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Highly symmetrical catenated and polymeric organic compounds of group IVB elements

See Yuen Sim
Iowa State University

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**HIGHLY SYMMETRICAL CATENATED AND
POLYMERIC ORGANIC COMPOUNDS OF GROUP
IVB ELEMENTS.**

**Iowa State University of Science and Technology,
Ph.D., 1966
Chemistry, organic**

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HIGHLY SYMMETRICAL CATENATED AND POLYMERIC
ORGANIC COMPOUNDS OF GROUP IVB ELEMENTS

by

See Yuen Sim

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

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Approved:

Signature was redacted for privacy.

In Charge of Major Work

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Dean of Graduate College

Iowa State University
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Ames, Iowa

1966

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INTRODUCTION

The chemistry of organic compounds of the Group IVB elements is very extensive and has been well studied. Nevertheless, it is still an extremely lively area of organic chemistry. Numerous compounds in this group have been of commercial importance for many years, and the development of other organic compounds of the Group IVB elements for industrial applications is still in progress.

The purpose of this present work is to supplement the organic chemistry of germanium, tin, and lead on lines parallel with that already relatively well studied for silicon. An attempt is made to generalize and to compare the organic chemistry of these four elements.

Triphenylsilyllithium and triphenylgermyllithium are highly versatile intermediates for the synthesis of many unsymmetrical tetraorganosilanes and -germanes as well as triorganosilanes and -germanes containing functional groups. It was of interest to examine the preparation and reactions of triphenyltinlithium and triphenylleadlithium, and to compare the relative reactivities of these Ph_3MLi reagents ($\text{M} = \text{Si}, \text{Ge}, \text{Sn}$ and Pb) with alkyl halides and trialkyl phosphates.

Various methods have been devised for the quantitative estimation of organometallic compounds. However, their suitabilities for the quantitative analysis of organic-substituted Group IVB lithium reagents (R_3MLi) are limited, and a simple and convenient, yet accurate, method for assaying such reagents is much desired. Thus, a double titration procedure has been evaluated.

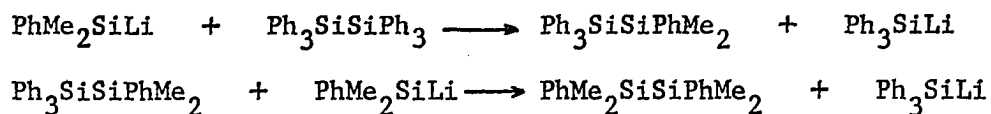
In general, the tendency of the Group IVB elements towards

catenation decreases markedly down the Group. It was of interest to examine some highly symmetrical catenated compounds of mixed atoms, such as Si-Ge, Ge-Sn, etc., in the neopentane structure as it is believed that the symmetry of these compounds would enhance their stability and impart certain special properties.

As a direct consequence of the present intense interest in the chemistry of the pentafluorophenyl derivatives of the Group IVB and other metallic and transition elements, the hitherto uninvestigated and potentially important pentachlorophenyl derivatives of silicon and tin were examined. These compounds can provide an avenue of approach to new polymers by selectively forming a Grignard or lithium reagent with one of the five functional C-Cl groups in the phenyl ring.

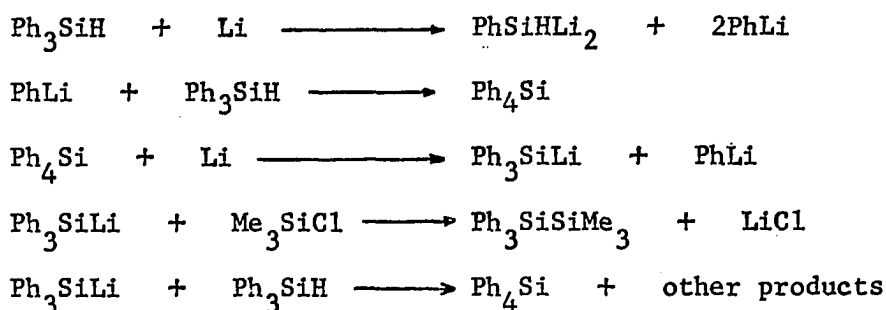
Triphenylsilyllithium was also obtained by the cleavage of hexaphenyldisilane with lithium in ethylene glycol dimethyl ether (5). Unfortunately, this solution was not stable and had to be used immediately after its preparation. When the same solution was refluxed for one hour, it gave a negative Color Test I (6). The ether cleavage product was methyltriphenylsilane (5). In 1958, tetrahydrofuran was introduced as the solvent in place of ethylene glycol dimethyl ether, making possible the preparation of many other organosilyllithium reagents containing aromatic groups with or without aliphatic groups. Triphenylsilyllithium in tetrahydrofuran is stable at room temperature for a long period of time (3), which provides a distinct advantage over the use of ethylene glycol dimethyl ether. In recent years, THF has been used almost exclusively as the solvent for the preparation of many organosilyllithium reagents and provides the foundation for the preparation of many other organo-Group IVB lithium derivatives.

By a process of interconversion between dimethylphenylsilyllithium and hexaphenyldisilane in tetrahydrofuran, triphenylsilyllithium and 1,1,2,2-tetramethyl-1,2-diphenyldisilane were obtained (3).



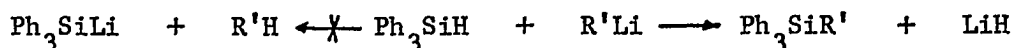
When 1,1,1-triethyl-2,2,2-triphenyldisilane was allowed to react with lithium in tetrahydrofuran, triethylsilane and triphenylsilane, in addition to a small amount of hexaethyldisilane, were isolated after acid hydrolysis. The isolation of these products indicates the formation of

Triphenylsilane has been shown to react with lithium in ether to give triphenylsilanol and hexaphenyldisilane on hydrolysis (8). The reaction is more rapid in THF and yields the corresponding silyllithium (4). The process appears to involve cleavage of phenyl groups from the silicon atom followed by reaction of the phenyllithium groups with the silicon-hydride bond to form tetraphenylsilane which in turn is cleaved by the lithium. On derivatization with trimethylchlorosilane, there was obtained tetraphenylsilane and 1,1,1-trimethyl-2,2,2-triphenyldisilane (4). The following reaction schemes were proposed.



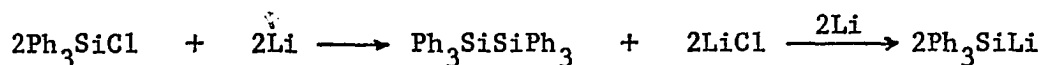
In addition to the tetraphenylsilane, Benkeser and co-workers isolated various other phenylsilanes (9,10,11).

However, when triphenylsilane was treated with an organolithium compound, the result was a displacement of a hydride ion with the formation of a new silicon-carbon bond (12,13,14,15).



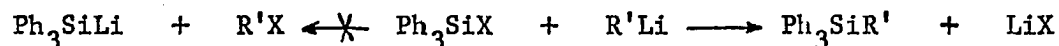
Tris(trimethylsilyl)silane reacts with n-butyllithium in a mixture of ether and THF to give the corresponding silyllithium compound which on derivatization with triphenylchlorosilane gave a 45% yield of tris(trimethylsilyl)(triphenylsilyl)silane (16).

A more recent development in the preparation of triphenylsilyllithium is that involving the direct reaction of triphenylchlorosilane with lithium in THF giving a 89.5% yield. The same product was obtained in 61.7 and 64.1% yield, by the use of 2-methyltetrahydrofuran and tetrahydropyran, respectively, as the solvents (17). Since it was found that the silyllithium reagents couple readily with chlorosilanes even at -70° , and that a 63.4% yield of hexaphenyldisilane was isolated after arresting the reaction before completion, the following mechanism was proposed.



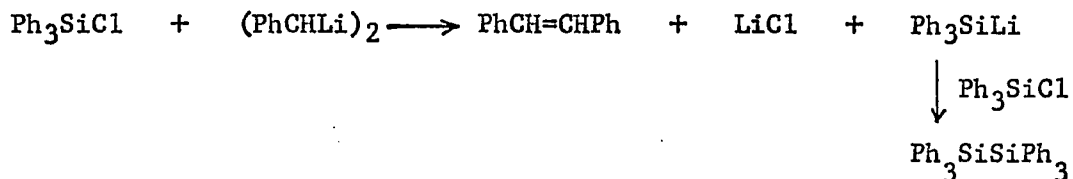
Triphenylsilyl fluoride has been reported as a starting material for the preparation of triphenylsilyllithium (18). The use of triphenylchlorosilane over hexaphenyldisilane may be advantageous in that the disilane is usually prepared from the chlorosilane with alkali metals; however, the yield of triphenylsilyllithium from the chlorosilane is often slightly lower than that from the disilane. Furthermore, the handling of triphenylchlorosilane, though commercially available, requires special precautions owing to its ease of hydrolysis.

Halogen-metal interconversion with a reactive organolithium compound has been employed successfully for the preparation of many compounds containing a carbon-lithium bond. However, triphenylchlorosilane forms exclusively coupling products with reactive organolithium compounds (19).



In one case where halogen-metal interconversion occurs in silicon

chemistry, namely in the reaction between a silyl halide and the stilbene dilithium adduct (20), the Si-Li intermediate couples immediately with the silyl halide to give the disilane as the final product.



The reactions of triphenylsilyllithium, conveniently prepared in high yield by treating lithium wire with either triphenylchlorosilane or hexaphenyldisilane in tetrahydrofuran, have been expanding rapidly both in scope and in significance. Many excellent reviews and papers have been written on this subject (21-26), so further discussion will not be included here.

Triphenylgermyllithium

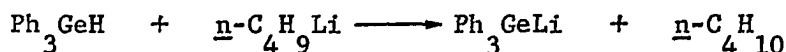
Triphenylgermyllithium was first reported in 1934 by Kraus and Nelson (27). These authors treated (triethylsilyl)triphenylgermane with lithium in an ethylamine solution with the formation of an equimolar mixture of triethylsilyllithium and triphenylgermyllithium, identified by derivatization with ethyl bromide to form tetraethylsilane and ethyltriphenylgermane, respectively. Treatment of these two lithium reagents with ammonium bromide solution yielded triethylsilane and triphenylgermane. The authors did not report the yields of these products.

In 1955, triphenylgermyllithium was prepared in These Laboratories by the cleavage of hexaphenyldigermane with lithium in ethylene glycol dimethyl ether, and identified by treatment with triethylchlorosilane to

give a yield of 39.8% of (triethylsilyl)triphenylgermane (28). Cleavage of hexaphenyldigermene by lithium in ether does not occur unless an "initiator", e.g. tetrahydrofuran, bromobenzene or tetraphenylgermane, is present (29). Cleavage of tetraphenylgermane with lithium in ethylene glycol dimethyl ether to form triphenylgermyllithium has also been reported (30). The yield of products from many reactions of triphenylgermyllithium indicated that the reagent could be obtained in about a 70% yield (30). No product from phenyllithium, which should be present from the cleavage of tetraphenylgermane with lithium, could be isolated from these reactions (30). Presumably the phenyllithium was destroyed by reaction with solvent. When tetrahydrofuran is used as the solvent, triphenylgermyllithium can be prepared in approximately 90% yield by the cleavage of either hexaphenyldigermene or tetraphenylgermane with lithium.

Triphenylgermyllithium was also prepared (17) directly from triphenylchlorogermene and lithium wire in tetrahydrofuran and the reagent was characterized by derivatization with triethylchlorosilane to give the expected (triethylsilyl)triphenylgermane in a yield of 52.5%. Triphenylbromogermene can be used in place of triphenylchlorogermene.

Finally, triphenylgermyllithium can be prepared by the metalation of triphenylgermane with n-butyllithium (31).

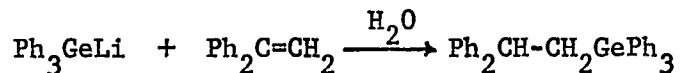


This method has many advantages over the others previously reviewed. Firstly, the reaction proceeds quantitatively and instantaneously; secondly, there are no complicated side reactions; thirdly, the

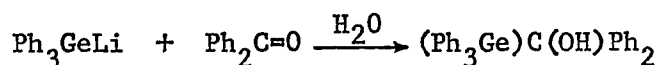
triphenylgermyllithium reagent is soluble in ether; fourthly, the reagent does not react with the solvent; fifthly, there is no need to remove unchanged metal and reactions may be carried out directly in the flask in which the reagent is prepared. However, the only disadvantage in this method is that triphenylgermane is usually prepared by reducing either triphenylbromogermane or hexaphenyldigermane with lithium aluminum hydride in diethyl ether (32).

In general, triphenylgermyllithium undergoes the same reactions as the analogous triphenylsilyllithium. Interaction of triphenylgermyllithium with organo halides or dihalides normally gives rise to the expected coupling products (33). When triphenylgermyllithium was added to triphenyltin chloride, the final reaction mixture was difficult to separate and was believed to be a mixture of $\text{Ph}_3\text{Ge-GePh}_3$, $\text{Ph}_3\text{Sn-SnPh}_3$ and $\text{Ph}_3\text{Ge-SnPh}_3$. The occurrence of these products can be explained by halogen-metal exchange between the two reactants, and subsequent coupling of the various compounds present in the reaction mixture (34,35). The ability of triphenylgermyllithium to metalate fluorene (containing an acidic hydrogen) was studied and compared with that of triphenylsilyl-, triphenylgermyl- and triphenylleadlithium (36). It was found that triphenylgermyllithium was an effective metalating reagent toward fluorene, giving fluorene-9-carboxylic acid in a 69% yield subsequent to carbonation (37), and that the relative metalating ability decreased in the order $\text{Ph}_3\text{Si}^- > \text{Ph}_3\text{Ge}^- > \text{Ph}_3\text{Sn}^- > \text{Ph}_3\text{Pb}^-$ (36).

In some cases, triphenylgermyllithium adds to olefinic double bonds (38).

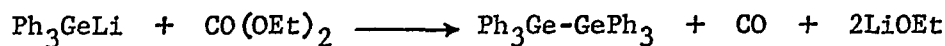
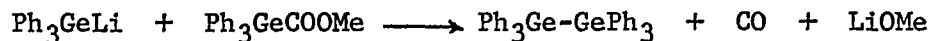


However, it fails to react with cyclohexene or 1-octene. There is no adequate explanation for this observation as yet. Triphenylgermyllithium was found to add to formaldehyde in ethylene glycol dimethyl ether to give triphenylhydroxymethylgermane. It also reacts with benzophenone to give (triphenylgermyl)diphenylcarbinol (30,39).



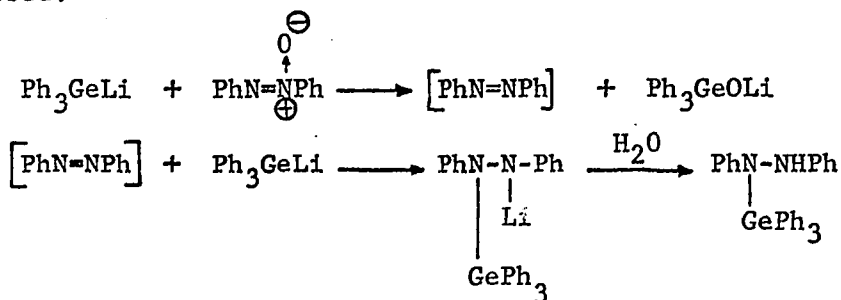
In contrast to this, Ph_3SiK reacts with benzophenone to give a siloxane: $\text{Ph}_3\text{Si}-\text{O}-\text{CHPh}_2$.

In the reaction between Ph_3GeLi and $\text{Ph}_3\text{GeCOOMe}$ or diethyl carbonate, decarbonylation occurs (30):



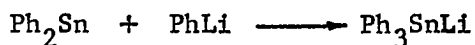
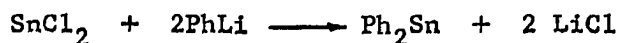
The reaction of Ph_3GeLi with azoxybenzene has also been studied (40).

The following scheme, with the formation of substituted hydrazines, was proposed:



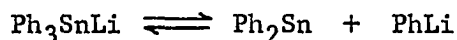
Triphenyltinlithium

Several methods have been reported for the preparation of triphenyltinlithium. Wittig and co-workers in 1951 reported (41) that it could be prepared by treating diphenyltin with one equivalent of phenyllithium in ether-benzene as solvent. The reagent was characterized by reaction with triphenyltin bromide to form hexaphenylditin. The same workers also reported (42) that triphenyltinlithium could be prepared by metalating triphenyltin hydride with methyllithium in diethyl ether, or by the interaction of triphenyltin bromide with lithium in liquid ammonia. No yield of triphenyltinlithium in these preparations was reported. A year later, it was found (43) that triphenyltinlithium could be synthesized in diethyl ether by treating finely ground anhydrous stannous chloride with three equivalents of phenyllithium at -10° thereby eliminating the preparation of diphenyltin. A series of color changes in the reaction mixture was observed as the addition of phenyllithium solution progressed. An orange color was obtained when one equivalent of phenyllithium was added. This developed into a reddish color after the second equivalent of phenyllithium had been added, and the third equivalent turned the color to light tan. The path of the reaction may be postulated as:



The structure of triphenyltinlithium has been a subject of discussion for some time. In order to explain the reaction of triphenyltinlithium with bromine to give diphenyltin dibromide, the existence of

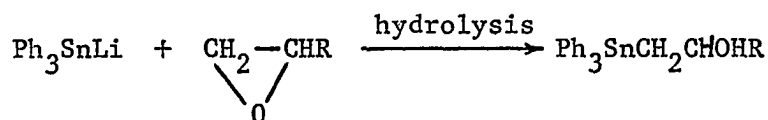
the following equilibrium was proposed (44).



However, evidence for such an equilibrium could not be detected by carbonation (45a) and other experiments (45b). Triphenyltinlithium reacts with fluorene in ether at room temperature for 18.5 hours to give, subsequent to carbonation, a 21.5% of 9-fluorene-carboxylic acid (34). The author (44) suggested that triphenyltinlithium is approximately 20% dissociated, and that it was the phenyllithium which actually metalates the acidic hydrogen of fluorene. However, it was reported later that in many cases triphenyltinlithium does not react with Dry Ice to form triphenyltin-carboxylic acid or benzoic acid. Only hexaphenylditin was isolated subsequent to reaction (45a,45b). These results proved conclusively that triphenyltinlithium does not dissociate in ether, so that triphenyltinlithium, and not phenyllithium, is the reagent responsible for the metalation of fluorene.

When triphenyltinlithium was prepared from stannous chloride and three equivalents of phenyllithium in ether, it reacted with benzyl chloride and ethyl iodide to give large amounts of tetraphenyltin (60% and 27%, respectively) as well as some coupling products, such as benzyltriphenyltin (21.7%) and ethyltriphenyltin (36.4%) (43). Perhaps the more important reactions of triphenyltinlithium are those with alkyl halides to form the corresponding alkyltriphenyltin; however, halogen-metal exchange, resulting in the formation of hexaphenylditin, is a significant side-reaction. Triphenyltinlithium in ether also reacts with

organotin chlorides and organic sulphates (45b, 46, 47, 48). Under similar conditions, it does not react with chlorobenzene, Dry Ice, benzophenone or trans-stilbene. When an ethereal solution of triphenyltinlithium was hydrolyzed, a mixture of tetraphenyltin and hexaphenylditin was obtained (42,47). Tetraphenyltin and hexaphenylditin are also formed when ethyl carbonate or ethyl chloroformate is treated with triphenyltinlithium in ether (49). Triphenyltinlithium also reacts with epoxides, which upon hydrolysis, gives β -hydroxyalkyl derivatives (45b,48).

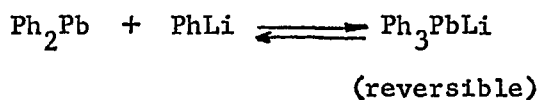
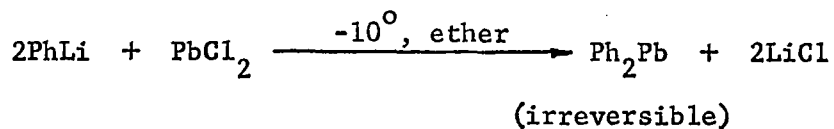


Triphenylleadlithium

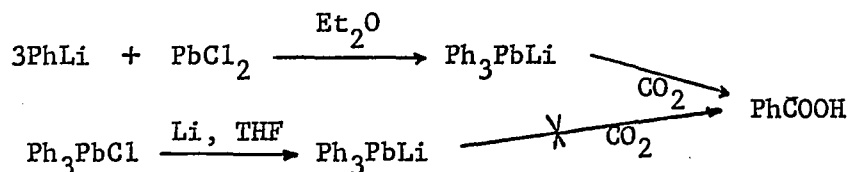
Organolead compounds of the general formula R_3PbM (M=reactive metal) were first reported in 1939 when the preparation of triphenyllead-sodium by the action of sodium in liquid ammonia on hexaphenyldilead or triphenyllead halide was described (50a, 50b, 51). Further investigation showed that lithium, potassium, rubidium, calcium, strontium and barium would react in similar fashion with hexaphenyldilead (52). It was also found that triethylleadlithium could be obtained from triethyllead chloride with lithium in liquid ammonia.

The preparation of triphenylleadlithium from lead chloride and three equivalents of phenyllithium in ether at -10°C was reported from These Laboratories in 1952 (53). The triphenylleadlithium was characterized by reaction with benzyl chloride to give benzyltriphenyllead (69% yield). The mechanism of the reaction was believed to proceed in

two stages:

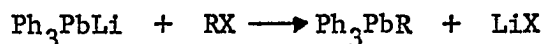


These stages can be distinguished by color phenomena. The authors regarded the triphenylleadlithium preparations as an equilibrium system, containing diphenyllead and phenyllithium. Carbonation experiments which gave benzoic acid, support this belief (53,54). Qualitative observations indicated that the equilibrium at -10° was displaced at least 80% towards triphenylleadlithium. This result is to be contrasted with that of triphenylleadlithium prepared from lithium and triphenyllead chloride in tetrahydrofuran, which, after carbonation, did not yield any detectable amount of benzoic acid (55). This result suggested that for triphenylleadlithium



prepared from triphenyllead chloride and lithium in tetrahydrofuran, the equilibrium system, if it exists at all, is displaced principally toward the triphenylleadlithium.

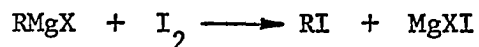
The most important reaction of triphenylleadlithium is its reaction with reactive halides, yielding unsymmetrical tetra-organolead compounds.



