. Org. Chem., 26,1309 (1961).

167. D. Seyferth and H. M. Cohen, J. Organometal. Chem., 1, 15 (1963).

168. H. Gilman and D. Aoki, J. Org. Chem., 24, 426 (1959).

169. S. J. Cristol, J. W. Ragsdale and J. S. Meek, J. Am. Chem. Soc., 73, 810 (1951).

170. J. O. Edwards and R. G. Pearson, J. Am. Chem. Soc., 84, 16 (1962).

171. W. J. Trepka. Aryloxy and related organosilicon chemistry. Unpublished Ph.D. thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1960.

172. A. D. Petrov and T. I. Chernysheva, Dokl. Akad. Nauk S.S.S.R., 89, 73 (1953). Original available, but not translated; abstracted in Chem. Abstr., 48, 3916 (1954). J. J. Eisch and W. C. Kaska, J. Org. Chem., 27, 3745 (1962).

173. D. Wittenberg and H. Gilman, J. Am. Chem. Soc., 80, 2677 (1958).

174. H. Gilman, R. A. Klein and H. J. S. Winkler, J. Org. Chem., 26, 2474 (1961).

175. F. Glockling and K. A. Hooten, J. Chem. Soc., 1963, 1849.

176. L. C. Willemsens. Organolead chemistry. Utrecht, Holland, International Lead Zinc Research Organization. 1964.

177. J. J. Goodman. Some correlations between structure and thermal stability of organosilicon compounds. Unpublished Ph.D. thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1955.

178. H. Gilman and C. L. Smith, *J. Am. Chem. Soc.*, *86*, 1454 (1964).

179. H. Gilman and J. C. Bailie, *J. Am. Chem. Soc.*, *61*, 731 (1939); G. Bähr and G. Zoche, *Chem. Ber.*, *88*, 542 (1955).

130. D. Wittenberg, M. V. George, and H. Gilman, *J. Am. Chem. Soc.*, *81*, 4812 (1959).

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