The metalating properties of triphenylleadlithium have been studied, but contradicting results were obtained. D'Ans and co-workers (44) found that triphenylleadlithium, prepared from lead dichloride and phenyllithium, could metalate fluorene to the extent of 52%, whereas triphenylleadlithium prepared from triphenyllead chloride and lithium in THF, metalated fluorene to a limit of 0.5% (56). It was suggested that the difference is due to the possibility that the above equilibrium exists only in diethyl ether and that then, the fluorene is metalated by phenyllithium.

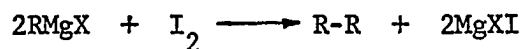
The Analysis of Organic-substituted Group IVB Lithium Reagents

The analysis and stability of organometallic compounds have been of profound interest for many years. Very often, an exact concentration is required for a stability test or a comparison of reactivity. For this reason, there are many published procedures for determining the concentration of solutions of Grignard reagents, organolithium reagents and organic-substituted Group IVB lithium reagents. The method first studied for the quantitative analysis of organomagnesium halides was based on a reaction described by Boudroux (57). This method involves the determination of the amount of iodine consumed according to the equation:



It has been found, however, that this is not the only possible reaction taking place (58,59), and a competing reaction is shown in the following

equation:



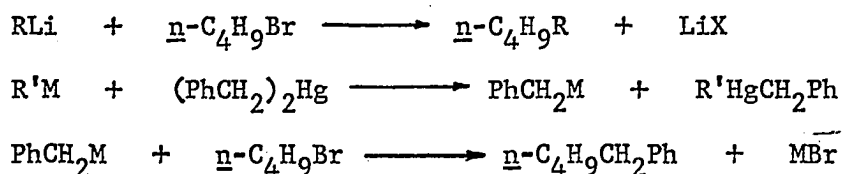
It requires only half the amount of iodine consumed by the previous reaction. Because of the interfering reaction, this method is not generally recommended (58, 59, 60). A second method commonly employed is the hydrolysis of an aliquot of the organometallic compound followed by titration with standard acid of the total base liberated (59,60,61,62, 63). This method is unacceptable for those organometallic compounds which react with the solvent, such as the cleavage of an ether leading to the formation of lithium alkoxide, which would increase the assay of the solution above the true value. A double titration has been devised to analyze quantitatively this class of organometallic compounds (64,65). This involves the determination of total base as described above, but a second aliquot is caused to react with benzyl chloride, consuming all the organometallic compounds. The alkoxides are then determined by a simple acid titration. This method has been studied in detail in These Laboratories and it has been found that benzyl chloride often does not react quantitatively with lithium derivatives of Group IVB elements, e.g. triphenyltinlithium. It tends to give a lower yield than the true value. The purity of the ether had been shown to have a marked effect on the result when the double titration procedure was used to analyze solutions of *n*-butyllithium (66). However, following this report (66), Eberly published his findings and concluded that the Gilman and Haubein double titration procedure (64,65) is the most reliable for the assay of alkyl-lithium reagents (67).

A gasometric method has been proposed for the analysis of organometallic compounds of low molecular weight (58). This method involves the decomposition of the organometallic compound by various compounds containing "active hydrogen", particularly water,



to give a hydrocarbon. This method is limited to Grignard reagents yielding, upon hydrolysis, hydrocarbons that are gases at ordinary temperatures. An objection to this method is based upon the claim that the gas evolved upon hydrolysis of ethylmagnesium bromide always contains a considerable proportion of ethylene (68).

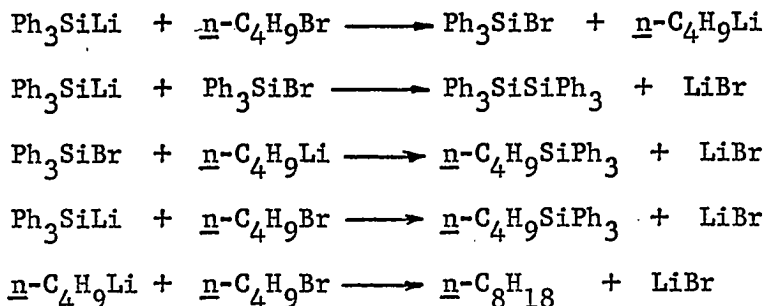
Organoalkali metal compounds have been analyzed by a method involving their reaction with n-butyl bromide followed by determination of the liberated alkali metal bromide according to the Volhard procedure (69). This method is useful only for organometallic compounds of high reactivity (R-Li). A procedure was described for the use of this method for the quantitative analysis of less reactive organometallic compounds (R'-M). In this procedure (69), dibenzylmercury was added dropwise to a mixture of the organometallic reaction and n-butyl bromide. Dibenzylmercury reacts with the less reactive organometallic compound to give a benzylmetallic intermediate which couples readily with the n-butyl bromide present. The alkali metal liberated was titrated with standard acid.



Halogen-metal interconversion reactions do not interfere with the determination, because an excess of n-butyl bromide is present. It was likewise established that alkoxides do not react rapidly enough with n-butyl bromide to liberate an excess of halide which would interfere with the determination.

An oxidative determination of n-butyllithium in hydrocarbon solvents using vanadium pentoxide was reported by Collins and co-workers (70). When a solution of n-butyllithium in n-heptane is treated with vanadium pentoxide, a rapid reaction takes place in which reduced vanadium compounds are formed in amounts equivalent to the n-butyllithium originally present. The reduced vanadium is determined by titration with standard sulfatoceric acid and from this the concentration of n-butyllithium can be accurately determined. The method gives reasonably accurate results, even in the presence of large amounts of alkoxides.

In 1961, a report describing a quantitative estimation of organosilylmetallic compounds in the presence of alkoxides was published from These Laboratories (71). It involves the reaction of the silyllithium compound with n-butyl bromide and subsequent determination of lithium bromide by the Volhard procedure. The Volhard procedure is known to be very accurate for determining bromides quantitatively and the end-point is clearly distinguishable even in the presence of organic compounds. The reaction of triphenylsilyllithium with n-butyl bromide proceeds to completion as shown by a negative Color Test I. There are several possible routes for the reaction:



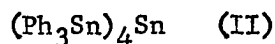
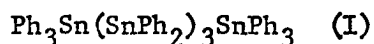
Regardless of the route of the reaction, the total lithium bromide liberated is the same. Two different procedures were reported (71). The less expedient process involves the addition of an aliquot of triphenylsilyllithium solution to an excess of n-butyl bromide. The amount of base is determined with standard sulfuric acid using phenolphthalein as indicator, and the organic layer is extracted with portions of water which are combined and diluted to a known volume in a volumetric flask. Aliquots of this solution are withdrawn and then the bromide content determined by the Volhard procedure. The more expedient procedure involves the same steps as above including the titration with standardized sulfuric acid but the extraction is not carried out, and the total amount of bromide is determined in the presence of the organic layer.

Recently, a variety of alkyl halides, polyhaloalkanes and substituted benzyl halides were examined as possible reagents to replace benzyl chloride in the standard double titration procedure for the analysis of organolithium compounds (72). The authors found that replacement of benzyl chloride with 1,2-dibromoethane or 1,1,2-tribromoethane improves the accuracy of the method while retaining its convenience and rapidity.

Some Tetrakis Organo-Group IVB Compounds

Catenated organic compounds of Group IVB elements have been of great interest lately. In general, the tendency to catenation decreases markedly down the group. Silicon has some tendency to catenation, with many organic linear and cyclic polysilanes having been synthesized. However, the stability of these compounds is very low compared with their carbon analogues. For the heavier elements (Ge, Sn and Pb) of Group IVB, the tendency to catenation and the stability of the resultant bond decrease rapidly. Recently, a considerable number of attempts has been made to synthesize these compounds having a chain of three or more Group IVB elements, particularly the tetrakis compounds with five Group IVB atoms. The spectral and chemical properties, and stability of some of these compounds have been studied. An excellent review on the catenation of organic compounds of Group IVB elements will soon be available (73). Thus, this portion of the review will cover only those tetrakis compounds containing Si, Ge, Sn and Pb.

One of the compounds in this group, tetrakis(triphenylstannyl)tin, was first reported by Böeseken in 1923 (74). He repeated Krause's experiment (75), by refluxing diphenyltin with an excess of phenylmagnesium bromide. He isolated not only hexaphenylditin and metallic tin, but a compound specified as dodecaphenylpentatin. These authors proposed two structures for their pentatin compound:



Structure (II) was preferred because of the stability of this compound. It is a solid which does not melt, but begins to decompose at 280°.

Recently, this compound was investigated in detail in These Laboratories (76), and the tetrakis structure for the pentatin compound was established beyond doubt (77). The conclusion was based on the methods of preparation, the results of its chemical reactions, the quantitative analyses of its carbon, hydrogen and tin content, and the comparison of its X-ray powder diffraction pattern with those of other similar compounds. Four different routes to this tetrakis compound were found:

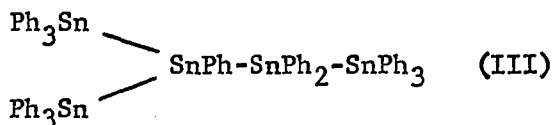
(a) by the treatment of triphenyltinlithium with stannous chloride, followed by triphenyltin chloride.

(b) by the treatment of triphenyltinlithium with stannic chloride.

(c) by the treatment of phenylmagnesium bromide with stannous chloride.

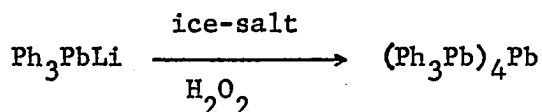
(d) by the reaction of stannic chloride, triphenyltin chloride and lithium.

Method (a) gave a 70% yield of tetrakis(triphenylstannyl)tin. Two of the more interesting chemical properties of this tetrakis compound are its reaction with four equivalents of iodine to give 83% of triphenyltin iodide and its reaction with 1,2-dibromoethane to give 63% of triphenyltin bromide. Only the tetrakis structure with its four triphenylstannyl ligands can give such a high yield. Furthermore, no diphenyltin diiodide was reported.



Both structures (I) and (III) do not have enough triphenylstannyl ligands to give an 63% yield of triphenyltin bromide.

At about the same time that tetrakis(triphenylstannyl)tin was reported (76,77), van der Kerk and co-workers (78a,78b,79) re-investigated the red-colored diphenyllead and di-*p*-tolyllead mentioned by Krause and Reissaus (80) in the reaction between lead dichloride and the appropriate Grignard reagents. It was found that when vacuum-dried triphenyllead lithium was treated with an ice-salt mixture containing a small amount



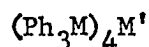
of hydrogen peroxide, a red compound was obtained. The analyses point to the empirical formula $\text{Ph}_{12}\text{Pb}_5$. The pure compound is rather unstable, exposure to air for a few days resulting in substantial decomposition to hexaphenyldilead and lead oxide. The structure of $\text{Ph}_{12}\text{Pb}_5$ was established as tetrakis(triphenylplumbyl)lead by its reaction with iodine. It was found that the amount of iodine consumed was 6 to 8 atoms per mole of the red compound. Furthermore, the iodination product consisted of nearly four moles of triphenyllead iodide per mole of the red compound. These results indicated that the compound had a highly-branched structure. The authors attributed the relatively high stability of this



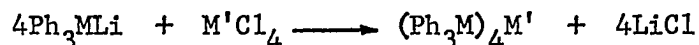
compound to its symmetry, since organic-substituted lead chains of more than two lead atoms were not known. The red compound of Krause's

experiment was said by these authors to contain a mixture of tetrakis-(triphenylplumbyl)lead and hexaphenyldilead.

Subsequently, attempts were made to prepare a series of compounds with the general formula:



in which M and M' are Si, Ge, Sn and Pb in all possible combinations. These known compounds are listed in Table 1. A point of special interest was that they would represent the first compounds with lead-tin and lead-germanium bonds. For the preparation of any of the tetrakis compounds in which the central atom is Si, Ge or Sn, the general procedure is the interaction of four equivalents of Ph_3MLi with $\text{M}'\text{Cl}_4$ in diethyl ether or tetrahydrofuran.



Varying amounts of Ph_6M_2 were always formed as a side-product from halogen-metal exchange. For compounds containing lead as the central atom, the procedure has to be slightly different. Lead(II) chloride is used as the starting material instead of lead tetrachloride; the diorganolead compound initially formed easily disproportionates into the tetraorgano-lead compound and lead.

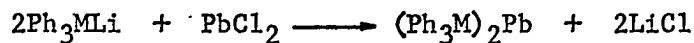


Table 1. Perphenylated tetrakis compounds

| $(\text{Ph}_3\text{M})_4\text{M}'$ | M.p. °C | Reference |
|-------------------------------------|-----------------|-------------|
| $(\text{Ph}_3\text{Si})_4\text{Sn}$ | 390-394° (dec.) | This thesis |
| $(\text{Ph}_3\text{Ge})_4\text{Sn}$ | 407-410° (dec.) | This thesis |
| $(\text{Ph}_3\text{Ge})_4\text{Pb}$ | --- | 78a |
| $(\text{Ph}_3\text{Sn})_4\text{Si}$ | 390-395° (dec.) | This thesis |
| $(\text{Ph}_3\text{Sn})_4\text{Ge}$ | $\pm 324^\circ$ | 78a |
| $(\text{Ph}_3\text{Sn})_4\text{Sn}$ | $\pm 280^\circ$ | 76, 77, 78a |
| $(\text{Ph}_3\text{Sn})_4\text{Pb}$ | $\pm 200^\circ$ | 78a |
| $(\text{Ph}_3\text{Pb})_4\text{C}$ | 292-294° | 78b |
| $(\text{Ph}_3\text{Pb})_4\text{Ge}$ | $\pm 210^\circ$ | 78a |
| $(\text{Ph}_3\text{Pb})_4\text{Sn}$ | $\pm 160^\circ$ | 78a |
| $(\text{Ph}_3\text{Pb})_4\text{Pb}$ | --- | 78a, 79 |

However, $(\text{Ph}_3\text{Pb})_4\text{Pb}$ cannot be prepared from triphenylleadlithium and lead dichloride because of its instability in an ethereal medium, although it can be obtained from the simultaneous hydrolysis and oxidation of ether-free triphenylleadlithium or diphenyllead at low temperature.

The ultraviolet properties of some of these known perphenylated tetrakis compounds, $(\text{Ph}_3\text{M})_4\text{M}'$, have been reported (81), and are given in Table 2.

Table 2. Ultraviolet data of some perphenylated tetrakis compounds

| Compound | Solvent | $\lambda_{\text{max.}}$ $m\mu$ | $\epsilon_{\text{max.}}$ |
|-------------------------------------|------------------------|--------------------------------|--------------------------|
| $(\text{Ph}_3\text{Sn})_4\text{Pb}$ | CHCl_3 | 298 | 59,500 |
| $(\text{Ph}_3\text{Sn})_4\text{Sn}$ | CHCl_3 | 277 | 79,000 |
| $(\text{Ph}_3\text{Sn})_4\text{Ge}$ | CHCl_3 | 276 | 73,000 |
| $(\text{Ph}_3\text{Pb})_4\text{Pb}$ | C_6H_6 | 358 444 | 56,000 29,000 |
| $(\text{Ph}_3\text{Pb})_4\text{Sn}$ | C_6H_6 | 319 | 67,000 |
| $(\text{Ph}_3\text{Pb})_4\text{Ge}$ | CHCl_3 | 328 | 63,000 |

The authors indicated that each of these molecules contained four equivalent metal-metal σ -bonds and that the electrons in these bonds were responsible for the long wavelength absorptions. Two suggestions were made to explain these observations.

- 1) Considering the symmetry of these compounds, it can be shown

that the valence electrons of the metal-metal bonds can give rise to such absorptions.

2) Absorptions may be due to the interaction between the filled 5d-orbital of the central lead atom and the empty orbitals of the surrounding metal atoms. The central lead atom is surrounded by four electro-positive atoms. In this situation, expansion of its orbitals and increase overlap of its 5d-orbital with empty orbitals of the outer metal atoms might occur. Thus, a set of molecular orbitals could be formed. The long wavelength bands could be connected with a transition between these molecular orbitals.

Other tetrakis compounds, $(R_3M)_4M'$, where R is methyl and M and M' may be Si, Ge or Sn, are also known. Some of them will be described in the experimental procedure. Several attempts were made to synthesize compounds where R is ethyl; however, they have not been successful.¹ The known compounds are listed in Table 3.

¹H. Gilman and J. M. Holmes, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Information on the reaction of triethylchlorosilane with lithium and silicon tetrachloride. Private communication. 1965.

Table 3. Compounds of Group IVB elements of the neopentyl type and containing methyl groups

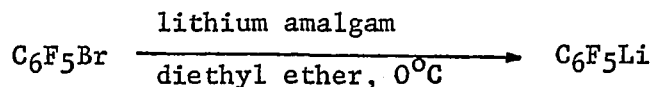
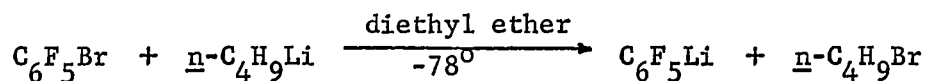
| $(R_3M)_4M'$ | M.p. (b.p.) ^o C | Reference |
|---------------------------|---|------------------|
| $(Me_2HSi)_4C$ | 115 ^o | 82 |
| $(Me_2MeOSi)_4C$ | sublimed | 83 |
| $(Me_2EtOSi)_4C$ | 114-115 ^o | 83 |
| $(Me_3Si)_4C$ | 305-307 ^o | 84, 85 |
| $(Me_2HSi)_4Si$ | 40-42 ^o , (77 ^o /1.4 mm.) | 86 |
| $(Me_2HSi)_3Si(SiEt_3)$ | 125-128 ^o | --- ^a |
| $(Me_2HSi)_3Si(SiMePhH)$ | (115 ^o /0.03 mm.) | --- ^a |
| $(Me_2HSi)_3Si(SiMe_2Ph)$ | (101 ^o /0.01 mm.) | --- ^a |
| $(Me_2HSi)_3Si(SiMePh_2)$ | (173 ^o /0.5 mm.) | --- ^a |
| $(Me_2HSi)_3Si(SiPh_3)$ | 135-137 ^o | --- ^a |
| $(Me_2PhSi)_4Si$ | 133-134 ^o | 16 |
| $(Me_3Si)_4Si$ | 319-321 ^o | 16, 86, 87 |
| $(Me_3Si)_3Si(SiPhMe_2)$ | 190-190.5 ^o | 16 |
| $(Me_3Si)_3Si(SiPh_2Me)$ | 187-187.5 ^o | 16 |
| $(Me_3Si)_3Si(SiPh_3)$ | 287-289 ^o | 16 |
| $(Me_3Si)_4Ge$ | 296-299 ^o | This thesis |
| $(Me_3Si)_4Sn$ | 245-248 ^o | This thesis |

^aH. Gilman and J. M. Holmes, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Information on the reactions of tetrakis(dimethylsilyl)silane. Private communication. 1965.

Perhalogenated Phenyl Derivatives of Group IVB Elements

Pentafluorophenyl derivatives

In 1962, pentafluorophenyllithium was first reported (88). It was prepared from bromopentafluorobenzene by halogen-metal interconversion with *n*-butyllithium and by direct metalation with lithium amalgam. It has been characterized by reactions with water, ethyl formate, *N*-methylformanilide, bromine, chlorine and mercury. The intermediate formation of tetrafluorobenzene has been indicated in reactions with chlorine, bromine and furan.

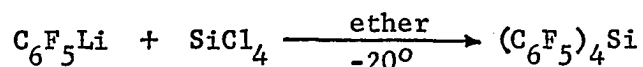


Both the pentafluorophenylmagnesium iodide and bromide have also been reported (89). They can be synthesized by the interaction of magnesium with the corresponding iodide or bromide in dry ether. The use of very pure magnesium is not necessary as is the case for the preparation of the Grignard reagents of the perfluoroalkyl series. Pentafluorophenylmagnesium bromide undergoes several reactions expected for Grignard reagents.

With the advent of the Grignard and the lithium reagents, many new compounds containing the pentafluorophenyl moiety have been reported. Pentafluorophenyl derivatives of Ti, Zr, Mn, Fe and several other transition metals have been studied (90-97). In this part of the review, only

the derivatives of group IVB elements will be discussed.

So far only two pentafluorophenyl derivatives of Si have been reported, namely tetrakis(pentafluorophenyl)silane (96,98) and pentafluorophenyltrimethylsilane (97,98). These compounds were easily prepared in ether at -20° to -65°C by reacting either the Grignard or the lithium reagent with the corresponding chlorosilane. An unsuccessful attempted

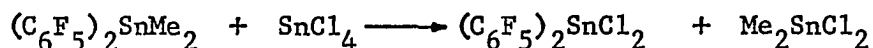


preparation of bis(pentafluorophenyl)dichlorosilane, $(\text{C}_6\text{F}_5)_2\text{SiCl}_2$, by the reaction between pentafluorophenyllithium and silicon tetrachloride in a 2:1 molar ratio has also been reported (96). In this reaction, only the tetrakis compound (35%) and a black tar which was probably a polymer of the desired product were isolated. The author suggested that the first pentafluorophenyl group, upon becoming attached to the silicon atom, activates the remaining chlorine atoms towards coupling with the Grignard or the lithium reagents.

When pentafluorophenyllithium was caused to react with germanium tetrachloride in the molar ratios of 4.5:1 in ether and 3.5:1 in pentane, tetrakis(pentafluorophenyl)germane and tris(pentafluorophenyl)chloro-germane were obtained, respectively (95). However, when the Grignard reagent was used, the reaction, after hydrolysis, gave a white powder for which was proposed the formula $[\text{OGe}(\text{C}_6\text{F}_5)_2]_x$ on the basis of its infrared spectrum and C, H, and F analyses. Recently, the same authors (99) reported that both the Grignard and the lithium reagents have been made to react with GeCl_4 to form the series of compounds $(\text{C}_6\text{F}_5)_n\text{GeX}_{4-n}$.

(X=Br and Cl). Halogen-metal exchange occurs to some extent when the Grignard reagent is used. By variation of the ratio of the reactants and the solvent, the value of n may be changed from 1 to 4. Compounds with the general formula $R \text{Ge}(\text{C}_6\text{F}_5)_{4-n}$, where R = Me, Et, and Ph, have also been reported.

Compounds of tin containing the pentafluorophenyl moiety have recently been reported by three groups of workers (93,98,100). Tatlow et al. briefly reported the reaction between pentafluorophenylmagnesium bromide with stannic chloride to give tetrakis(pentafluorophenyl)tin, tris(pentafluorophenyl)tin chloride and bis(pentafluorophenyl)tin dichloride. The bis(pentafluorophenyl)tin dichloride can also be obtained by an exchange reaction (93,100)



The bis(pentafluorophenyl)dimethyltin can be obtained by the reaction between dimethyltin dichloride and two equivalents of pentafluorophenylmagnesium bromide. A most remarkable property of these compounds was noted by Chambers and Chivers (92). They found that, when pure, these compounds are stable in aqueous ethanol. However, they are rapidly hydrolyzed on addition of catalytic quantities of halide or cyanide ion, to give pentafluorobenzene. The overall average order of cleavage of groups from tin by the electrophiles, hydrogen chloride and boron halides, is $p\text{-tolyl} > \text{Ph} > \text{C}_6\text{F}_5 > \text{Me}$. Cleavage of $p\text{-CH}_3\text{C}_6\text{H}_4\text{Sn}(\text{C}_6\text{F}_5)_3$ by HCl gives $(\text{C}_6\text{F}_5)_3\text{SnCl}$, exclusively, which can be hydrolysed to tris(pentafluorophenyl)tin oxide by ammonium hydroxide without

significant cleavage of the pentafluorophenyl groups.

For the lead derivatives, Tamborski et al. found that PbCl_2 and PbCl_4 were unsuitable starting materials for reaction with the lithium reagent, $\text{C}_6\text{F}_5\text{Li}$ (98). The reaction between $\text{C}_6\text{F}_5\text{Li}$ and PbCl_4 gave 1-3% $(\text{C}_6\text{F}_5)_4\text{Pb}$ with the major product being an intractable material of high melting point. Infrared analysis indicated this product to be a poly-fluorophenylene polymer (98). Fortunately, a 15.5% yield of $(\text{C}_6\text{F}_5)_4\text{Pb}$ was obtained by the action of the lithium reagent, $\text{C}_6\text{F}_5\text{Li}$, on lead tetraacetate. All the known pentafluorophenyl derivatives of Si, Ge, Sn and Pb are listed in Table 4.

Interest in these pentafluorophenyl derivatives has been varied and studies such as thermal stability, nuclear magnetic resonance and reactions towards various reagents have been made. Tamborski and co-workers (98) have recently studied and compared the relative thermal stabilities of $(\text{C}_6\text{F}_5)_4\text{M}$, where $\text{M} = \text{Si}, \text{Ge}, \text{Sn}$ and Pb . The decomposition temperatures of the fluorocarbon and hydrocarbon derivatives are listed in Table 5. Judging from the decomposition temperatures, the silicon member of the fluorocarbon series is the least thermally stable; however, the other members of the series have equal or increased stability over their hydrocarbon analogs. Wall et al. (96) qualitatively studied the stability of $(\text{C}_6\text{F}_5)_4\text{Si}$ and $(\text{C}_6\text{H}_5)_4\text{Si}$ (as shown in Table 6).

In contrast to $(\text{C}_6\text{H}_5)_4\text{M}$ ($\text{M} = \text{Si}, \text{Ge}, \text{Sn}$ and Pb) which reacts with lithium in THF to give phenyllithium and $(\text{C}_6\text{H}_5)_3\text{MLi}$, and with bromine to give bromobenzene and $(\text{C}_6\text{H}_5)_3\text{MBr}$, Tamborski and co-workers found that the pentafluorophenyl derivatives of Si, Ge and Sn do not react with

Table 4. C_6F_5 derivatives of Group IVB elements

| Compound | M.p. (b.p./mm.) ^o C | Reference |
|--------------------------|--------------------------------|-----------|
| Silicon | | |
| $(C_6F_5)Si(CH_3)_3$ | (64 ^o /14mm.) | 97, 98 |
| $(C_6F_5)_4Si$ | 245-246 ^o | 98 |
| | 248-250 ^o | 96 |
| Germanium | | |
| $(C_6F_5)GeCl_3$ | | 99 |
| $(C_6F_5)GeBr_3$ | | 99 |
| $(C_6F_5)Ge(CH_3)_3$ | | 99 |
| $(C_6F_5)Ge(C_2H_5)_3$ | | 99 |
| $(C_6F_5)Ge(C_6H_5)_3$ | | 99 |
| $(C_6F_5)_2GeCl_2$ | | 99 |
| $(C_6F_5)_2GeBr_2$ | | 99 |
| $[(C_6F_5)_2GeO]_x$ | | 95 |
| $(C_6F_5)_2Ge(CH_3)_2$ | | 99 |
| $(C_6F_5)_2Ge(C_2H_5)_2$ | | 99 |
| $(C_6F_5)_2Ge(C_6H_5)_2$ | | 99 |
| $(C_6F_5)_3GeCl$ | | 95 |
| $(C_6F_5)_3GeBr$ | | 99 |
| $(C_6F_5)_3GeCH_3$ | | 99 |
| $(C_6F_5)_3GeC_2H_5$ | | 99 |
| $(C_6F_5)_3GeC_6H_5$ | | 96 |
| $(C_6F_5)_4Ge$ | 246.5-247.5 ^o | 95 |

Table 4. (Continued)

| Compound | M.p. (b.p./mm.) ^o C | Reference |
|---|--------------------------------------|-----------|
| Tin | | |
| $(C_6F_5)Sn(CH_3)_2Cl$ | | 94 |
| $(C_6F_5)Sn(CH_3)_3$ | | 92 |
| $(C_6F_5)Sn(C_6H_5)_3$ | | 92 |
| $(C_6F_5)_2SnCl_2$ | | 93,100 |
| $(C_6F_5)_2Sn(CH_3)_2$ | (94-96 ^o /1.7) | 92 |
| $(C_6F_5)_2Sn(C_6H_5)_2$ | | 92 |
| $(C_6F_5)_2Sn(C_6H_4\text{-}p\text{-}CH_3)_2$ | | 92 |
| $(C_6F_5)_3SnCl$ | 106 ^o | 93,100 |
| $(C_6F_5)_3SnCH_3$ | | 92 |
| $(C_6F_5)_3SnC_6H_5$ | 100-102 ^o | 92 |
| $(C_6F_5)_3Sn\text{-}(C_6H_4\text{-}p\text{-}CH_3)$ | | 92 |
| $(C_6F_5)_4Sn$ | 221 ^o | 93,98,100 |
| Lead | | |
| $(C_6F_5)Pb(CH_3)_3$ | (40 ^o /10 ⁻²) | 91 |
| $(C_6F_5)Pb(C_6H_5)_3$ | 85-87 ^o | 91 |
| $(C_6F_5)_4Pb$ | 199-200 ^o | 91 |

Table 5. Relative thermal stabilities of Group IVB compounds

| Compound | Decomposition temperature °C | |
|--------------------|-----------------------------------|----------------------------------|
| | Ar= C ₆ H ₅ | Ar=C ₆ F ₅ |
| Ar ₄ Si | 468° | 382° |
| Ar ₄ Ge | 421° | 416° |
| Ar ₄ Sn | 352° | 399° |
| Ar ₄ Pb | 232° | 260° |

Table 6. Stability study on (C₆F₅)₄Si and (C₆H₅)₄Si

| Compound | m.p. | Heating temp (°C) | Heating time (hr.) | Conditions of sample |
|--|------|-------------------|--------------------|-------------------------|
| (C ₆ F ₅) ₄ Si | 249° | 500° | 1 | charred, not coked |
| | | 500° | 2 | charred, some etching |
| | | 500° | 3 | coked, etched tube |
| (C ₆ H ₅) ₄ Si | 232° | 500° | 1 | yellow color |
| | | 500° | 2 | yellow, decomp. started |

bromine (98). They also studied the hydrolysis of the compounds $(C_6F_5)_4M$ ($M = Si, Ge$ and Sn) and found that they are unaffected at reflux temperature in a heterogeneous acid medium (6N. HCl). The silane and germane are also stable to basic hydrolysis (6N. NaOH) in a heterogeneous system at reflux temperature but the tin and lead compounds are hydrolyzed. In a homogeneous hydrolytic medium (THF) under acidic or basic conditions, the only compound resistant to hydrolysis was the germanium whereas the silicon, tin and lead were unstable. No attempt was made to identify the hydrolysis products besides pentafluorobenzene (98).

Pentachlorophenyl derivatives

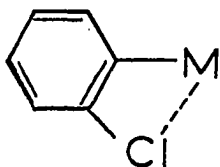
The preparation of pentachlorophenylmagnesium chloride was first reported in 1959 by Ramsden and co-workers (101,102,103). It was made by the interaction of a 4-fold excess of magnesium turnings on hexachlorobenzene in tetrahydrofuran, using a small crystal of iodine and ethyl bromide to initiate the reaction. The Grignard reagent was characterized by hydrolysis with dilute hydrochloric acid to give pentachlorobenzene in 60% yield. Pearson and co-workers (104) were able to prepare the Grignard reagent in diethyl ether by a modified entrainment method using ethylene bromide instead of ethyl bromide. The yield by carbonation, followed by hydrolysis, to give pentachlorobenzoic acid, was 71%.

The lithium derivative, pentachlorophenyllithium, was reported recently by Rausch and co-workers (105). It was made by halogen-metal

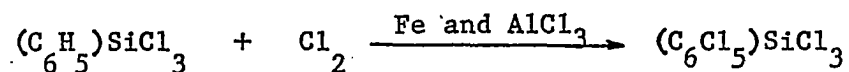
interconversion between hexachlorobenzene in either diethyl ether or tetrahydrofuran, with commercial *n*-butyllithium in hexane. The lithium reagent was characterized by forming pentachlorophenyl derivatives of Hg, Si, P, Co, Ni and other elements. Carbonation and hydrolysis lead to pentachlorobenzoic acid and pentachlorobenzene, respectively.

The same intermediate, pentachlorophenyllithium, can also be prepared by metalating pentachlorobenzene with *n*-butyllithium at -65° (106). Extensive hydrogen-lithium exchange to give pentachlorophenyllithium was observed, giving, after carbonation and hydrolysis, 91% of pentachlorobenzoic acid. Small amounts of products due to chlorine-lithium interconversion were also obtained.

Recently, the reaction of pentachlorophenylmagnesium chloride with mercuric chloride to form bis(pentachlorophenyl)mercury was reported (107). Mono-substituted pentachlorophenyl derivatives of mercury could be made by prolonged heating at temperatures above 200° of bis(pentachlorophenyl)mercury with other organomercury compounds. The following pentachlorophenyl derivatives of mercury have been prepared: $(C_6Cl_5)_2Hg$, $(C_6Cl_5)HgCl$, $(C_6Cl_5)HgCH_3$ and $(C_6Cl_5)Hg(C_6H_5)$. The same authors found that these compounds have very high thermal stabilities. When attacked by acid, the ease of cleavage from mercury is in the following order: $C_6H_5 > C_6Cl_5 > CH_3$. The authors suggested possible interaction between mercury and the ring halogen atoms.



The only compound, reported to date, containing a pentachlorophenyl-silicon bond is (pentachlorophenyl)trichlorosilane. This compound was prepared by the chlorination of phenyltrichlorosilane in the presence of a catalyst (Fe and AlCl_3 , or I_2 and SbCl_3) (108). By using different temperatures and reagent ratios, it is possible to isolate



the entire series from the mono- to pentachlorophenyl derivatives. Attempts made by the same authors to prepare bis(pentachlorophenyl)dichlorosilane by the chlorination of diphenyldichlorosilane have not been successful (108).

EXPERIMENTAL

All reactions involving reactive organometallic reagents were carried out in an atmosphere of dry, oxygen-free nitrogen. The nitrogen was dried and deoxygenated by passing the gas through a train containing activated 'BTS-Katalysator', sulfuric acid and anhydrous calcium chloride (109).

The apparatus normally consisted of a 250 ml., three-necked, round-bottomed flask equipped with a Trubor stirrer, an addition funnel and a Friedrichs condenser. The condenser and addition funnel were connected to nitrogen inlets. The flask and its attachments were dried in an oven at 110° for at least one hour before use. A positive pressure of nitrogen was maintained at all times during a reaction involving a reactive organometallic reagent.

The reagents and solvents used in the experiments were commercially available materials. Tetrahydrofuran (THF) was dried and purified by refluxing over sodium wire, followed by distillation into lithium aluminum hydride, and was then distilled from the hydride immediately before use. For the latter part of the experimental work, the THF used was of better commercial grade so that drying over sodium wire alone was sufficient to remove all the moisture. Diethyl ether and hydrocarbon solvents were dried by storage of the solvents over sodium wire.

Lithium wire was obtained commercially from Lithium Corporation of America. Before its use, it was wiped to remove its protective oil and cut into small pieces directly into the reaction flask which had been flushed with nitrogen. Magnesium metal turnings of Grignard grade were

purchased from Mallinkrodt Chemical Works. Organosilicon compounds were obtained from Dow Corning Corp., Midland, Michigan, and Union Carbide Corp., Tonawanda, N.Y. Organogermanium compounds were purchased from Reaction Products, Inc., Painesville, Ohio. 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. Hexachlorobenzene was obtained from Eastman Organic Chemicals, Rochester 3, N.Y. or Stauffer Chemical Co., New York 17, N.Y.

Both the melting points and the boiling points were uncorrected. Melting points were determined with an electrically heated oil bath or a Mel-Temp apparatus. Infrared Spectra were determined with a Perkin-Elmer spectrophotometer, model 21, and ultraviolet spectra with a Beckman DK-2A spectrophotometer. Molecular weights were determined with a Mechrolab osmometer Model 301A, using benzene solutions of benzil as standards.

Silicon, germanium, tin or a combination of any two elements were quantitatively analyzed by the following procedure. A sample of the unknown, weighing about 0.2 g., was placed in a Vycor crucible. The lid of the crucible was so arranged that a small opening was formed. About 1 ml. of concentrated sulfuric acid and a few drops of fuming nitric acid were then introduced. In most cases a reaction was started within a few seconds. The crucible with its contents were then heated gently over a Rogers ring burner until all of the nitric acid had evaporated and white fumes appeared. After the mixture had cooled, about 1 ml. of

fuming nitric acid was added, and the contents again gently heated. This process was repeated until the residue became white. After evaporating all of the acids, the crucible with its contents were ignited with a Meeker burner until a constant weight was obtained. The residue was weighed as the dioxides.

Preparation and Reactions of Ar_3MLi Reagents

Preparation of triphenyltinlithium in tetrahydrofuran

(A) From triphenyltin chloride and lithium A solution of 11.56 g. (0.03 mole) of triphenyltin chloride in 30 ml. of tetrahydrofuran (THF) was stirred with 0.7 g. (0.1 g.-atom) of finely-cut lithium wire until the reaction had begun, as evidenced by the evolution of heat and the formation of a tan color. An additional 45 ml. of THF was added at a moderate rate. The mixture was stirred for 8 hr. at room temperature and then allowed to stand for 12 hr. (Subsequent studies indicated that the formation of the tin-lithium compound is complete in 3-4 hr.) The dark green solution was filtered through a glass-wool plug and added to 4.4 g. (0.035 mole) of benzyl chloride. The reaction mixture was refluxed for 1 hr. and then it was poured into an aqueous ammonium chloride solution. The organic layer was separated, dried, and concentrated. Addition of ethanol to the residue gave 10.0 g. of benzyltriphenyltin, m.p. 86-89°. Recrystallization from ethanol gave 9.07 g. (68.6%) of pure product, m.p. and mixed m.p. 89.5-90.5°. The ethanol-insoluble material weighed 0.3 g. (2.9%) and melted at 226-230°. This was identified as hexaphenylditin by a mixed m.p. with an authentic sample.

(B) From hexaphenylditin and lithium A mixture of hexaphenylditin (7.0 g., 0.01 mole) and finely-cut lithium wire (0.7 g., 0.1 g.-atom) was treated with a small amount of tetrahydrofuran (THF) to form a paste. The mixture was stirred at room temperature until the cleavage had started (heat evolved and a dark brown color developed) after which time the remainder of the 50 ml. of THF was added. After the mixture had been stirred for 7 hr. at room temperature, it was filtered into an addition funnel and added to 3.17 g. (0.025 mole) of benzyl chloride in 20 ml. of THF. Subsequent to refluxing 1 hr., hydrolysis was effected with an aqueous ammonium chloride solution, and ether added. The organic layer was separated and dried. The concentrated oil was seeded with benzyltriphenyltin to give 6.27 g. of solid, m.p. 88-91°. Recrystallization from ethanol gave 5.72 g. (64.8%) of pure product, m.p. 89-91°, identified as the benzyl derivative by mixed melting point.

Attempted preparation of triphenyltinlithium in ethylene glycol dimethyl ether

Ethylene glycol dimethyl ether was dried over sodium before use. Finely-cut lithium wire, 0.7 g. (0.1 g.-atom) and 1 g. of triphenyltin chloride were placed in a 250 ml. flask. The rest of the triphenyltin chloride (a total of 11.56 g., 0.03 mole) was dissolved in 95 ml. of ethylene glycol dimethyl ether in an addition funnel. Stirring was started, and enough ethylene glycol dimethyl ether was added to form a paste. No indication of a reaction was observed after stirring for 3 hr. although external heat was applied. The rest of the triphenyltin chloride solution was added and the solution became chalky after about 30

minutes. The white precipitate formed was filtered off and the unchanged lithium was separated. This precipitate, after one recrystallization from benzene, melted at 231-232.5°, and was identified, by mixed m.p. with an authentic sample, as hexaphenylditin. The yield was 7.60 g. (72.4%).

Attempted preparation of triphenyltinlithium in 2,2,4,4-tetramethyl-tetrahydrofuran

2,2,4,4-Tetramethyltetrahydrofuran was obtained from Tennessee Eastman Company, Kingsport, Tennessee. It was freed from moisture before use by refluxing over sodium wire, followed by distillation from lithium aluminum hydride immediately before use.

A mixture of triphenyltin chloride (11.57 g., 0.01 mole) and finely-cut lithium wire (1.0 g., 0.142 g.-atom) was treated with a small amount of 2,2,4,4-tetramethyltetrahydrofuran to form a paste. The mixture was stirred at room temperature; however, no indication of a reaction was observed after 15 minutes. External heat was applied and still no reaction was observed. Additional 2,2,4,4-tetramethyltetrahydrofuran did not initiate a reaction. The unchanged lithium wire was separated by filtration and the filtrate, upon concentration, gave the starting material, triphenyltin chloride.

Hydrolysis of triphenyltinlithium

A tetrahydrofuran (THF) solution containing 0.026 mole of triphenyltinlithium, prepared from 10.0 g. (0.026 mole) of triphenyltin chloride and 0.7 g. (0.1 g.-atom) of finely-cut lithium wire in 60 ml. of THF, was divided into two equal portions and one portion poured into an

aqueous ammonium chloride solution. Ether was added and the layers separated. The combined organic layer was concentrated to give 1.68 g. of a solid, m.p. 229-231°. Recrystallization from petroleum ether (b.p. 100-120°) gave 1.58 g. (34.8%) of hexaphenylditin, m.p. and mixed m.p. 229-231°.

The second portion of the triphenyltinlithium solution was added to an excess of benzyl chloride. After the usual work-up, 0.47 g. (10.3%) of hexaphenylditin, m.p. and mixed m.p. 225-228°, and 3.19 g. (55.6%) of pure benzyltriphenyltin (4.24 g. or 74% of crude material), m.p. and mixed m.p. 89-91°, were isolated.

Approximately the same yield (44%) of hexaphenylditin was isolated when the hydrolysis was carried out under nitrogen.

Carbonation of triphenyltinlithium

A solution of triphenyltinlithium, prepared from 5.0 g. (0.013 mole) of triphenyltin chloride and lithium wire in 30 ml. of tetrahydrofuran, was poured jet-wise onto a slurry of Dry Ice and ether. After hydrolysis with water, the layers were separated. The organic layer was filtered to give 1.5 g. of a solid, m.p. 224-228°, identified as hexaphenylditin by mixed melting point.

Acidification of the aqueous layer, which was basic, did not give any insoluble products.

The organic layer was dried over magnesium sulfate and distilled. Treatment of the residual solid with petroleum ether (b.p. 60-70°) afforded an additional 1.1 g. of hexaphenylditin. The combined fractions were recrystallized from a petroleum ether-benzene mixture to give 2.25 g.

(49.6%) of pure product, m.p. 231-233°.

Interrupted triphenyltinlithium preparation

Five grams (0.013 mole) of triphenyltin chloride and 0.7 g. (0.1 g.-atom) of finely-cut lithium were dissolved in 10 ml. of THF at which time the reaction began and a solid was formed. Before the cleavage began (formation of a dark brown color), the mixture was diluted with 30 ml. of THF and the lithium removed by filtration through a loose glass-wool plug. The filtrate was filtered through a Büchner funnel to give a solid which was taken up in water to dissolve any lithium chloride. Subsequent filtration gave 3.7 g. (81.3%) of hexaphenylditin, m.p. and mixed m.p. 231-233° after recrystallization from a petroleum ether (b.p. 100-120°)-benzene mixture.

Reaction of triphenyltinlithium with n-butyl chloride

Triphenyltinlithium (0.03 mole) in THF was prepared by the usual procedure of reacting 11.56 g. (0.03 mole) of triphenyltin chloride with lithium wire. It was then transferred into an addition funnel.

Into another 250 ml. flask were placed 2.8 g. (0.03 M.) of n-butyl chloride and 20 ml. of THF. Stirring was started and the triphenyltinlithium solution was added dropwise. After the addition, the reaction mixture was refluxed for 3 hr. Upon cooling, it was hydrolyzed with aqueous ammonium chloride solution. The organic layer was separated from the aqueous layer, and the aqueous layer was again extracted with ether. The organic fraction was dried over sodium sulfate and then distilled to remove the solvents. A precipitate weighing 0.8 g. was filtered off. It

melted over the range 200-210° and was suspected to be a mixture of tetraphenyltin and hexaphenylditin, representing a 6.3% yield (based on hexaphenylditin). The filtrate, upon addition of 95% ethanol, gave white crystals, m.p. 56-58°. It was identified as n-butyltriphenyltin by mixed m.p. with an authentic sample, and it weighed 5.35 g. (44.6%).

Reaction of triphenyltinlithium with phenyllithium

To a THF solution of triphenyltinlithium, prepared by the lithium cleavage of 7.0 g. (0.01 mole) of hexaphenylditin in 27 ml. of THF, was added 0.02 mole of phenyllithium in 100 ml. of ether. A solid was formed during the addition. The mixture was stirred over night and then filtered under nitrogen. The insoluble material was recrystallized from a benzene-petroleum ether (b.p. 60-70°) mixture to give 0.23 g. of tetraphenyltin, m.p. and mixed m.p. 230-231°.

The filtrate was treated with 5.0 g. (0.04 mole) of benzyl chloride. The reaction mixture was refluxed for 3 hr. and then it was hydrolyzed with an aqueous ammonium chloride solution and filtered. The solid was recrystallized from a mixture of benzene and petroleum ether (b.p. 60-70°) to afford 3.85 g. of tetraphenyltin, m.p. and mixed m.p. 229-230.5°. The total yield of tetraphenyltin was 47.8%.

The organic layer was separated and dried over sodium sulfate. The solvent was evaporated and ethanol added to the residue to give 1.1 g. (12.5%) of benzyltriphenyltin, m.p. and mixed m.p. 91.5-92.5°.

The results of three runs in which the ratios of phenyllithium to triphenyltinlithium were 1:1, 2:1 and 3:1 are shown in Table 7.

Table 7. Reaction of phenyllithium with triphenyltinlithium

| PhLi:Ph ₃ SnLi ratio | Yield of Ph ₄ Sn, % | Yield of Ph ₃ SnCH ₂ Ph |
|---------------------------------|--------------------------------|---|
| 1:1 | 47.8 | 12.5 |
| 2:1 | 39.8 | None |
| 3:1 | 73.6 | None |

Triphenyltinlithium refluxed for 8 hours

Triphenyltinlithium (0.03 mole) was prepared by reacting 11.5 g. (0.03 mole) of triphenyltin chloride with 0.7 g. (0.1 g.-atom) of finely cut lithium wire in 75 ml. of THF. After the reaction mixture had been stirred for 3 hr., the unchanged lithium wire was filtered off. The filtrate was then refluxed under an atmosphere of nitrogen for 8 hr. After the refluxing period the reaction mixture was allowed to cool. The fine white crystals that settled down in the flask were filtered under nitrogen.

The residue melted over a range at ca. 220°. When it was recrystallized from a mixture of petroleum ether (b.p. 60-70°) and benzene, tetraphenyltin (2.5 g., 19.5%), m.p. and mixed m.p. at 229-230°C., was obtained.

The filtrate was added dropwise to 3.4 g. of (0.03 mole) of PhCH₂Cl in 20 ml. of THF. After the addition, the reaction mixture was refluxed for 2 hr. and then hydrolyzed with aqueous ammonium chloride solution.

The organic layer was separated and on subsequent work-up, no benzyltriphenyltin was obtained.

Stability of triphenyltinlithium

Triphenyltinlithium (0.01 mole) in THF was placed in a sealed tube under nitrogen. The tube was shaken for 1 week at room temperature and then stored at room temperature for 8 months. During this period, crystals of Ph_4Sn (identified by triple melting-point method with an authentic sample) were formed. After the period of standing, the crystals were separated and the filtrate added to benzyl chloride. After the reaction mixture had been refluxed for 2 hr., the solution was hydrolyzed with aqueous ammonium chloride solution. On subsequent work-up, a mixture of Ph_6Sn_2 and Ph_4Sn was obtained. The weight was 0.6 g. and the melting range was 200-210°.

Allyl bromide double titration of triphenyltinlithium

Triphenyltinlithium (0.03 mole) in THF was prepared by treating 11.56 g. (0.03 mole) of triphenyltin chloride with an excess of lithium wire in 100 ml. of THF. The solution was decanted into an addition funnel, removing any unchanged lithium at the same time. The solution was kept under nitrogen and aliquots were withdrawn for titration at various intervals. The total base of the solution remained constant over the period while the base due to triphenyltinlithium decreased over a period of 300 hr. The titration results are shown in Table 8.

Table 8. Titration results of triphenyltinlithium

| Time (hr.) | Mole of Ph_3SnLi | % of Ph_3SnLi |
|------------|----------------------------------|-------------------------------|
| 10 | 0.2820 | 94.0 |
| 22 | 0.2755 | 91.8 |
| 34 | 0.2660 | 88.6 |
| 58 | 0.2575 | 85.8 |
| 70 | 0.2518 | 84.5 |
| 94 | 0.2505 | 83.5 |
| 118 | 0.2320 | 77.3 |
| 148 | 0.2170 | 72.2 |
| 176 | 0.213 | 71.1 |
| 196 | 0.191 | 63.7 |
| 220 | 0.161 | 53.6 |
| 244 | 0.141 | 46.9 |
| 258 | 0.105 | 35.0 |
| 299 | 0.0899 | 29.3 |

Reaction of triphenyltinlithium with allyl chloride

To a well-stirred THF solution containing 2.3 g. (0.03 mole) of allyl chloride in 20 ml. THF, triphenyltinlithium (0.03 mole) in THF was added at a slow rate. The reaction was exothermic. At the end of the addition, the reaction mixture was refluxed for 3 hr. and then hydrolyzed with aqueous ammonium chloride solution. After the usual work-up, the

organic fraction gave a pale yellow, oily residue. Upon addition of 95% ethanol, this oil solidified. The mixture was then heated to boiling and the allyltriphenyltin was dissolved, separating it from any insoluble hexaphenylditin and tetraphenyltin. The insoluble materials were recrystallized once from a mixture of benzene and petroleum ether (b.p. 60-70°) to give crystals melting at 231-234°. A mixed m.p. with tetraphenyltin was depressed to 210-215° and with hexaphenylditin, no depression was observed. The total weight of hexaphenylditin obtained was 0.95 g (9.0%). The ethanol filtrate, upon cooling, gave 6.50 g. of allyltriphenyltin, m.p. 71-73°. A second crop, 0.85 g., was also obtained. The total yield of allyltriphenyltin obtained was 7.35 g. (70.0%) and was identified by mixed m.p. with an authentic sample.

Reaction of triphenyltinlithium with allyl bromide

Following the same procedure used for the reaction between triphenyltinlithium and allyl chloride, the work-up of the reaction mixture from triphenyltinlithium and allyl bromide gave 3.33 g. (28.4%) of allyltriphenyltin, m.p. 74-75° and 0.89 g. (8.5%) of hexaphenylditin m.p. 228-230°. These compounds were identified by mixed m.p. with authentic samples.

Reaction of triphenyltinlithium with 1-chloropropene

Into a 250 ml. flask, 1.2 g (0.015 mole) of 1-chloropropene and 25 ml. THF were introduced and cooled to 0°C. in a salt-ice bath. At this time, triphenyltinlithium (0.03 mole) in THF was added dropwise to the reaction flask, keeping the temperature at 0°C. during the whole

addition. After the addition, the reaction mixture was allowed to stir for 1.5 hr. and then hydrolyzed with 400 ml. aqueous ammonium chloride solution. The organic layer was separated and the aqueous layer was extracted with ether once more. The combined organic layers were dried over sodium sulfate. When the solvent was distilled, 6.25 g. (59.4%) of hexaphenylditin was obtained. The compound was identified by mixed m.p. with an authentic sample of hexaphenylditin. No coupling product, (1-propenyl)triphenyltin, was isolated.

Reaction of triphenyltinlithium and 1-bromopropene

The procedure for this reaction was similar to that of the reaction between triphenyltinlithium and 1-chloropropene, except that the reaction mixture was heated to reflux for 1.5 hr. before it was hydrolyzed with aqueous ammonium chloride solution. After the usual work-up, the organic fraction was distilled to remove the solvents. To the brown residue, 95% ethanol was added and the precipitate formed was filtered off. This precipitate was then recrystallized once from benzene to give 3.9 g. (37.2%) of hexaphenylditin, m.p. and mixed m.p. 232-234^o with an authentic sample. The ethanol filtrate was then distilled until a polymeric brown residue was obtained. This solid was then chromatographed on activated alumina, using petroleum ether (b.p. 60-70^o) as eluent, to give 1.0 g. of a white solid, melting at 85-88^oC. After three recrystallizations from ethanol, it melted constantly at 100-101^oC. This compound was assumed to be propenyltriphenyltin, which was later confirmed by its mixed m.p. with the product obtained from the reaction of triphenyltin chloride with propenyllithium, and by analyses of its tin content.

Preparation of propenyltriphenyltin from the interaction of triphenyltin chloride and propenyllithium

Propenyllithium (0.03 mole) in diethyl ether was prepared by reacting 3.63 g. (0.03 mole) of 1-bromopropene in 30 ml. diethyl ether with a well-stirred mixture of 0.42 g. (0.06 g.-atom) of finely-cut lithium wire and 50 ml. of ether. It was an exothermic reaction. After the addition, the reaction mixture was allowed to stir until it reached room temperature. Color Test I (8) was positive. The unchanged lithium was filtered off, and a 3 ml. aliquot was titrated with standard acid indicating a 79% (0.023 mole) yield of propenyllithium.

Into a 250 ml. flask, 8.55 g. (0.023 mole) of triphenyltin chloride and 30 ml. diethyl ether were introduced. Stirring was started and the 0.023 mole propenyllithium (previously prepared) was added dropwise to the reaction flask. At the end of the addition, the reaction mixture was stirred for 15 min. at room temperature and then for 1 hr. at the reflux temperature. It was then hydrolyzed with aqueous ammonium chloride solution. The organic fraction was separated and the aqueous layer further extracted with ether. The organic fractions were combined and dried over sodium sulfate. Upon removal of the ether solvent, a viscous liquid was obtained. It solidified when methanol was added to give a solid crude product which melted in the range 75-100°. Recrystallization from propanol gave 1.45 g. of crystals, m.p. 74-80°. Another recrystallization from methanol raised the melting point to 95-98°. Further recrystallization raised the melting point to 101-103°. Its mixed melting point with the compound obtained from the reaction of triphenyltinlithium and 1-bromopropene was 101-102°. The methanol filtrate, when concentrated,

gave 0.8 g. of a compound, m.p. 78-83.5°.

The compound which had a m.p. 101-102° was identified as propenyl-triphenyltin. The infrared spectra of the compounds obtained from the two different methods of preparations were identical. They showed absorption bands at 6.25 μ and 9.33 μ , indicating the presence of a C=C bond and a phenyl-tin bond, respectively.

Anal. Calcd. for $C_{21}H_{20}Sn$: Sn, 30.35%. Found: Sn, 30.19%, 30.80%

Reaction of triphenyltinlithium with epichlorohydrin (molar ratio 1:1)

Into a 250 ml. three-necked flask, 2.8 g. (0.03 mole) of epichlorohydrin in 25 ml. of THF were cooled to 0°. Triphenyltinlithium (0.03 mole) in THF was then added to the reaction flask at a moderate rate. The addition was completed in 15 min. and stirring was continued for 1 hr. at 0°. The reaction mixture was then hydrolyzed with aqueous ammonium chloride solution and the organic layer was separated. Another extraction of the aqueous fraction with diethyl ether was made and the organic layers were combined and dried with sodium sulfate. The solvent was distilled and a pale yellow oil remained. About 100 ml. of methanol was added, and the solid formed was filtered off. This solid weighed 2.9 g. (27.6%) and was identified as hexaphenylditin, mixed m.p. with an authentic sample. The methanol filtrate, upon concentration, gave a solid residue, m.p. 120-124°. After three recrystallizations from petroleum ether (b.p. 60-70°), its m.p. was 122.5-123.5°. It was later identified as bis(triphenyltin) oxide. The weight obtained was 0.55 g. (5.12%)

Anal. Calcd. for $C_{36}H_{30}O_2Sn_2$: Sn, 33.18%. Found: Sn, 33.05%, 33.13%

A second run was made; however, the addition temperature was kept at room temperature instead of 0°C. The products obtained were hexaphenylditin (4.25 g., 40.6%) and bis(triphenyltin) oxide (1.6 g., 14.9%).

Reaction of triphenyltinlithium with n-octyl fluoride

Triphenyltinlithium (0.03 mole) in 110 ml. of THF was added dropwise to 4.0 g. (0.03 mole) of n-octyl fluoride in 60 ml. of the same solvent. The reaction mixture was allowed to stir at room temperature overnight, and finally at the reflux temperature for 2 hr. Color Test I was negative. Work-up of the reaction mixture by hydrolysis with aqueous ammonium chloride solution, separation of the layers, extraction of the aqueous layer with diethyl ether, drying of the organic fraction with sodium sulfate, and removal of the solvents, left a residue which solidified on addition of 95% ethanol. The m.p. of the solid was 52-55°. After one recrystallization from 95% ethanol, 5.5 g. (39.2%) of octyltriphenyltin, m.p. and mixed m.p. 53-55°, were obtained. The insoluble material from the ethanol solution was filtered and recrystallized from benzene to give 1.3 g. (12.4%) of hexaphenylditin.

Reaction of triphenyltinlithium with trimethyl phosphate (1:1)

Triphenyltinlithium (0.03 mole) in 70 ml. of THF was added dropwise to 4.2 g. (0.03 mole) of trimethyl phosphate. During the addition, heat was evolved. The reaction mixture was stirred for 12 hr. at room temperature and then at the reflux temperature for 1.5 hr. After the reaction mixture had reached room temperature, it was hydrolyzed with 80 ml. of aqueous ammonium chloride solution. The organic fraction was separated,

dried over sodium sulfate and concentrated to give a semisolid residue. Methanol was then added. The resultant precipitate started to melt at 58° and did not completely melt until 90°. One recrystallization from methanol gave 8.84 g. (80.6%) of methyltriphenyltin, m.p. 60-62° which was identified by mixed m.p. with an authentic sample.

A second run with the same amount of starting materials, was carried out. After the usual work-up, 6.97 g. (65.4%) of methyltriphenyltin, melting at 61-62.5°, was obtained and identified by mixed m.p. with an authentic sample. In this work-up, 1.4 g. (13.3%) of hexaphenylditin m.p. 230-232°, was also obtained and was identified by mixed m.p. with an authentic sample.

Reaction of triphenyltinlithium with tri-n-butyl phosphate

Triphenyltinlithium (0.03 mole) in 70 ml. of THF was added dropwise to a stirred solution of 8.0 g. (0.03 mole) of tri-n-butyl phosphate in 30 ml. of the same solvent. Stirring at room temperature was continued for 3 hr. The reaction mixture was then heated at the reflux temperature for 1 hr. At this time Color Test I was negative. Work-up in the manner described for trimethyl phosphate gave a solid melting at about 54-60°. One recrystallization of the solid from methanol raised the m.p. to 60-62°. It was identified by mixed m.p. with an authentic sample as n-butyltriphenyltin. The yield was 7.55 g. (61.8%).

A second run using 0.04 mole of triphenyltinlithium and 0.04 mole of tri-n-butyl phosphate, gave a 63% yield of n-butyltriphenyltin.

Reaction of triphenyltinlithium with benzoyl chloride

Triphenyltinlithium (0.03 mole) in THF which was prepared by the usual procedure, was decanted into a 250 ml. flask. From an addition funnel 4.2 g. (0.03 mole) of benzoyl chloride in 50 ml. THF was added slowly. Heat was evolved during the addition and the reaction mixture turned a dark brown color. The reaction mixture was stirred for 2 hr. at room temperature and then 3.8 g. (0.03 mole) of benzyl chloride in THF was added dropwise. It was then allowed to stir for an additional 3 hr. and then hydrolyzed with aqueous ammonium chloride solution. After the usual work-up, 6.4 g. (64 %) of hexaphenylditin m.p. 229-232^o, was obtained and identified by mixed m.p. with an authentic sample. Another fraction of lower melting solid was also isolated. It weighed 1.45 g. and melted over the range 136-170^o. After recrystallization from petroleum ether (60-70^o), the melting point range was 145-160^o. Further recrystallization from petroleum ether (60-70^o) raised the m.p. to 161-164^o. This compound was later identified as the dibenzoate of stilbenediol by mixed m.p. with a sample prepared by another route (110).

Reaction of triphenyltinlithium with 1,2-dibromoethane

Triphenyltinlithium (0.03 mole) in 100 ml. of THF was added dropwise to 2.82 g. (0.03 mole) of 1,2-dibromoethane in 20 ml. of THF. Heat was evolved during the addition. The dark brown color which was characteristic of triphenyltinlithium, was discharged. The reaction mixture was allowed to stir for 3 hr. at room temperature and was then hydrolyzed with aqueous ammonium chloride solution. Work-up by the usual method gave 4.15 g. (39.5%) of hexaphenylditin, m.p. and mixed m.p. 228-230^o. Another

fraction was recrystallized from petroleum ether (b.p. 60-70°) to give 2.46 g. of a white solid, m.p. 106.5-108°. The tin analyses of this compound gave 30.0% and 30.18% of Sn. Triphenyl(2-hydroxyethyl)tin has a tin content of 30.02% but its reported m.p. is 66-67°. Triphenyl-(2-bromoethyl)tin has a tin content of 25.6% and its m.p. has not yet been reported. 1,2-Bis(triphenylstannyl)ethane requires a tin content of 32.6%. Triphenyltin chloride has the same m.p. 106-108°, but with a tin content of 30.8%.

The reaction was carried out a second time and 3.65 g. (34.6%) of hexaphenylditin and 3.7 g. of a solid m.p. 106-108° were obtained.

Reaction of triphenyltinlithium with 1,2-dibromopropane

Triphenyltinlithium (0.03 mole) in 109 ml. of THF was added dropwise to 3.03 g. (0.015 mole) of 1,2-dibromopropane in 20 ml. of THF. At the end of the addition, a milky suspension was formed. The reaction mixture was stirred for 2 hr. at room temperature, followed by 1 hr. at the reflux temperature. It was then hydrolyzed with aqueous ammonium chloride solution. Work-up by the usual method gave 0.92 g. (7.4%) of tetraphenyltin, m.p. and mixed m.p. 226-228°, and 5.85 g. (55.6%) of hexaphenylditin, m.p. and mixed m.p. 230-234° with an authentic sample.

The reaction was repeated and the same work-up gave 3.1 g. (38.5%) of tetraphenyltin and 4.95 g. (47.0%) of hexaphenylditin. These compounds were identified by mixed m.p. with respective authentic samples.

Reaction of triphenyltinlithium with 1,2,4-tribromobenzene

The starting material, 1,2,4-tribromobenzene, was obtained from Dow Chemical Co. (order #688439). It was recrystallized from petroleum ether

(b.p. 30-40°) before it was used for reaction with triphenyltinlithium.

Triphenyltinlithium (0.03 mole) in 80 ml. of THF was added dropwise to 9.35 g. (0.03 mole) of 1,2,4-tribromobenzene in 40 ml. of THF over 20 minutes. The reaction mixture was allowed to stir for 3 hr. at room temperature and then hydrolyzed with aqueous ammonium chloride solution. The organic layer was separated, and the aqueous layer was further extracted with 100 ml. of diethyl ether. The combined organic fraction was distilled to remove the solvents, leaving behind a thick brown residue. Upon addition of petroleum ether (b.p. 60-70°) to the residue, white crystals formed. They were filtered and dried, giving 3.7 g. (35.2%) of hexaphenylditin, m.p. 291-231°. It was identified by mixed m.p. with an authentic sample.

Reaction of triphenyltinlithium with octaphenylcyclotetrasilane

Triphenyltinlithium (0.025 mole) in 50 ml. of THF and 3.05 g. (0.0042 mole) of octaphenylcyclotetrasilane, were placed in a sealed tube. The tube, with its contents, were placed in a shaker for 10 days and no apparent reaction was observed. It was then allowed to stand at room temperature for 12 months. After this time, some relatively large crystals had formed besides the powdery starting material, octaphenylcyclotetrasilane. The tube was opened and the reaction mixture was hydrolyzed with aqueous ammonium chloride solution. After the usual work-up, 2.2 g. (72%) of unchanged octaphenylcyclotetrasilane was recovered. This was identified by mixed m.p. with an authentic sample. In the benzene filtrate, a total of 3.85 g. (36.5% based on the total amount of available tin) of tetraphenyltin was obtained. The m.p. was

226-230° and the mixed m.p. with an authentic sample was 225-228°. A mixed m.p. with hexaphenylditin was depressed to about 200°. Also isolated in the work-up was 0.62 g. of a solid compound which had a decomposition temperature of 315°. At 326° the solid in the melting-point tube turned black. Its infrared spectrum showed a Sn-Ph absorption band at 9.32 μ . The tin analyses for the compound gave 38.04 and 38.38% Sn. The required values for $\text{Ph}_3\text{Sn}(\text{SnPh}_2)_2\text{SnPh}_3$ and $\text{Ph}_3(\text{SnPh}_2)_3\text{SnPh}_3$ are 37.80 and 39.0%, respectively.

Reaction of triphenyltinlithium with decaphenylcyclopentasilane

Triphenyltinlithium (0.03 mole) in THF was added dropwise to 4.4 g. (0.004 mole) of decaphenylcyclopentasilane. The reaction mixture was allowed to stir for 4 hr. and then at the reflux temperature over night. At the end of the reflux period, the suspension was passed through a sintered-glass filter crucible under nitrogen. The filtrate was then hydrolyzed with aqueous ammonium chloride solution. After the usual work-up, the organic fraction was distilled to remove the solvents. The residue was a solid with m.p. range 190-210°. It was chromatographed on alumina, and elution with carbon tetrachloride gave 4.2 g. of white crystals melting at 203-210°. Recrystallization from benzene did not change the m.p., and the product formed two different shapes of crystals. No effort was made to separate these crystals, but by means of a pair of forceps, a small amount of each of these crystals were isolated and their melting points taken. The higher melting solid was identified by mixed m.p. with an authentic sample as hexaphenylditin. Similarly, the lower melting solid was identified by mixed m.p. with an authentic sample as

tetraphenyltin. The solid residue which was removed from the reaction mixture previously, did not have a definite m.p. It was boiled with benzene and part of it dissolved. The solution was filtered and the benzene filtrate gave, upon concentration, 1.3 g. (10.1%) of tetraphenyltin, m.p. and mixed m.p. 228-230°. A mixture of tetraphenyltin and hexaphenylditin melts at 200-210°. The insoluble material was identified, by mixed m.p., as the starting material, decaphenylcyclopentasilane, m.p. 445-450°. The amount of starting material recovered was 1.0 g. (20%).

Preparation of triethyltinlithium

Into a 250 ml. flask, equipped with a stirrer and a condenser, 0.7 g. (0.1 g.-atom) of finely-cut lithium wire was introduced. This amount represented a 33% excess. From an addition funnel, 75 ml. of a THF solution which contained 7.24 g. (0.03 mole) of triethyltin chloride was added at a moderate rate. Stirring at room temperature was continued for 4 hr. The brown solution was filtered through glass wool under nitrogen to remove any unchanged lithium wire. Triethyltinlithium gives a positive Color Test I and a weakly positive Color Test II (111). Titration with standard acid indicated a yield of 85.0% total base.

A second preparation of triethyltinlithium was carried out and titration with standard acid indicated the following results:

| | |
|--------------------------------|-------------------|
| Total base | 123.5% and 125.0% |
| Allyl bromide double titration | 65.2% and 64.0% |

Reaction of triethyltinlithium with ethyl bromide

Triethyltinlithium (0.03 mole) in 75 ml. of THF was caused to react with 3.27 g. (0.03 mole) of ethyl bromide. The reaction mixture was stirred over night and then hydrolyzed with aqueous ammonium chloride solution. The organic layer was separated and dried over sodium sulfate. The solvent was distilled off and the product which boiled at 96-98°/1 mm. (reported b.p. 153-155°/17mm.) was collected. From the b.p. and refractive index, it was identified as hexaethylditin, 1.5 g. (25%). The refractive index at 20° was 1.5358 while the reported value is 1.5373 (112).

Preparation of triphenylleadlithium and its reaction with benzyl chloride

Tetrahydrofuran (150 ml.) was added rapidly to 21.2 g. (0.04 mole) of triphenyllead chloride and 0.7 g. (0.1 g.-atom) of finely-cut lithium wire. After a short induction period, heat was evolved and a dark-colored suspension rapidly formed. The mixture was stirred for 4 hr. at room temperature and decanted into an addition funnel. One-half of the dark solution was added to 3.42 g. (0.027 mole) of benzyl chloride. The color was partially discharged and, after heating 1 hr. at the reflux temperature, the reaction mixture was poured into an aqueous ammonium chloride solution. The aqueous layer was separated, extracted with ether and discarded. The organic layer was dried over sodium sulfate and distilled. The residual oil was treated with ethanol to give 10.3 g. (98.2%) of benzyltriphenyllead, m.p. 91-93°. A mixed m.p. with an authentic sample was not depressed.

A second run was carried out and, after similar work-up, 78% of

benzyltriphenyllead was obtained.

Carbonation of triphenylleadlithium

The second portion of the above triphenylleadlithium solution was poured onto a slurry of Dry Ice and ether. After acid hydrolysis, the layers were separated and filtered to give 3.9 g. of a solid which did not melt below 360° . The organic layer was extracted with sodium hydroxide. Acidification of the basic extracts gave no products. The organic layer was dried over magnesium sulfate and the solvent was evaporated. The residue was treated with petroleum ether (b.p. $60-70^{\circ}$) to afford 2.95 g. (16.8%) of the pure dilead compound which turned black at 153° and completely melted at 220° . There was no change in these properties when admixed with an authentic sample, which also showed these melting characteristics.

Reaction of triphenylleadlithium with n-butyl chloride

Triphenylleadlithium (0.03 mole) in 100 ml. of THF was added slowly to 2.79 g. (0.03 mole) of n-butyl chloride in 20 ml. of THF. Heat was evolved during the addition and the reaction mixture was stirred for 3 hr. at room temperature and then for 1 hr. at the reflux temperature. When cool, it was hydrolyzed with aqueous ammonium chloride solution. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic fractions were dried over sodium sulfate, and distillation to remove the solvents left a light yellow oil. Addition of petroleum ether (b.p. $60-70^{\circ}$) to the residue gave 9.95 g. (65.6%) of n-butyltriphenyllead, m.p. $50-78^{\circ}$. Recrystallization from ethanol

gave 8.7 g. (58.6%) of pure n-butyltriphenyllead, m.p. 47-48° which was identified by mixed m.p. with an authentic sample.

Reaction of triphenylleadlithium with n-butyl bromide

Triphenylleadlithium (0.02 mole) in 106 ml. of THF was added slowly to 2.74 g. (0.02 mole) of n-butyl bromide in 10 ml. of THF. The procedure for this reaction is similar to that with n-butyl chloride. The work-up gave 6.35 g. (64.0%) of n-butyltriphenyllead, m.p. 47-48°. It was identified by mixed m.p. with an authentic sample. In this work-up a small amount (0.2 g.) of hexaphenyldilead, which turned black at about 150° and melted at 220°, was also obtained and identified.

Reaction of triphenylleadlithium with ethylene bromide

Triphenylleadlithium (0.03 mole) in THF was added dropwise to 2.82 g. (0.015 mole) of ethylene bromide. Heat was given out and the dark color of triphenylleadlithium was partially discharged. The reaction mixture was stirred over night at room temperature and then at the reflux temperature for 2 hr. before it was hydrolyzed with aqueous ammonium chloride. After the usual work-up, 6.82 g. (42.0%) of tetraphenyllead was obtained, m.p. and mixed m.p. 229-239°. No hexaphenyldilead was isolated.

Reaction of triphenylleadlithium with 1,4-dibromobutane

Triphenylleadlithium (0.02 mole) in THF was added slowly to 2.16 g. (0.01 mole) of 1,4-dibromobutane in 10 ml. of THF. After the usual reaction procedure and work-up, a compound melting at 137.5-138° was obtained. The lead analyses for this compound were 43.7% and 43.54%, and the required value for 1,4-bis(triphenyllead)butane is 44.37%. The

infrared spectrum of the compound showed absorption bands at 3.3μ and 9.3μ , indicative of phenyl and phenyl-lead groups, respectively.

Reaction of hexaphenyldigermane with lithium

Into a 250 ml. flask, 7.6 g. (0.0125 mole) of hexaphenyldigermane and 0.7 g. (0.1 g.-atom) of lithium wire were introduced. Enough THF was added to the reaction mixture so that a paste was formed. Stirring was started and a ten-minute induction time was usually required before any reaction (cleavage of Ph_6Ge_2) occurred. This was indicated by the appearance of a yellow color. The rest of the 100 ml. of THF was added slowly. Stirring was continued at room temperature. After 1.5 hr. of stirring, a 3 ml. aliquot of the reaction mixture was removed and analyzed according to the allyl bromide double titration procedure indicating an 84.6% yield of triphenylgermyllithium. The same analyses were performed after 4 hr. and after 5 hr. of stirring, and the results were 89.0% and 89.6%, respectively. These results indicated that 4 to 5 hr. of stirring was needed to give maximum yield of triphenylgermyllithium.

Reaction of tetraphenylgermane with lithium

Into a 250 ml. flask, 9.52 g. (0.025 mole) of tetraphenylgermane and 0.7 g. (0.1 g.-atom) of lithium wire were introduced. About 5 ml. of THF was added and after a few minutes the reaction started. About 90 ml. of THF was added slowly. The reaction mixture was stirred at room temperature for 13 hr. after which time the allyl bromide double titration indicated a yield of 74.5% of triphenylgermyllithium. Four-fifths of the solution (equivalent to 0.02 mole of Ph_3GeLi) was added dropwise

to 15.42 g. (0.04 mole) of triphenyltin chloride in 20 ml. of THF. Heat was evolved during the addition of triphenylgermyllithium. The reaction mixture was stirred at room temperature for 3 hr. and then at the reflux temperature for 1 hr. After this time some solids were formed in the reaction mixture. Subsequent to the usual work-up, a total of 16 g. of solids were obtained. The m.p. range was 160-230°. They were recrystallized several times from benzene in which tetraphenyltin was more soluble. Finally, 5.5 g. (66.0%) of tetraphenyltin of m.p. 224-226°, and 10.0 g. (70.5%) of (triphenylgermyl)triphenyltin of m.p. 293-297° were isolated. These products showed no depression in their mixed m.p. with respective authentic samples.

Reaction of triphenylgermyllithium with trimethyl phosphate

Triphenylgermyllithium (0.02 mole) in THF was added slowly to 3.5 g. (0.02 mole + an excess of 50%) of trimethyl phosphate in 20 ml. of THF. Color Test I was negative 40 minutes after the addition. The reaction mixture was then hydrolyzed with aqueous ammonium chloride solution and worked up by the usual procedure to give 3.5 g. (54.8%) of methyltriphenylgermane. The compound was recrystallized from methanol and melted at 67-69°. It was identified by mixed m.p. with an authentic sample.

Reaction of triphenylgermyllithium with tri-n-butyl phosphate

Triphenylgermyllithium (0.02 mole) in THF was added dropwise to 5.3 g. (0.02 mole) of tri-n-butyl phosphate. Color Test I was negative 30 minutes after the addition and the solution was hydrolyzed with aqueous ammonium chloride. The organic layer was separated from the aqueous layer

which was twice extracted with diethyl ether. The combined organic fractions were dried over sodium sulfate and then distilled to give a solid residue melting at 83-88°. Recrystallization from methanol raised the m.p. to 87-88°. It weighed 4.8 g. (66.7%) and was identified as n-butyl-triphenylgermane by mixed m.p. with an authentic sample.

Reaction of triphenylgermyllithium with triphenyltin chloride

Triphenylgermyllithium (0.025 mole) in THF was prepared by treating 9.6 g. (0.025 mole) of triphenylbromogermane with 0.7 g. (0.1 g.-atom) of finely-cut lithium wire in 100 ml. of THF. At the end of the reaction, the allyl bromide double titration indicated a yield of 83.2% and 82.5% of triphenylgermyllithium. The solution was decanted into an addition flask, removing any of the unchanged lithium wire.

The THF solution containing 0.02 mole of triphenylgermyllithium, was added slowly to 9.6 g. (0.025 mole) of triphenyltin chloride in 20 ml. THF. Color Test I on the reaction mixture was negative 15 minutes after completion of the addition. The reaction mixture was then hydrolyzed with aqueous ammonium chloride solution. The organic fraction, after separation from the aqueous fraction, was dried over sodium sulfate and distilled to remove the solvents. The solid residue had a wide m.p. range, and was recrystallized several times from benzene to give 6.75 g. (47.5%) of (triphenylgermyl)triphenyltin, m.p. 291-293° and was identified by mixed m.p. with an authentic sample. Finally, the benzene solution was concentrated and the residue was recrystallized from petroleum ether (b.p. 60-70°) to give 1.6 g. of bis(triphenyltin) oxide, m.p. and mixed m.p. 155-158°.

The Analysis of Organic-substituted Group IVB Lithium Reagents

Triphenylsilyllithium (3), methyldiphenylsilyllithium (3), dimethylphenylsilyllithium (3), triphenylgermyllithium (39), triphenyltinlithium (55a), and triphenylleadlithium (55a) were prepared in tetrahydrofuran solution according to published procedures. The tetrahydrofuran was purified by refluxing over sodium wire, followed by distillation into lithium aluminum hydride, and distillation from the hydride immediately before use. Phenyllithium was also prepared in diethyl ether according to a published procedure (113) or obtained commercially from Foote Mineral Company in ether/benzene solution. The diethyl ether employed was dried by storage over sodium wire. The solution to be analyzed was filtered under dry, oxygen-free nitrogen through a sintered-glass funnel in order to remove insoluble material. Alternatively, the solution could be allowed to stand so that the insoluble material could settle down. The pipettes and flasks were dried in an oven at 140° and flushed with a stream of nitrogen until cool. The halides used in the titration were dried over phosphorus pentoxide and then distilled. The 0.1 N. sodium hydroxide was standardized by titration against potassium acid phthalate and the 0.1 N. HCl was titrated against standardized sodium hydroxide.

Analytical Procedures

For the double titrations, a 3 ml. aliquot of the solution to be analyzed was withdrawn by pipette with a suction bulb and added to 10 ml. of diethyl ether in an atmosphere of nitrogen. The solution was

hydrolyzed with 10 ml. of distilled water and titrated with standard 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 halide, under an atmosphere of nitrogen. The solution was swirled gently and allowed to stand for two minutes, after which time it was hydrolyzed with distilled water and titrated immediately with standard acid, again using phenolphthalein as indicator, to give the alkali due to lithium oxide and lithium alkoxide.

In titrating the latter solution, the end-point is easily overstepped since the aqueous layer decolorizes before the ether layer. Vigorous shaking when near the end-point is recommended. There is the possibility of interference from hydrolysis of the halide, so that titration should be carried out within a reasonable length of time.

Preparation and reaction of lithium ethoxide with allyl bromide

Lithium ethoxide (0.003 mole) in ether was prepared by reacting 0.47 g. (0.003 mole) of ethanol in 100 ml. of diethyl ether with lithium. The unchanged lithium was filtered off. The double titration procedure, using allyl bromide as described above, was then carried out with this solution.

Reaction of phenyllithium with triphenyltin chloride

Phenyllithium (0.1 mole) in diethyl ether was prepared according to a published procedure (113) by reacting 2 g. (0.29 g.-atom) of finely-cut lithium wire with 15.7 g. (0.1 mole) of bromobenzene in ether. The total volume was 101 ml. When it was titrated with the different

halides, the following results were obtained:

| | |
|-----------------------------------|-------|
| Total base: | 95.4% |
| Allyl bromide double titration: | 87.2% |
| Benzyl chloride double titration: | 77.5% |

An ethereal solution which contained 0.04 mole of phenyllithium was added dropwise to a stirred THF solution of triphenyltin chloride which contained 15.4 g. (0.04 mole) of triphenyltin chloride in the minimum amount of THF required for dissolution. During the addition, heat was evolved. After the completion of the addition, stirring was continued for 2 hr. at room temperature and 1 hr. at the reflux temperature. The tetraphenyltin formed was filtered off on a sintered glass funnel and washed twice with water and once with methanol. It was then dried in an oven and weighed (11.0 g., 85.7%). The product melted at 228-230° (mixed m.p. with an authentic sample of tetraphenyltin). The ether layer was evaporated, but no additional tetraphenyltin was obtained.

Some Tetrakis Organo-Group IVB Compounds

Preparation of tetrakis(triphenylsilyl)tin

(A) From triphenylsilyllithium and stannous chloride, followed by triphenylchlorosilane Triphenylsilyllithium (0.1 mole) was prepared in THF by treating 25.8 g. (0.05 mole) of hexaphenyldisilane with an excess of lithium wire in 200 ml. of THF by the usual, published procedure (3). The unchanged lithium wire was removed by filtration through glass wool and the THF solution of triphenylsilyllithium was transferred to an addition funnel. The allyl bromide double

titration (114) indicated a yield of 92.6% of triphenylsilyllithium.

Into a 500 ml. flask, equipped with a mechanical stirrer and a low temperature thermometer, 6.05 g. (0.032 mole) of stannous chloride and 60 ml. of THF were placed. The mixture was then cooled to -40° in a Dry Ice-acetone bath. Stirring was started and 0.1 mole of triphenylsilyllithium, prepared previously, was added dropwise. Care was taken to prevent settling of the dense stannous chloride. After all the triphenylsilyllithium had been added, the reaction mixture was allowed to come to room temperature and was stirred at this temperature for an additional 12 hr. Some solids had then settled to the bottom of the flask. The solution was decanted into another addition funnel under an atmosphere of dry nitrogen and then added dropwise to 8.35 g. (0.03 mole) of triphenylchlorosilane dissolved in 100 ml. of THF. The reaction mixture was stirred for an additional 12 hr. at room temperature and then hydrolyzed by pouring it into a stirred, saturated aqueous ammonium chloride solution. The solids in the hydrolyzed mixture were removed by filtration. The organic fraction of the filtrate was separated from the aqueous fraction, dried over sodium sulfate, and concentrated on a rotary evaporator. The solid-residue thus obtained was identified as triphenylsilanol by its mixed m.p. with an authentic sample. The insoluble material from the hydrolyzed mixture was boiled with xylene, the whole filtered and the filtrate concentrated to give a small amount of white crystalline powder. A sample was heated in an open capillary and it turned yellow at $330-335^{\circ}$. Sintering and shrinking were noted at 380° and the compound melted with decomposition at

390-394°. The rest of the solid was recrystallized by means of a Soxhlet extraction apparatus with carbon tetrachloride as the solvent to give 3.0 g. (8.8%) of tetrakis(triphenylsilyl)tin. The X-ray powder diffraction pattern is very similar to that of tetrakis(triphenylstannyl)tin.

Anal. Calcd. for $C_{72}H_{60}Si_4Sn$: Si, 19.98; Si, 9.71; Sn, 10.26.
Found: Si_4Sn , 19.90, 19.91; Si, 9.16; Sn, 9.48, 9.63%

(B) From triphenylsilyllithium and stannic chloride (attempted)

Into a 500 ml. flask, equipped with a mechanical stirrer and a low temperature thermometer, 6.5 g. (0.025 mole) of stannic chloride and 100 ml. of sodium-dried pentane were placed. The mixture was cooled to -60° in a Dry Ice-acetone bath. Triphenylsilyllithium (0.1 mole) in THF was added dropwise to the vigorously stirred stannic chloride solution. The temperature of the reaction mixture was maintained at -60° throughout the addition and then allowed to slowly attain room temperature. Stirring at room temperature was continued over night and then the reaction mixture was hydrolyzed with 200 ml. of saturated aqueous ammonium chloride solution. The solid formed during the reaction was removed by filtration. After separation of the organic layer of the filtrate from the aqueous layer, the latter was extracted twice with diethyl ether. The solids were recrystallized in a Soxhlet extraction apparatus with xylene-carbon tetrachloride mixture as the solvent. Although the major portion was inorganic material, 2.4 g. (9.3%) of organic material was isolated and identified as hexaphenyldisilane (mixed m.p. $365-368^\circ$). The organic fraction, upon concentration, gave a small amount of triphenylsilanol (1.0 g., 3.62%), the major portion being unidentified polymeric material.

No tetrakis(triphenylsilyl)tin was isolated.

(C) From triphenylsilyllithium and tetravinyltin (attempted) Into a 500 ml. flask, 0.0925 mole of triphenylsilyllithium in 168 ml. of THF was placed and 4.45 g. (0.02 mole) of tetravinyltin in 30 ml. of THF added dropwise. No immediate reaction was observed. The reaction mixture was stirred at room temperature for 15 hr. and then the solvent was removed on a rotary evaporator. The residue was a reddish oil but after hydrolysis with dilute acid, the red color was discharged and a light yellow oil was obtained. After extraction of the aqueous mixture with diethyl ether, the organic fraction was separated and the ether removed on a rotary evaporator. Petroleum ether (b.p. 60-70°) was added to the residual oil. The mixture was allowed to stand over night and a small amount of solid melting at 149-153° was obtained. A mixed m.p. with triphenylsilanol was not depressed. The remainder of the oil was of a polymeric nature and was not further examined.

(D) From triphenylsilyllithium and tetraphenyltin (attempted) Into a 250 ml. flask, 4.27 g. (0.01 mole) of tetraphenyltin and 20 ml. of THF, were placed and 0.04 mole of triphenylsilyllithium in 90 ml. of THF, was added dropwise. The reaction mixture was stirred at room temperature over night, refluxed for 3 hr. and then hydrolyzed with aqueous ammonium chloride solution. After the usual work-up a yellowish solid (4.7 g.), melting over the range of 180-220° was obtained. This was recrystallized from a petroleum ether (b.p. 60-70°) and benzene mixture to give 4.0 g. (13.5%) of tetraphenylsilane, m.p. 235-236°. It was identified by mixed

m.p. with an authentic sample.

Preparation of tetrakis(triphenylstannyl)silane

Triphenyltinlithium was prepared by treating 46.3 g. (0.12 mole) of triphenyltin chloride with lithium in THF according to the published procedure (55a). Aliquots of the resultant solution were analyzed by the allyl bromide double titration method indicating a yield of 0.109 mole of triphenyltinlithium in 229 ml. THF (114).

The triphenyltinlithium/THF solution was decanted into another 500 ml. flask, 4.4 g. (0.026 mole) of silicon tetrachloride in 40 ml. of THF added dropwise. Stirring was continued for 24 hr. at room temperature and then the solvent was removed on a rotary evaporator. Benzene was added to the dry residue and the mixture was heated to dissolve any hexaphenylditin and tetrakis(triphenylstannyl)silane. The insoluble lithium chloride was removed by filtration. Concentration of the filtrate gave a mixture of hexaphenylditin and tetrakis(triphenylstannyl)silane. Both were redissolved in benzene and, upon standing, the hexaphenylditin crystallized. The tetrakis(triphenylstannyl)silane was precipitated out as a powder after further concentration of the benzene solution. This work-up of the reaction mixture gave 17.8 g. (42.4%) of hexaphenylditin, m.p. 226-230°, and 10.95 g. (29.7%) of tetrakis(triphenylstannyl)silane, m.p. 390-395° with decomposition. The X-ray powder diffraction pattern is very similar to that of tetrakis(triphenylstannyl)silane.

Anal. Calcd. for $C_{72}H_{60}SiSn_4$: $SiSn_4$, 35.22%; mol. wt. 1428.
Found: $SiSn_4$, 35.66%; mol. wt. (vapor pressure osmometer) 1442, 1451.

A repeat of the experiment using the same amount of starting materials was carried out. In the first experiment, silicon tetrachloride was added dropwise to triphenyltinlithium; in the second, the manner of addition was reversed. Work-up of the reaction mixture gave 27.5 g. (65.5%) of hexaphenylditin, identified by mixed m.p. with an authentic sample. No tetrakis(triphenylstannyl)silane was isolated.

Reaction of tetrakis(triphenylstannyl)silane with methyllithium (1:1 molar ratio)

Methyllithium (0.002 mole) in 1.47 ml. of diethyl ether was added dropwise with stirring to 2.85 g. (0.002 mole) of tetrakis(triphenylstannyl)silane in 50 ml. of THF. Heat was evolved during the addition. No attempt was made to cool the reaction mixture. After 10 minutes, 0.253 g. (0.002 mole) of benzyl chloride in 10 ml. of THF was added in one portion. The reaction mixture was hydrolyzed with ammonium chloride solution after it had been allowed to stir at room temperature for a further 30 minutes. Work-up gave 1.35 g. (50%) of hexaphenylditin, m.p. 226-230°. A mixed m.p. with an authentic sample showed no depression.

Preparation of tetrakis(triphenylgermyl)tin

Triphenylgermyllithium (0.64 mole) was prepared by treating 19.44 g. (0.032 mole) of hexaphenyldigermene with an excess of finely-cut lithium wire in 120 ml. of THF. The allyl bromide double titration indicated an 88.6% yield of triphenylgermyllithium (39). The unchanged lithium wire was removed by filtration.

To stannous chloride (3.6 g., 0.019 mole) in 100 ml. of THF, 0.057 mole of triphenylgermyllithium in 134 ml. of THF was added dropwise. The temperature of the reaction mixture was kept at 0° during the addition. Vigorous stirring was maintained to prevent the dense stannous chloride from settling to the bottom of the flask. The reaction mixture was stirred over night at room temperature and a light yellow precipitate was formed. The solution was decanted into an addition funnel under an atmosphere of nitrogen, and then added dropwise to triphenylchlorogermane (6.5 g., 0.019 mole). Stirring was continued for an additional 12 hr. and then the reaction mixture was hydrolyzed with 250 ml. aqueous ammonium chloride solution. The solid formed was removed by filtration, and the organic layer of the filtrate separated from the aqueous fraction. The organic fraction was dried over sodium sulfate and the solvent removed by distillation to give a solid residue which melted at 340° with decomposition. All the solids isolated in the work-up were combined and purified by recrystallization from xylene. The solubility of these solids in xylene was very low. A recrystallized solid melted with decomposition at 388-390°. Further recrystallization from xylene raised the m.p. to 407-410°, and the compound was identified as tetrakis(triphenylgermyl)tin (7.08 g., 27.0%). Also obtained was hexaphenyldigermane (2.75 g., 15.9%) m.p. and mixed m.p. 340-343°. The X-ray powder diffraction pattern of tetrakis(triphenylgermyl)tin is very similar to that of tetrakis(triphenylsilyl)tin.

Anal. Calcd. for $C_{72}H_{60}Ge_4Sn$: Ge_4Sn , 30.68. Found: $Ge\ Sn$, 30.89, 30.81%.

Attempted preparation of tetrakis(triphenylgermyl)germane by the treatment of triphenylgermyllithium with germanium tetrachloride

Triphenylgermyllithium (0.064 mole) in THF was prepared by treating 19.44 g. (0.032 mole) of hexaphenyldigermane with an excess of lithium in 120 ml. of THF. The allyl bromide double titration showed a yield of 0.0583 mole (91.0%) of triphenylgermyllithium. The solution was decanted into an addition funnel.

Into a 250 ml. flask were placed 3.3 g. (0.014 mole) of germanium tetrachloride and 10 ml. of THF. Triphenylgermyllithium (0.0583 mole) was added dropwise with stirring. Heat was evolved during the addition and solids were formed. The reaction mixture was stirred over night and then hydrolyzed with 200 ml. of aqueous ammonium chloride solution. After the usual work-up, 7.3 g. (42.7%) of hexaphenyldigermane, m.p. 340-342°, was obtained. It was identified by mixed m.p. with an authentic sample. Also obtained from the reaction mixture was a small amount of unidentified material melting at 244-248°. The X-ray powder diffraction pattern of this unidentified material showed no similarity to that of tetrakis(triphenylgermyl)tin.

Attempted preparation of tetrakis(triphenylsilyl)lead

(A) By treating triphenylsilyllithium with tetraphenyllead Triphenylsilyllithium (0.04 mole) in 100 ml. of THF was added dropwise to 5.15 g. (0.01 mole) of tetraphenyllead in 50 ml. of THF. Heat was evolved during the addition and solids were formed. The reaction mixture was stirred over night at room temperature and then at the reflux temperature for 2 hr. The mixture was hydrolyzed with aqueous ammonium

chloride solution and the insoluble greyish material was removed by filtration. A sample of this greyish material was heated in a Bunsen burner but it did not ignite. Hence the material was probably inorganic and was discarded. The organic fraction of the filtrate was separated from the aqueous fraction and, after drying over sodium sulfate, was distilled to give 4.7 g. of material melting at 230-235°. This solid was recrystallized from benzene to give 3.5 g. (33.6%) of tetraphenylsilane, m.p. and mixed m.p. 235-236°. The infrared spectrum of the compound was identical with that of an authentic sample of tetraphenylsilane. Some solids (3.4 g.) melting at 132-137° were also isolated from the reaction mixture. After several recrystallizations from petroleum ether (b.p. 60-70°) the m.p. was raised to 152-154° and the compound was identified by mixed m.p. as triphenylsilanol.

(B) By treating triphenylsilyllithium with lead(II) chloride,
followed by triphenylchlorosilane Triphenylsilyllithium (0.046 mole) in 167 ml. of THF was added dropwise to 4.3 g. (0.0153 mole) of lead(II) chloride in 60 ml. of THF. The temperature of the reaction mixture was kept at -30° for 3 hr. and then 4.4 g. (0.015 mole) of triphenylchlorosilane in 20 ml. of THF was added. The reaction mixture was allowed to come to room temperature slowly and was then worked up anhydrously by evaporation of the THF on a rotary evaporator. Sodium-dried benzene was added to the residue and the insoluble inorganic salts were removed by filtration. The benzene filtrate was again evaporated on a rotary evaporator and a semi-solid residue obtained. Petroleum ether (b.p. 60-70°) was added to the residue. The solid thus formed (3.5 g.) was

isolated by filtration and showed signs of decomposition at 240° , melting with decomposition at 290° . This compound was insoluble in boiling benzene, carbon tetrachloride or xylene. The infrared spectrum of the compound showed a phenyl-silicon absorption band at 8.95μ . The combined Si and Pb analysis gave 24.45% and 24.65% (based on 4 SiO_2 and 1 PbSO_4), the required value for Si_4Pb in $(\text{Ph}_3\text{Si})_4\text{Pb}$ being 26.50%. No further work was done to identify this compound.

Attempted preparation of tetrakis(triphenyllead)silane by the treatment of triphenylleadlithium with silicon tetrachloride

Triphenylleadlithium (0.1 mole) in 150 ml. of THF was added dropwise to 4.4 g. (0.025 mole) of silicon tetrachloride in 50 ml. of THF. After the reaction mixture had been stirred over night at room temperature, it was refluxed for 2 hr. and then worked up anhydrously by stripping the THF on a rotary evaporator. Sodium-dried benzene was added to the residue. After heating the benzene mixture to the reflux temperature, it was filtered to remove the inorganic salts. The benzene filtrate was again evaporated and a black solid residue was obtained. This residue was dissolved in a mixture of benzene and petroleum ether (b.p. $60-70^{\circ}$) and then decolorized with Norit-A. The final work-up gave 19.5 g. (37.1%) of solid which turned black at 163° and completely melted at 215° (dec.). A mixed m.p. with hexaphenyldilead did not change the melting behavior.

Preparation of tetrakis(trimethylsilyl)germane

A mixture of trimethylchlorosilane (52.1 g., 0.48 mole) and finely-cut lithium wire (8.4 g., 1.2 g.-atom) was introduced into a 500 ml.

flask. A small portion (12 ml.) of a germanium tetrachloride solution which contained 21.4 g. (0.1 mole) of germanium tetrachloride in 100 ml. of THF, was added. After the mixture had been stirred for about two minutes, heat was evolved indicating the start of a reaction and the rest of the germanium tetrachloride solution was then added dropwise. The reaction mixture was stirred for 12 hr. at room temperature and then the unchanged lithium wire was removed by filtration through a funnel loosely packed with glass wool. The filtrate was hydrolyzed with 400 ml. of 10% hydrochloric acid and the brown insoluble material formed was removed by filtration. The organic layer was separated from the aqueous layer and, after drying over sodium sulfate, was distilled to remove the solvents. A white solid which had no definite melting point was obtained. It was soluble in petroleum ether (b.p. 30-40°) and in diethyl ether. When heated at 130°/3 mm., the solid sublimed. The sublimed material sintered and shrank at 275-285° and melted to a clear liquid at 290-295° in a vacuum-sealed capillary tube. Recrystallization from methanol and petroleum ether raised the m.p. to 296-299° in a vacuum sealed capillary. The yield was 4.0 g. (10.95%). The molecular weight of this compound, as determined by vapor pressure osmometer, was 367.5, and the required value for tetrakis(trimethylsilyl)germane is 365.37. The X-ray powder diffraction pattern of tetrakis(trimethylsilyl)germane is isomorphous with those of tetrakis(trimethylsilyl)silane and tetrakis(trimethylsilyl)tin.

Preparation of tetrakis(trimethylsilyl)tin

A mixture of trimethylchlorosilane (52.1 g., 0.48 mole), finely-cut lithium wire (8.4 g., 1.2 g.-atom) and 100 ml. of THF, was introduced into a 500 ml. flask. Stannic chloride (26.0 g., 0.1 mole) in 50 ml. of sodium-dried petroleum ether (b.p. 30-40°) was added slowly to the reaction mixture. Heat was evolved during the addition and the reaction mixture was kept at 56-60° by means of a water bath. The solution was stirred at room temperature for 12 hr. and then filtered through a funnel loosely packed with glass wool to remove the unreacted lithium wire. The filtrate was hydrolyzed with 250 ml. of 10% hydrochloric acid. The organic fraction of the filtrate was separated from the aqueous fraction, dried over sodium sulfate and then distilled to remove the solvents. The residue, weighing 2.3 g., melted over the range 200-220°. It was sublimed to give 1.9 g. (4.6%) of tetrakis(trimethylsilyl)tin, m.p. 245-248°. The molecular weight of this compound, as determined by vapor pressure osmometer, was 421 and 420, the required value for tetrakis(trimethylsilyl)tin being 411. The X-ray powder diffraction pattern of tetrakis(trimethylsilyl)tin was isomorphous with those of tetrakis(trimethylsilyl)silane and tetrakis(trimethylsilyl)germane.

Pentachlorophenyl Derivatives of Silicon and TinPreparation of pentachlorophenylmagnesium chloride

(A) From hexachlorobenzene and magnesium A 250 ml., three-necked flask was equipped with a mechanical stirrer, a condenser and an addition funnel. Into the flask, 3.6 g. (0.1 g.-atom + an excess of 50%)

of magnesium ribbon, which had been dried in an oven at 100°, and about 6 drops of dry ethylene bromide, were introduced. From the addition funnel, a small amount of the slurry, which contained 28.5 g. (0.1 mole) of hexachlorobenzene and 120 ml. of sodium-dried THF, was added to the flask and stirring was started. After about 5 minutes the reaction started as indicated by the evolution of heat and the appearance of a dark brown color. The rest of the hexachlorobenzene/THF slurry was added in small portions to maintain the reaction mixture at gentle reflux. After the addition of the slurry, the reaction mixture was allowed to stir at room temperature for 3 hr. to complete the reaction. The Grignard solution was then filtered through glass wool into an addition funnel in order to remove any unchanged magnesium. The solution gave a weakly positive Color Test I. Several 2 ml. aliquots of this solution were hydrolyzed and their total bases were determined by titrating against standard acid. The results ranged from 98% to 105%. VPC analysis of a hydrolyzed aliquot indicated the presence of pentachlorobenzene and 1,2,4,5-tetrachlorobenzene in the ratio of about 20:1. The results from the titration and the VPC analyses suggest that the mono-Grignard reagent can be formed in yields of 90% or more, and that it is accompanied by about 5% of the para-di-Grignard reagent.

(B) From hexachlorobenzene and benzylmagnesium chloride A 0.25 mole benzylmagnesium chloride solution was prepared according to published procedure (58) by reacting 31.6 g. (0.25 mole) of benzyl chloride with an excess of magnesium in 120 ml. diethyl ether. A total base titration gave a 95.2% yield of the Grignard reagent. A slurry, which

contained 28.5 g. (0.1 mole) of hexachlorobenzene and 100 ml. of THF, was placed in a 250 ml. flask. After stirring had been started, 0.1 mole of benzylmagnesium chloride in 75 ml. of diethyl ether was added over a 2 minute period. The reaction was very exothermic and the color of the reaction mixture was dark brown. Color Test I on the reaction mixture was negative 30 minutes after the addition of the benzylmagnesium chloride. The reaction mixture was carbonated by pouring it into a slurry of Dry Ice in ether. After it had come to room temperature, the solution was hydrolyzed with dilute acid. The organic fraction was separated and dried over sodium sulfate. Removal of the organic solvents on a rotary evaporator, gave 2.0 g. of pentachlorobenzoic acid, m.p. 204-206°, and a small amount of 2,3,5,6-tetrachlorobenzenedicarboxylic acid, m.p. 339-342°. The reported melting point of pentachlorobenzoic acid (115) and 2,3,5,6-tetrachlorobenzenedicarboxylic acid (116) are 208-209° and 343-345° (dec.), respectively. Pentachlorobenzoic acid was also obtained from the carbonation, followed by acid hydrolysis, of pentachlorophenyllithium and a mixed melting point of the acid obtained from the two routes showed no depression. However, the major product of this latter reaction was a polymeric brown material which melted between 340-345° and which was soluble in benzene at room temperature. No further work was performed to identify this polymeric product.

Preparation of (pentachlorophenyl)triphenylsilane

A THF solution which contained 0.1 mole of pentachlorophenylmagnesium chloride was added in a dropwise manner to a THF solution which contained 29.5 g. (0.1 mole) of triphenylchlorosilane in 30 ml. of THF.

The addition was completed within 30 minutes and heat was evolved during this time. The reaction mixture was allowed to stir over night at room temperature and then for 2 hr. at the reflux temperature. Upon cooling, it was hydrolyzed with 200 ml. aqueous ammonium chloride solution. The precipitate formed was filtered, and the organic fraction of the filtrate was separated from the aqueous fraction. It was dried over sodium sulfate and then concentrated to give a solid residue. The solid residues were combined and boiled with petroleum ether (b.p. 60-70°) to remove any hexachlorobenzene which might be formed from halogen-metal interconversion. The insoluble materials were then recrystallized from benzene to give 27.55 g. (50.5%) of (pentachlorophenyl)triphenylsilane. Two recrystallizations from benzene and decolorization with Norit-A were necessary to purify the compound to constant melting point of 217-220°. A small amount of hexachlorobenzene was also isolated and identified. The ultraviolet spectrum of (pentachlorophenyl)triphenylsilane in cyclohexane gave λ_{max} . 218 m μ ($\epsilon=64,930$), 297 m μ ($\epsilon=1040$), 307 m μ ($\epsilon=1250$).

Anal. Calcd. for C₂₄H₁₅Cl₅Si: Si, 5.51; mol. wt. 508.6. Found: Si, 5.67, 5.47%; mol. wt. (vapor pressure osmometer) 518. (When the Si analysis was carried out on (pentachlorophenyl)triphenylsilane which had been recrystallized from benzene, the results were 5.11 and 5.11%. These low results suggested that the compound formed a complex with benzene. When the compound was recrystallized from petroleum ether (b.p. 80-115°), the results obtained from two Si analyses were acceptable with errors of +3% and -1% from the calculated value.)

A second preparation of the compound was carried out. The scale of the preparation was doubled and the manner of addition was reversed, i.e. dropwise addition of triphenylchlorosilane to the Grignard reagent. The reaction mixture was worked up in the usual manner to give 73.0 g. (73%) of crude (pentachlorophenyl)triphenylsilane 210-215°. It was recrystallized from benzene to give 70 g. (70%) of pure (pentachlorophenyl)triphenylsilane melting at 217-220°. The compound was identified by mixed m.p. with an authentic sample.

Preparation of bis(pentachlorophenyl)diphenylsilane

A 0.1 mole pentachlorophenylmagnesium chloride solution in 100 ml. of THF was added slowly to 10.13 g. (0.04 mole) of diphenyldichlorosilane in 30 ml. of THF. An excess of 20% of the Grignard reagent was used in the reaction. Heat was evolved during the addition and solid particles precipitated out during the stirring period. After the reaction mixture had been stirred over night at room temperature it was refluxed for 1 hr. to ensure completion of the reaction. The suspension was hydrolyzed with aqueous ammonium chloride and the insoluble materials were separated by filtration. The organic fraction of the filtrate was separated from the aqueous fraction and dried over sodium sulfate. The organic solvents were removed on a rotary evaporator and a black oil remained. Upon addition of petroleum ether (b.p. 60-70°) to the black oil, solids were formed which showed signs of melting at about 100°, and at about 200°, white solids sublimed onto the inner wall of the capillary tube. At about 210°, melting of the solids occurred. This behavior suggested the presence of hexachlorobenzene and pentachlorobenzene. The

insoluble materials separated by filtration at the beginning also showed the same melting point behavior. All the solids isolated from the reaction were combined and recrystallized from benzene, using Norit-A to remove the black color. Upon concentration, solids were obtained. Petroleum ether (b.p. 60-70°) was added and the whole boiled to dissolve the hexachlorobenzene and pentachlorobenzene. The insoluble material was separated and redissolved in benzene. After two recrystallizations from benzene, the compound melted constantly at 239-240°. The total yield was 10.5 g. (38.5%) of bis(pentachlorophenyl)diphenylsilane. The ultraviolet spectrum in cyclohexane gave λ_{\max} . 221 m μ ($\epsilon=100,000$), 297 m μ ($\epsilon=1516$), 308 m μ ($\epsilon=1842$). The infrared spectrum (in CS₂) contained absorptions in μ at: 3.4, 7.7, 8.6, 9.15 and 11.6.

Anal. Calcd. C₂₄H₁₀Cl₁₀Si: Si, 4.13; mol. wt. 681. Found: Si, 4.00, 3.94%; mol. wt. (vapor pressure osmometer) 687.

Preparation of tris(pentachlorophenyl)phenylsilane (attempted)

A 0.1 mole pentachlorophenylmagnesium chloride solution in 100 ml. THF was added dropwise to 5.72 g. (0.027 mole) of phenyltrichlorosilane in 20 ml. THF. The reaction mixture was stirred for several hours at room temperature and then for 3 hr. at the reflux temperature. The solution was hydrolyzed with aqueous ammonium chloride and the organic fraction was separated from the aqueous fraction. After drying the organic fraction over sodium sulfate, it was distilled to remove the organic solvents. The black, polymeric residue was chromatographed on activated alumina, using a mixture of petroleum ether (b.p. 60-70°) and benzene as eluent, to give only hexachlorobenzene, m.p. 224-226°. The compound was

identified by mixed m.p. with an authentic sample. The other product was a polymeric oil which failed to give any crystalline material in several different organic solvents.

A second attempt to prepare tris(pentachlorophenyl)phenylsilane was made, but, only hexachlorobenzene was isolated and identified by mixed m.p. with an authentic sample. All attempts to isolate any crystalline compound from the black, polymeric residue were unsuccessful.

A third attempt was then made to prepare tris(pentachlorophenyl)-phenylsilane by the treatment of 5.3 g. (0.025 mole) of phenyltrichlorosilane in 30 ml. of THF with 0.1 mole of pentachlorophenyllithium. The pentachlorophenyllithium was prepared by treating 28.5 g. (0.1 mole) of hexachlorobenzene in 120 ml. of THF with 0.1 mole of n-butyllithium in 66 ml. of diethyl ether at -50° in a Dry Ice-acetone bath. Within 10 minutes of the addition of n-butyllithium Color Test II (111) was negative indicating the consumption of n-butyllithium. Color Test I (6) was positive. One hour after the addition of pentachlorophenyllithium to phenyltrichlorosilane, Color Test I was negative. The reaction mixture was worked up anhydrously by removing the organic solvents (THF and diethyl ether) on a rotary evaporator, leaving behind a black oil. Sodium-dried benzene was added to dissolve the organic material and the insoluble MgCl_2 was separated by filtration. The benzene filtrate was concentrated and a black oil obtained. Petroleum ether (b.p. $60-70^{\circ}$) was added to solidify the black oil. The resultant light brown solid had no definite m.p. and part of it sublimed on the walls of the capillary tube at about 160° . These solids were then sublimed to give 4.2 g. of white

hexachlorobenzene, m.p. 226-228^o, and was identified by mixed m.p. with an authentic sample. The remaining 9.3 g. of light brown solid which softened at 100^o and had no definite m.p., was dissolved in benzene to give an oil. No further attempts were made to identify this oil.

Reaction between pentachlorophenylmagnesium chloride and silicon tetrachloride

A 0.1 mole of pentachlorophenylmagnesium chloride solution in 100 ml. of THF was added dropwise to 4.25 g. (0.025 mole) of silicon tetrachloride in 25 ml. THF. During the addition a white solid precipitated out which was identified by mixed m.p. as hexachlorobenzene. The reaction mixture was stirred for three hours at room temperature and then for two hours at the reflux temperature. It was worked up anhydrously by removing the organic solvent on a rotary evaporator, and 35 g. of a mixture of magnesium chloride, hexachlorobenzene and some coupling products were obtained. Benzene was added to these solids and the mixture was boiled to dissolve the hexachlorobenzene. The insoluble material was separated by filtration and the benzene filtrate, upon concentration, gave 4.0 g. (14.5%) of hexachlorobenzene, m.p. 226-228^o, which was identified by mixed m.p. with an authentic sample. The insoluble material was boiled with xylene and filtered. The xylene filtrate, upon concentration, gave a small amount of solid melting at 380-386^o. This was recrystallized from benzene several times until the constant m.p. 402-404^o was obtained. The weight of the pure compound obtained was 0.77 g. (3%, based on tetrakis(pentachlorophenyl)silane). The ultraviolet spectrum in cyclohexane gave λ_{\max} . 220 m μ ($\epsilon=134,000$), 305 m μ ($\epsilon=12,100$), 314 m μ ($\epsilon=13,850$).

The infrared spectrum (in CS₂) contained absorptions in μ at: 3.3, 7.75, 8.6, 8.7, 9.0, 9.15 and 11.45.

Anal. Calcd. C₂₄Cl₂₀Si: Si, 2.69; mol. wt. 1026. Found: Si, 2.73, 3.19%; mol. wt. (mass spectrum) 954. (The compound was too insoluble to allow determination of its molecular weight osmometrically in benzene. The value of 954 obtained from the mass spectrum indicates that the compound has two chlorine atoms less than the required number.)

Preparation of (pentachlorophenyl)triphenyltin

A 0.05 mole pentachlorophenylmagnesium chloride solution in 80 ml. of THF was added slowly to 19.3 g. (0.05 mole) of triphenyltin chloride in 30 ml. of THF. The reaction mixture warmed slightly during the addition. The solution was stirred over night at room temperature and then for two hours at the reflux temperature. It was hydrolyzed with aqueous ammonium chloride solution. The organic fraction was separated and dried over sodium sulfate. Removal of the organic solvents on a rotary evaporator gave 24.25 g. of solids melting over the range of 180-190°. Petroleum ether (b.p. 60-70°) was added to these solids and the mixture was boiled to remove the hexachlorobenzene which was formed in the reaction. The less soluble material was separated by filtration. The petroleum ether filtrate was concentrated to give 3.1 g. (21.8%) of hexachlorobenzene melting at 225-228° and identified by mixed m.p. with an authentic sample. The less soluble material was recrystallized from benzene several times until a constant m.p. 170-172° was attained. The yield was 20.1 g. (67.3%) of (pentachlorophenyl)triphenyltin. The ultraviolet spectrum in cyclohexane gave λ_{\max} , 218 m μ ($\epsilon=85,830$),

292 m μ ($\epsilon=8,150$) and 307.5 m μ ($\epsilon=8,150$).

Anal. Calcd. C₂₄H₁₅Cl₅Sn: Sn, 19.82; mol. wt. 599. Found: Sn, 19.80, 20.20%; mol. wt. (vapor pressure osmometer) 582.

Preparation of bis(pentachlorophenyl)diphenyltin

Pentachlorophenylmagnesium chloride (0.1 mole) in 100 ml. of THF was added dropwise to 17.1 g. (0.05 mole) of diphenyltin dichloride in 20 ml. THF. The addition was made over 1 hr. The reaction mixture was allowed to stir over night at room temperature and then at the reflux temperature for 3 hr. The reaction mixture was worked up anhydrously by removing the organic solvent on a rotary evaporator. Sodium-dried benzene was added to the residue and the insoluble inorganic material was separated by filtration. The filtrate, upon concentration, gave a solid melting at 233-237°. After two recrystallizations from benzene, the m.p. was raised to 237-240°. The yield was 15.1 g. (39.7%) of bis(pentachlorophenyl)diphenyltin. The ultraviolet spectrum in cyclohexane gave λ_{\max} . 219 m μ ($\epsilon=116,900$), 291 m μ ($\epsilon=1,255$) and 301 m μ ($\epsilon=1,255$).

Anal. Calcd. C₂₄H₁₀Cl₁₀Sn: Sn, 15.36; mol. wt. 772. Found: Sn, 14.88, 14.95%; mol. wt. (vapor pressure osmometer) 841. (The low Sn analyses and the high result for the molecular weight determination suggested that the compound contained a small percentage of hexachlorobenzene or that the compound formed a complex with benzene. The sample was dried in a "drying piston" at 100° over night before the analyses were made.)

Reaction between pentachlorophenylmagnesium chloride and phenyltin trichloride

Pentachlorophenylmagnesium chloride (0.1 mole) in 100 ml. of THF was added slowly to 9.06 g. (0.03 mole) of phenyltin trichloride in 40 ml. sodium-dried xylene. Heat was evolved during the addition and solids were precipitated. The reaction mixture was stirred over night at room temperature and then for 3 hr. at the reflux temperature. The THF was removed from the reaction mixture and replaced by xylene. The mixture was refluxed for an additional 3 hr. and then filtered to separate the insoluble material, m.p. 400-401^o (0.8g.). The xylene filtrate, upon concentration, gave an oily residue. No further work was carried out with this black oil.

Preparation of tetrakis(pentachlorophenyl)tin

Pentachlorophenylmagnesium chloride (0.1 mole) in 100 ml. of THF was added dropwise to 4.0 g. (0.015 mole) of stannic chloride in 20 ml. of sodium-dried hexane. Heat was evolved and much white solid was formed. The reaction mixture was stirred at room temperature for 3 hr. and at the reflux temperature for 2 hr. At this stage, sodium-dried xylene was added and the THF was distilled off slowly. Again, the reaction mixture was refluxed for 2 hr. with xylene as the solvent. Finally, the solution was hydrolyzed with aqueous ammonium chloride solution and the insoluble material was separated by filtration. When heated in a capillary tube, it decomposed without melting at 300^o. It was insoluble in the common organic solvents and only slightly soluble in the high boiling xylene (about 0.5 g. per 100 ml. xylene). It was then extracted

several times with water and then ethanol to assure the complete removal of any inorganic salts. When a sample was ignited it burned, showing the presence of carbon. A sample was boiled in xylene and then filtered. The filtrate, upon concentration, gave some fine, light brown, powdery solids, m.p. 446-449° (decomposed to a black solid).

Anal. Calcd. C₂₄Cl₂₀Sn: Sn, 10.62; mol. wt. 1106. Found: Sn, 10.76, 10.56%; mol. wt. (mass spectrum) 1100 ± 10. (The compound was too insoluble to allow determination of its molecular weight osmometrically in benzene. The uncertainty of the molecular ion at 1100±10 of the mass spectrum was due to the upper limit of the usability of the machine. Confirmatory evidence was provided by a fragment ion cluster at 858 corresponding to loss of a pentachlorophenyl group.)

Reaction between pentachlorophenylmagnesium chloride and tetraethoxysilane

A 0.1 mole pentachlorophenylmagnesium chloride solution in 100 ml. of THF was added dropwise to 4.2 g. (0.02 mole) of tetraethoxysilane in 20 ml. of THF. The reaction mixture was stirred over night at room temperature and then for 3 hr. at the reflux temperature. The THF was removed on a rotary evaporator and replaced with sodium-dried toluene. The reaction mixture was again refluxed for 4 hr. Upon cooling, it was hydrolyzed with dilute HCl and the organic fraction was separated from the aqueous fraction. It was worked up in the usual manner to give an oily, black residue. Attempts to solidify this residue were unsuccessful, but it was finally sublimed at reduced pressure to give 2.0 g. of

pentachlorobenzene, m.p. 85-86°. It was identified by mixed m.p. and V.P.C. retention time with an authentic sample. No further work was done to identify the oil.

Reaction between pentachlorophenylmagnesium chloride and trichlorosilane

A 0.1 mole of pentachlorophenylmagnesium chloride solution in 100 ml. of THF was added dropwise to 4.3 g. (0.032 mole) of trichlorosilane in 25 ml. of THF. Heat was evolved during the addition and the reaction mixture turned black. After the reaction mixture had been stirred over night at room temperature, it was refluxed for 2 hr. Upon cooling, it was hydrolyzed with dilute acid. The organic fraction was separated from the aqueous fraction and worked up in the usual manner. The residue was a black, polymeric oil. V.P.C. analysis of this residue showed retention times corresponding to those of pentachlorobenzene and 1,2,4,5-tetrachlorobenzene. No further work was done to separate these compounds or to identify the polymeric material.

Reaction between methyltrichlorosilane and pentachlorophenylmagnesium chloride

A 0.1 mole of pentachlorophenylmagnesium chloride solution in 100 ml. of THF was added dropwise to 5.0 g. (0.033 mole) of methyltrichlorosilane in 20 ml. of THF. Solids started to precipitate out from the solution after half of the Grignard reagent had been added. At the end of the addition, part of the solids redissolved into the reaction mixture. The reaction mixture was stirred over night at room temperature and then refluxed for 1 hr. before it was hydrolyzed with dilute

acid. The organic fraction was separated and dried over sodium sulfate. Evaporation of the solvent on a rotary evaporator gave a semi-solid residue. Benzene was added to dissolve this residue and the solution was filtered. On standing, hexachlorobenzene crystallized out as needles and was identified by mixed m.p. with an authentic sample. After removing the hexachlorobenzene, the oily residue was chromatographed on neutral alumina. Using a mixture of benzene and petroleum ether (b.p. 60-70°) as eluent, crystalline solids were obtained, melting in the range 140-180°. Several recrystallizations from benzene and petroleum ether (b.p. 60-70°) finally raised the m.p. to 271-273°. The yield was 2.3 g. (8.5%) of tris(pentachlorophenyl)methylsilane. The ultraviolet spectrum in cyclohexane gave λ_{\max} . 223 m μ ($\epsilon=153,000$), 301 m μ ($\epsilon=30,600$) and 311 m μ ($\epsilon=36,300$).

Anal. Calcd. C₁₉H₃Cl₁₅Si: Si, 3.14; mol. wt. 793. Found: Si, 3.35, 3.33%; mol. wt. (vapor pressure osmometer) 811. (The determined molecular weight of 811 is +2% higher than the calculated value. This is within the allowable error for the osmometer. However, a small impurity of hexachlorobenzene might be in the sample as it was very difficult to separate from the product during the work-up.)

Reaction of (pentachlorophenyl)triphenylsilane with magnesium, followed by trimethylchlorosilane

A mixture of (pentachlorophenyl)triphenylsilane (7.3 g., 0.0134 mole) and magnesium (1.0 g., 0.04 g.-atom) was placed in a 250 ml. flask and about 10 ml. of THF was added from an addition funnel. About 5 drops of ethylene bromide was added to initiate the reaction. Heat was

evolved after 5 minutes and 75 ml. of THF was added slowly. The mixture was stirred at room temperature for 3 hr. and then decanted into an addition funnel, thus removing any unchanged magnesium. The solution gave a positive Color Test I and, when a 2 ml. aliquot was hydrolyzed and titrated, the result indicated a total base content of 109%.

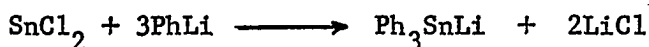
This Grignard reagent, (triphenylsilyl)tetrachlorophenylmagnesium chloride, was then added dropwise to 1.45 g. (0.0134 mole) of trimethylchlorosilane in 20 ml. of THF. The reaction mixture was stirred at room temperature for 3 hr. and then hydrolyzed with aqueous ammonium chloride solution. The organic fraction was separated from the aqueous fraction, dried over sodium sulfate and evaporated on a rotary evaporator to give a semi-solid residue. This residue dissolved in benzene at room temperature but crystallized as a needle-shaped solid from 95% ethanol. After two recrystallizations from 95% ethanol, the compound melted at 170-172° and amounted to 0.9 g. (12.3%) of (triphenylsilyl)-(trimethylsilyl)tetrachlorobenzene. The position of the trimethylsilyl group has not yet been established. The n.m.r. spectrum (cyclohexane as internal standard at 1.43 δ) showed two peaks at 0.565 δ and 7.40 δ indicative of methylsilyl protons and aromatic protons in a ratio of 1:1.71. The calculated ratio for (triphenylsilyl)(trimethylsilyl)-tetrachlorobenzene is 1:1.67. The ultraviolet spectrum of the compound in cyclohexane gave λ_{\max} 221 m μ ($\epsilon=60,000$), 305 m μ ($\epsilon=1883$) and 315 m μ ($\epsilon=2020$).

Anal. Calcd. for C₂₇H₂₄Cl₄Si₂: Si, 10.26. Found: Si, 10.15, 10.25%.

DISCUSSION

Preparation and Reactions of Ar_3MLi Reagents

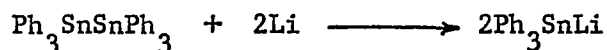
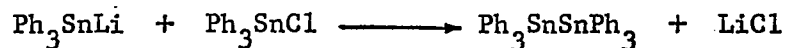
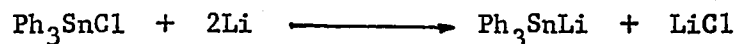
Triphenyltinlithium has previously been prepared from phenyllithium and stannous chloride in ether (43). The temperature of the reaction mixture has to be maintained at -10° throughout the preparation and the solution is heterogenous. Apart from these two limitations, the method gives a moderate yield of triphenyltinlithium (ca. 60%) and is a good example of the conversion of inorganic salt (SnCl_2) to an organometallic compound.



However, the recently reported (17) preparations of triphenylsilyl- and triphenylgermyllithium from triphenylchlorosilane and triphenylbromogermane in tetrahydrofuran (THF) prompted the use of this solvent for similar preparations of triphenyltinlithium and triphenylleadlithium from triphenyltin chloride and triphenyllead chloride, respectively. Subsequently, by allowing the THF solution of these halogen compounds to react with lithium at room temperature, homogenous solutions of the lithium derivatives were obtained in good yields ($> 90\%$).



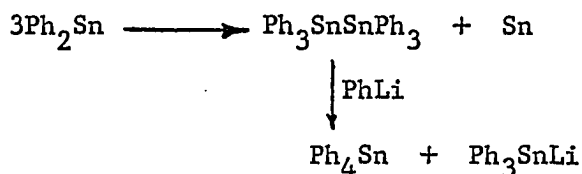
The mechanism of this reaction appears to follow the same course as that proposed for the formation of triphenylsilyllithium from triphenylchlorosilane (17, 117).



Hexaphenylditin (81.3%) was obtained when the reaction was arrested before the cleavage had begun. In fact, hexaphenylditin may be used to replace triphenyltin chloride if the presence of lithium chloride is undesirable in the triphenyltinlithium solution with no drop in yield. Attempts were made to replace THF with either 2,2,4,4-tetramethyltetrahydrofuran or ethylene glycol dimethyl ether as the solvent for the preparation of triphenyltinlithium from triphenyltin chloride and lithium. However, no indication of a reaction was observed when 2,2,4,4-tetramethyltetrahydrofuran was used as the solvent, the starting material being recovered quantitatively. With ethylene glycol dimethyl ether as the solvent, the reaction was very slow at room temperature. When external heat was applied, the triphenyltin chloride coupled to form hexaphenylditin which precipitated. No cleavage of the hexaphenylditin by lithium was observed after further heating and stirring. Thus, triphenyltinlithium must have been formed in the reaction but subsequent coupling with the triphenyltin chloride in the reaction mixture occurred. The yield of hexaphenylditin isolated was 72.4%.

When triphenyltinlithium, prepared from phenyllithium and stannous chloride, was hydrolyzed, tetraphenylditin (10%) and hexaphenylditin (14%) were obtained (45b). However, when triphenyltinlithium, prepared from triphenyltin chloride and lithium, was hydrolyzed, hexaphenylditin was obtained, the yields from two experiments being 44% and 35%. No

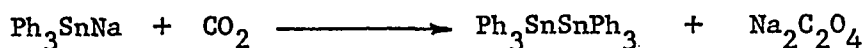
detectable amounts of tetraphenyltin were isolated. The formation of hexaphenylditin in these hydrolyses probably results from the triphenyltinlithium acting as a reducing agent. This has been proposed by Blake, Coates and Tate (118) for the formation of hexaphenylditin from triphenyltinsodium during carbonation and other reactions. Since tetraphenyltin was not formed on hydrolysis of triphenyltinlithium prepared directly from triphenyltin chloride, it was postulated that tetraphenyltin was formed, at least in part, during the preparation of triphenyltinlithium from phenyllithium and stannous chloride in ether. Subsequently, an ether solution of triphenyltinlithium was prepared from phenyllithium and stannous chloride as described (43) and filtered. A 4.1% of tetraphenyltin was obtained, together with a mixture of tetraphenyltin and hexaphenylditin. The result indicated that tetraphenyltin was present in the reaction mixture prior to hydrolysis. The mode of formation of the tetraphenyltin is not clear, but, since diphenyltin is an intermediate in the preparation of triphenyltinlithium by this method, the diphenyltin may disproportionate to tetraphenyltin and metallic tin. It has been observed that when diethyltin is heated above 150° , tin and tetraethyltin are formed (119). Diphenyltin, when refluxed with an excess of phenylmagnesium bromide, deposits metallic tin and forms hexaphenylditin (74). In one case, Böeseken isolated tetraphenyltin and dodecaphenylpentatin (74). Recent investigation in These Laboratories showed Böeseken's "dodecaphenylpentatin" to be the tetrakis(triphenylstannyl)tin. In turn, hexaphenylditin and tetrakis(triphenylstannyl)tin were cleaved by phenyllithium. The cleavage of hexaphenylditin



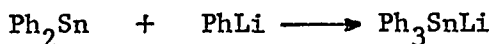
gave an 88.6% yield of tetraphenyltin (45a).

It should be emphasized that disproportionation of diphenyltin to tetraphenyltin and metallic tin, and cleavage of hexaphenylditin and tetrakis(triphenylstannyl)tin by phenyllithium may occur during the preparation of triphenyltinlithium from phenyllithium and stannous chloride. Since the direct preparation of triphenyltinlithium from triphenyltin chloride does not involve diphenyltin and phenyllithium as intermediates, such disproportionation and cleavage are not likely to occur. However, when a THF solution of triphenyltinlithium was refluxed or shaken at room temperature for about a week, tetraphenyltin was obtained.

When triphenyltinlithium, prepared directly from triphenyltin chloride, was carbonated with Dry Ice, a 49.6% yield of hexaphenylditin was obtained. No benzoic acid or addition products of benzoic acid could be isolated. Carbonation of triphenyltinlithium prepared from phenyllithium and stannous chloride has also been reported (45a), and in this case, the only compound formed was tetraphenyltin (4.7%). The mode of formation of hexaphenylditin and tetraphenyltin is believed to be similar to that of the hydrolysis reactions. Coates and co-workers isolated sodium oxalate and hexaphenylditin after carbonation of triphenyltinsodium (118), and explained their result by the reducing action of triphenyltinsodium.



In an attempt to explain the observation that triphenyltinlithium reacts with bromine to give diphenyltin dibromide, D'Ans and co-workers (44) proposed the existence of an equilibrium of diphenyltin and phenyllithium with triphenyltinlithium (44).



The fact that no benzoic acid or addition products of benzoic acid were isolated from these carbonation reactions tends to eliminate the possibility of such an equilibrium existing, since phenyllithium is known to give good yields of benzoic acid upon carbonation. Triphenyltin-carboxylic acid has not yet been reported and it is not known whether or not this compound is stable.

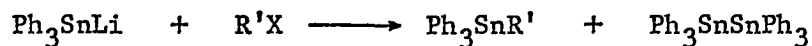
Tetraphenyltin has been isolated in varying amounts from reactions of several different alkyl halides with triphenyltinlithium prepared from phenyllithium and stannous chloride but none has been isolated from similar reactions from triphenyltinlithium prepared directly from triphenyltin chloride. For this reason, experiments were carried out to investigate the effect of phenyllithium on triphenyltinlithium prepared from hexaphenylditin using 1:1, 1:2, and 1:3 molar ratios, respectively, followed by the addition of benzyl chloride to derivatize any unchanged triphenyltinlithium. These results are shown in Table 7.

A satisfactory explanation for these results cannot be given at this time. The tetraphenyltin could arise, in part, by the cleavage with phenyllithium of hexaphenylditin remaining in the

triphenyltinlithium solution, by the coupling of triphenyltinlithium with any unchange bromobenzene present in the phenyllithium solution, and/or by the coupling of phenyllithium with triphenyltin hydride. The triphenyltin hydride might be formed during the course of the reaction, such as during the hydrolysis of triphenyltinlithium solution. Triphenyltin hydride has been reported to react with phenyllithium to give tetraphenyltin (120). However, the three proposed reactions would not be expected to be responsible for the formation of all the tetraphenyltin (48-74%) as high yields of triphenyltinlithium and phenyllithium were obtained in their respective preparations with very little hexaphenylditin and unchanged bromobenzene being present.

The stability of triphenyltinlithium in THF was studied by titrating aliquots of this solution according to the allyl bromide double titration procedure. The results are given in Table 8. It will be noted that the decomposition of triphenyltinlithium follows pseudo first order kinetics through the first 150 hr. and then the rate is accelerated, possibly by a catalytic effect of one of the products, until the deviation from first order kinetics is quite extreme. A comparison of these results for triphenyltinlithium with those of other organic-substituted Group IVB lithium derivatives has been reported (121).

An important reaction of triphenyltinlithium is with reactive organic halides, yielding unsymmetrical tetraorganotin compounds which are easily prepared in this way:



Hexaphenylditin was isolated from this reaction in varying amounts. With the more reactive chlorides such as benzyl chloride and allyl chloride, the yield of coupling products was about 70%, little of the halogen-metal exchange product (hexaphenylditin) being formed. When the corresponding bromides were used, the yield of coupling products decreased and that of hexaphenylditin increased. With polyhaloalkanes, the halogen-metal exchange product (hexaphenylditin) predominated. In the reaction of 1,2-dibromopropane with triphenyltinlithium, a 7.4% yield of tetraphenyltin and 55.6% of hexaphenylditin were obtained in one run, and a 38.5% yield of tetraphenyltin and 47.0% of hexaphenylditin in the second run. There is no satisfactory explanation for the formation of tetraphenyltin at this time. It is unlikely that 1,2-dibromopropane would cleave a phenyl group from triphenyltinlithium to form bromobenzene which would in turn couple with triphenyltinlithium to form tetraphenyltin.

It was observed in These Laboratories that 1,2,4-tribromobenzene was transformed to the symmetrical 1,3,5-tribromobenzene in the presence of triphenylsilyllithium.¹ When this reaction was repeated under the same conditions with triphenyltinlithium instead of triphenylsilyllithium, no sym-tribromobenzene was isolated; but a yield of 35.2% hexaphenylditin was obtained, together with a black oil.

It has been reported from These Laboratories (122) that triphenylsilyllithium reacts smoothly and promptly with trimethyl-, tri-n-butyl-,

¹H. Gilman and W. Steudel, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Information on the reaction of triphenylsilyllithium on 1,2,4-tribromobenzene. Private communication. 1960.

and tri-iso-butyl phosphates to give methyl, n-butyl, and isobutyltriphenylsilane in yields of 88, 97, and 88%, respectively. This method has the advantage of markedly reducing the formation of hexaphenylditin which may arise from phosphate-metal exchange (analogous to halogen-metal exchange). When triphenyltinlithium was treated with trimethyl phosphate, yields of 81 and 65% of methyltriphenyltin were obtained in two runs. In the second run, hexaphenylditin (13%) was also isolated. In two reactions of triphenyltinlithium with tri-n-butyl phosphate, the yields of n-butyltriphenyltin were 62 and 63%. This reaction affords a good method of preparation of unsymmetrical tetra-substituted organic compounds of the Group IVB elements.

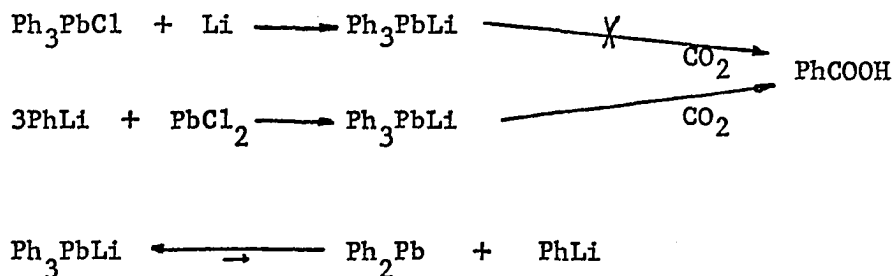
When triphenyltinlithium was treated with octaphenylcyclotetrasilane or with decaphenylcyclopentasilane, there was no indication of an immediate reaction. However, after these solutions had been refluxed, mixtures of tetraphenyltin and hexaphenylditin, respectively, were isolated. In one reaction, 72% of the starting material, octaphenylcyclotetrasilane, was recovered. Some unidentified products were isolated from these two reactions. The formation of tetraphenyltin might arise from either reflux of the triphenyltinlithium solution or the cleavage of the phenyl groups of the starting materials by triphenyltinlithium.

Triethyltinlithium has been prepared in These Laboratories (46) by the treatment of stannous chloride with three molar equivalents of ethyllithium, the reagent having been characterized by the formation of the derivative, tetraethyltin, in yields of 68.6 and 72.6%. The object of the present work was to prepare this reagent from triethyltin chloride

and lithium in THF and to find out whether the allyl bromide double titration could be applied for its analysis. The triethyltinlithium solution gave a positive Color Test I and weak Color Test II. This observation indicates the presence of triethyltinlithium and absence of ethyllithium. The allyl bromide double titration indicates yields of 65.2 and 64.0% of triethyltinlithium.

Triphenylleadlithium can be prepared in a similar manner as that for triphenyltinlithium by direct reaction of triphenyllead chloride and lithium in THF. The reaction with benzyl chloride proceeded with ease to give a good yield of benzyltriphenyllead (98.2%). When triphenylleadlithium, prepared by the direct method, was carbonated, benzoic acid was not detected and hexaphenyldilead was isolated.

Similarly, carbonation of triphenyltinlithium gave only hexaphenylditin and no benzoic acid was isolated. These results are to be contrasted with the isolation of benzoic acid from the carbonation of triphenylleadlithium prepared from phenyllithium and lead(II) chloride. Thus, in the case of triphenylleadlithium prepared from triphenyllead chloride and lithium in THF, the equilibrium system, if it exists at all, is displaced principally toward the triphenylleadlithium.



The Analysis of Organic-substituted Group IVB Lithium Compounds

The available methods of analysis for organometallic compounds have been investigated in relation to their suitability for estimation of organic-substituted Group IVB lithium compounds. It was found that the standard benzyl chloride double titration procedure (64, 65) for the analysis of organolithium compounds could not be applied to the analysis of R_3MLi type of compounds ($M = Si, Ge, Sn$ and Pb). The values obtained by this method were 10-20% lower and with no precision, than those obtained by the double titration procedure using other alkyl halides and polyhaloalkanes. Another method, using the *n*-butyl bromide-Volhard procedure (71) generally gave lower results and was inconvenient for normal work in the laboratory. It involved the use of three standard solutions (sulfuric acid, silver nitrate and thiocyanate) and the ferric alum end-point was difficult to detect for the tin and the lead-lithium derivatives. The object of this portion of the work was to develop a simple and convenient, yet accurate and precise method, for the analysis of organic-substituted Group IVB lithium compounds in the presence of lithium alkoxides and lithium oxide.

In the investigation of the double titration procedure for the analysis of organolithium compounds (72), a series of nineteen different substituted benzyl halides, alkyl halides and polyhaloalkanes was employed as potentially better organolithium consuming reagents than benzyl chloride. The first significant results were those obtained with phenyllithium, where the double titration values with several different halides were compared with the amount of tetraphenyltin formed on

treatment with triphenyltin chloride. It was concluded that, among the halides so far investigated, the titration values obtained with 1,1,2-tribromoethane were in closest agreement with actual concentration, whereas those with allyl bromide were several percent lower (72).

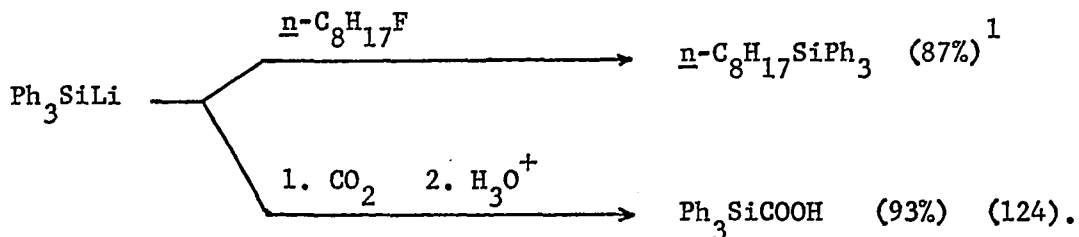
The investigation was then extended to include organic-substituted Group IVB lithium compounds, although it is difficult to assess a method of analysis when solutions of known concentration cannot be prepared. The ideal condition of preparing an organometallic compound is as solutions in hydrocarbon solvents under conditions rigorously controlled to exclude oxygen and moisture. In this way the amount of base from alkoxides is minimized by the lack of solvent cleavage and also by the low solubility of lithium alkoxides in hydrocarbons, so that the alkyl-lithium compound is almost the sole contributor to the total base content. Under these circumstances the titration of an aliquot previously caused to react with a halide should show very little base, a condition fulfilled very well by allyl bromide (72).

Recently it has been shown from competitive reactions (123) that the coupling reactions of triphenylsilyllithium with monohalosilanes is more facile than those of n-butyllithium or phenyllithium. Although this system is different from that existing in the double titration, it seems reasonable to suppose from the evidence above that the reaction of an organic halide with triphenylsilyllithium should go to completion if the same reaction is essentially complete with n-butyllithium and phenyllithium. It has been shown that the reactions of triphenylsilyllithium with alkyl bromides proceed largely through halogen-metal interconversion,

followed by a coupling reaction (22); however, the destruction of the Si-Li bond should still be complete.

Following the above conclusions, the present investigation was begun using the better titrating reagents previously tried (72). A given preparation of an R_3MLi compound was analyzed using several different halides in the double titration procedure as well as by the *n*-butyl bromide-Volhard method. The results of some of these determinations are shown in Tables 9-13.

It should first be noted that there is considerable reason to believe that the preparations of the R_3MLi compounds are accomplished in good yield. The particular case of triphenylsilyllithium has been investigated most thoroughly. It is common for products of reactions with triphenylsilyllithium to be isolated in yields of 80% or more, as illustrated in the following reactions. A particularly good method for forming derivatives of silyllithium compounds is the reaction with a trialkyl phosphate (122). With this reaction, yields in excess of 85% are normally obtained, and in one case a yield of 97% was reported (122). Another observation pointing to the same conclusion is that hexaphenyldisilane is not isolated in reactions of triphenylsilyllithium prepared from the



¹H. Gilman and G. M. Dappen, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Information on the reaction of triphenylsilyllithium with *n*-octyl fluoride. Private communication. 1959.

Table 9. Analyses of triphenylsilyllithium in tetrahydrofuran using the double titration procedure with several different organic halides and the Volhard procedure

| Halide | Yield, % | | | | |
|--|----------|--------|-------|-------|-------|
| | Run 1 | Run 2 | Run 3 | Run 4 | Run 5 |
| None | 139.7 | 128.0 | 134.8 | 134.8 | 112.2 |
| | 139.3 | --- | 135.7 | 134.8 | 112.4 |
| Allyl bromide | 81.2 | 91.7 | 87.0 | 91.6 | 95.6 |
| | 83.0 | 92.9 | 84.2 | 87.5 | 94.7 |
| <u>n</u> -Butyl bromide | 70.6 | 86.6 | 62.6 | 80.8 | 86.1 |
| | 76.0 | --- | 64.6 | 77.7 | 86.0 |
| Ethylene bromide | 93.0 | +100.0 | 134.0 | 95.4 | --- |
| | --- | --- | 135.3 | 104.5 | --- |
| Benzyl chloride | 60.7 | 82.2 | 63.7 | --- | 87.5 |
| | 61.9 | --- | 66.6 | --- | --- |
| 1,1,2-Tribromoethane | 120.5 | --- | --- | --- | --- |
| | 113.3 | --- | --- | --- | --- |
| Benzoyl chloride | 116.1 | --- | 117.4 | --- | --- |
| | 119.9 | --- | 119.3 | --- | --- |
| <u>n</u> -Butyl bromide- Volhard | 68.3 | 85.6 | 63.5 | --- | 87.8 |
| | 73.3 | --- | 69.4 | --- | 88.2 |
| Ethylene bromide- Volhard | --- | 93.1 | 143.4 | --- | --- |
| | --- | 96.6 | 141.2 | --- | --- |
| Derivative from tri- <u>n</u> -butyl phosphate | --- | 96.0 | 72.2 | --- | 92.6 |

Table 10. Analyses of triphenylgermyllithium in tetrahydrofuran using allyl bromide double titration

| Run | Total base (%) | Allyl bromide (%) |
|----------------|----------------|-------------------|
| 1 | 127.9 130.1 | 79.2 78.7 |
| 2 | 119.8 121.0 | 89.0 89.6 |
| 3 | 139.5 140.1 | 85.4 85.4 |
| 4 | 117.8 119.0 | 83.2 82.5 |
| 5 | 122.0 122.0 | 87.6 86.9 |
| 6 ^a | 113.0 --- | 74.5 --- |

^aRun 6: triphenylgermyllithium prepared from tetraphenylgermane and lithium.

Table 11. Analyses of triphenyltinlithium in tetrahydrofuran using the double titration procedure with several different organic halides, and the Volhard procedure

| Halide | Yield, % | | | | | |
|-------------------------------------|----------|-------|-------|-------|-------|-------|
| | Run 1 | Run 2 | Run 3 | Run 4 | Run 5 | Run 6 |
| None | 118.4 | 116.9 | 136.3 | 131.5 | 119.1 | 117.1 |
| | 118.1 | 117.3 | 137.0 | 132.7 | 118.8 | 119.0 |
| Allyl bromide | 93.1 | 94.4 | 95.0 | 99.0 | 96.0 | 93.5 |
| | 95.0 | 93.6 | 95.5 | 97.8 | 96.2 | 93.7 |
| <u>n</u> -Butyl bromide | 76.5 | 86.6 | --- | --- | 83.9 | 86.6 |
| | 72.9 | 85.5 | --- | --- | 83.8 | --- |
| Benzyl chloride | 74.4 | 90.9 | --- | --- | --- | --- |
| | 75.5 | 88.1 | --- | --- | --- | --- |
| Ethylene bromide | 83.6 | 90.5 | 92.5 | --- | --- | --- |
| | 80.2 | 90.0 | 91.5 | --- | --- | --- |
| 1,1,2-Tribromoethane | 86.6 | --- | --- | --- | --- | --- |
| | 87.1 | --- | --- | --- | --- | --- |
| Allyl bromide- Volhard | 90.1 | 94.0 | --- | --- | --- | --- |
| | 97.3 | 97.8 | --- | --- | --- | --- |
| <u>n</u> -Butyl bromide- Volhard | 89.0 | 86.0 | --- | 98.0 | 86.1 | 93.1 |
| | 86.4 | 82.9 | --- | 98.2 | 90.0 | 93.1 |

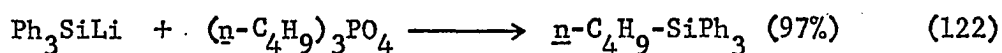
Table 12. Analyses of triphenylleadlithium in tetrahydrofuran using allyl bromide double titration

| Run | Total base (%) | Allyl bromide (%) |
|-----|----------------|-------------------|
| 1 | 155.0 | 101.0 |
| 2 | 199.0 | 128.0 |
| 3 | 184.0 | 110.0 |
| 4 | 183.2 | 102.0 |
| 5 | 173.3 | 117.6 |
| 6 | 136.4 | 91.5 |
| 7 | 126.0 | 104.1 |

Table 13. Analyses of R_3M-Li using the allyl bromide double titration procedure

| Compound | Total base (%) | Allyl bromide double titration (%) |
|--------------|----------------|------------------------------------|
| $MePh_2SiLi$ | 113.1 | 92.0 |
| | 112.4 | ----- |
| | 119.3 | 85.9 |
| | 119.3 | 84.7 |
| | 112.8 | 73.9 |
| | 113.8 | 74.8 |
| $Me_2PhSiLi$ | 91.2 | 52.7 |
| | 92.1 | 52.7 |
| Et_3SnLi | 123.5 | 65.2 |
| | 125.0 | 64.0 |
| | 82.6 | 57.1 |
| | 128.0 | 29.8 |
| | | |

disilane unless some side-reactions such as halogen-metal exchange, can take place. This is of particular significance because hexaphenyldisilane has a low solubility in tetrahydrofuran, making it difficult to overlook and very easy to isolate. There is reason to believe that



preparations of other R_3MLi compounds are equally good. In one study (117, 125) the Ph_3MLi ($\text{M} = \text{Si, Ge, Sn, Ph}$) reagents were prepared by lithium cleavage of the $\text{Ph}_3\text{M-MPh}_3$ compounds and also by direct reaction of lithium with the appropriate chloride, the resulting solutions being treated with benzyl chloride. The yields of benzyl derivatives were all good, except for triphenylsilyllithium, probably because of halogen-metal interconversion followed by formation of hexaphenyldisilane. The reaction conditions were not rigorously controlled in this study, nor was any attempt made to maximize the yields of the preparations. A further fact of some importance is that decomposition of R_3MLi compounds through reaction with the solvent (THF) is reasonably slow (71).

The observation above lead to the conclusion that titrations of fresh R_3MLi preparations may be expected to show yields consistently above 90%.

The data in Table 9 show high yields of triphenylsilyllithium in most cases and in general the observed yield is higher with the allyl bromide double titration than with the n-butyl bromide-Volhard analysis. In one preparation, the 1,1,2-tribromoethane double titration indicated yields of 120.5% and 113.3% while the allyl bromide double titration

indicated 81.2% and 83.0% of the theoretical value. Similarly, ethylene bromide double titration showed higher yields than those obtained by the allyl bromide double titration procedure and above 100% of the theoretical yield. The probable explanation for this observation is that the presence of organosilane compounds catalyze the reaction between ethylene bromide and the lithium alkoxides. The results obtained from the allyl bromide double titration agreed well with yields of derivatives from triphenylsilyllithium and tri-n-butyl phosphate.

It will be noticed from Tables 9-11 that the titration with no halide present gave values considerably more than 100% of the theoretical R_3MLi content. It has been suggested that this may be in part due to lithium alkoxide; however, the reagents were prepared in good yield, and cleavage of the solvent was slow. It is possible that the extra base content was due to very finely divided lithium metal, which would interfere with the titration. It seems unlikely, however, that anything of this nature takes place with allyl bromide, for, in the period of more than four years during which the allyl bromide method of assay has been in regular use in These Laboratories, no anomalous results have been encountered in a large number of preparations, principally of triphenylsilyllithium and triphenyltinlithium.

As cleavage of the solvent proceeds, the increasing concentration of lithium alkoxide is a major potential source of interference. It has been suggested (126) that there is no reaction between allyl bromide and lithium alkoxide under the conditions of the double titration. In the present work, lithium alkoxide solutions in diethyl ether were

treated in the same manner as the R_3MLi solutions to be analyzed. The results from the double titration using several organic halides indicated that a reaction took place to the extent of about 2% or less. Since the alkoxide concentrations in the R_3MLi solutions were considerably less than that of the alkoxide solution examined, the amount which would react with allyl bromide would be considerably less than 2% and, therefore, could be negligible.

The precision which may be expected with the allyl bromide double titration procedure of triphenylsilyl-, triphenylgermyl-, and triphenyltinlithium solutions is about 1%. Titrations of triphenylleadlithium in tetrahydrofuran solutions by the allyl bromide double titration have not proved satisfactory. The results in Table 12 indicate yields consistently higher than the theoretical value for triphenylleadlithium. In titrations of hydrolyzed aliquots without halide added, the end-point is not clearly defined by the phenolphthalein indicator. Also, the reaction of triphenylleadlithium with allyl bromide produces a highly colored solution which masks the end-point. Bromocresol Green seems to give a more distinct end-point.

The allyl bromide double titration procedure was employed for the analyses of methyldiphenylsilyllithium, dimethylphenylsilyllithium and triethyltinlithium. The results are shown in Table 13, and indicate that the method can be applied with precision of within 1%.

The analyses of phenyllithium using the double titration procedure with three different organic halides, and the gravimetric method with triphenyltin chloride were studied. The results, tabulated in Table 14,

Table 14. Analyses of phenyllithium using the double titration procedure with several different organic halides, and the gravimetric method by derivatization with triphenyltin chloride

| Halide | Yield, % | | | | | |
|-------------------------------|----------------|-------|-------|-------|-------|--------------------|
| | Run 1 | Run 2 | Run 3 | Run 4 | Run 5 | Run 6 ^a |
| None | 100.0 100.0 | 95.4 | 93.6 | 97.8 | 89.5 | 100.0 |
| Allyl bromide | 83.6 82.0 | 87.2 | 85.2 | 90.8 | 81.0 | 86.7 86.3 |
| Ethylene bromide | 88.6 89.2 | --- | --- | --- | --- | 93.6 93.4 |
| Benzyl chloride | 75.6 75.5 | 77.5 | 75.2 | --- | --- | 83.5 84.0 |
| Ph ₄ Sn derivative | --- | 85.7 | --- | 89.1 | 82.4 | --- |

^aPhenyllithium from Foote Mineral Company, Exton, Penna. in benzene/ether, 75%/25% by volume. Concentration: 20% or 2.1 mole.

agree well with those previously studied in These Laboratories (72). The results in Table 14 clearly show that ethylene bromide gives higher results than allyl bromide and benzyl bromide. Those from the ethylene bromide double titration checked well with the gravimetric method using triphenyltin chloride.

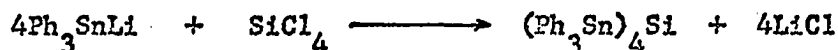
In conclusion it can be stated that, of the several different organic halides so far examined for the double titration procedure, allyl bromide gave the most reliable results which were in good agreement with the yields of derivatives obtained from these R_3MLi compounds by reaction with tri-n-butyl phosphate. This procedure also gives consistently good precision. The method is simple and convenient, and the chemicals needed are allyl bromide, standard dilute hydrochloric acid and phenolphthalein indicator all readily available in an ordinary research laboratory. Allyl bromide should be dried over phosphorus pentoxide and distilled before use; however, it retains its efficacy for several months. Its use may be extended to the titration of alkyllithium compounds, but accuracy will be less satisfactory. For more accurate results in the titration of alkyllithium compounds, the 1,2-dibromoethane double titration procedure should be employed.

Some Tetrakis Organo-Group IVB Compounds

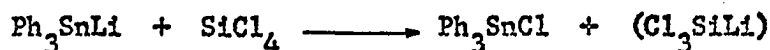
In connection with the studies of cationation and polymerization of compounds of the Group IVB elements, an attempt was made to synthesize a series of compounds with the general formula $(Ph_3M)M'$ in which M and M' were Si, Ge, Sn or Pb in all possible combinations. The formation of one

of these compounds, tetrakis(triphenylstannyl)tin, reported in the literature in 1923 by Boeseken and Rutgers (74) was from the reaction between stannous chloride and phenylmagnesium chloride, hexaphenylditin being the main product. The structural assignment was based on analyses and thermal decomposition behavior. Recently the preparation and properties of this compound were re-investigated in These Laboratories (76,77).

For the preparation of these compounds, $(Ph_3M)_4M'$, the usual method is to treat the tetrachloride of a Group IV element with four equivalents of Ph_3MLi ($M = Si, Ge, Sn$ or Pb) in tetrahydrofuran. Varying amounts of the compounds Ph_6M_2 have always formed as a by-product resulting from halogen-metal interconversion. For example, in the preparation of tetrakis(triphenylstannyl)silane, silicon tetrachloride was added dropwise to triphenyltinlithium. The work-up gave tetrakis(triphenylstannyl)silane (30%) and hexaphenyldisilane (42%).

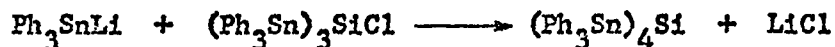


The hexaphenylditin isolated may be formed by halogen-metal interconversion according to the following equations.

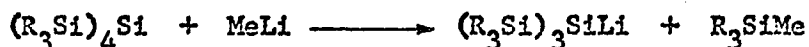


A slow rate of addition of silicon tetrachloride is important to minimize the formation of hexaphenylditin. In a second experiment on the same scale in which the manner of addition of the reactants was reversed, the reaction failed to give any tetrakis(triphenylstannyl)silane. Instead,

a yield of 50% of hexaphenylditin was obtained. By adding silicon tetrachloride dropwise to triphenyltinlithium, there was always an excess of triphenyltinlithium to couple with the silicon tetrachloride, this condition being especially important during the last stage, i.e., the addition of triphenyltinlithium to tris(triphenylstannyl)chlorosilane.



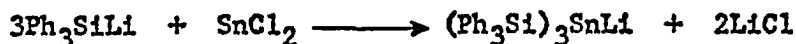
An attempt made to cleave one of the triphenyltin groups from tetrakis(triphenylstannyl)silane by methylolithium, resulted in the complete breakdown of the molecule, hexaphenylditin (50%) being isolated. Similar results have been noted (77) for the reaction between tetrakis(triphenylstannyl)tin and methylolithium. These observations are in contrast with those for the permethylated tetrakis analogs, as methylolithium is known to cleave tetrakis(trimethylsilyl)silane (86) and tetrakis(dimethylsilyl)silane (86) to give



tris(trimethylsilyl)silyllithium and tris(dimethylsilyl)silyllithium, respectively. However, the formation of tris(triphenylstannyl)tinlithium and tris(triphenylgermyl)silyllithium has also been reported. Tris(triphenylstannyl)tinlithium was prepared from triphenyltinlithium and stannous chloride (77), and tris(triphenylgermyl)silyllithium from the interaction of tris(triphenylgermyl)silane with lithium (127).

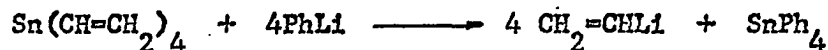
Several different methods were attempted for the preparation of tetrakis(triphenylsilyl)tin, but only in one case was the tetrakis compound isolated (8.8% yield). This was achieved by the reaction of

triphenylsilyllithium with stannous chloride, followed by the addition of triphenylchlorosilane,

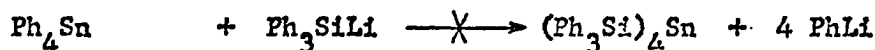
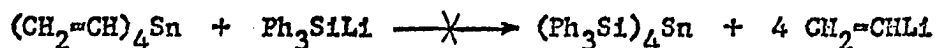


When four equivalents of triphenylsilyllithium was treated with stannic chloride, hexaphenyldisilane (9.3%) was isolated in addition to a large amount of unidentified polymeric material.

In order to overcome this undesired halogen-metal interconversion, it was proposed that tetraphenyltin or tetravinyltin be used in place of stannous chloride or stannic chloride in the preparation of tetrakis compounds with tin as the central atom. This is based on the fact that symmetrical organotin compounds are cleaved by organolithium reagents (128,129). When phenyllithium reacts with tetravinyltin, in ether or hydrocarbon solvents, tetraphenyltin is precipitated almost quantitatively (129). This is a very satisfactory method of preparing vinylolithium. Attempts were made to react triphenylsilyllithium with tetravinyltin, and



triphenylsilyllithium with tetraphenyltin. However, these two reactions



failed to give any tetrakis compound. Triphenylsilanol and hexaphenyldisiloxane were isolated from both of these reactions.

An attempt was made to prepare tetrakis(triphenylgermyl)germane by the treatment of four equivalents of triphenylgermyllithium with germanium tetrachloride, but only hexaphenyldigermene (42.7%) was isolated. Similarly, several unsuccessful attempts were made to prepare tetrakis(triphenylsilyl)lead by the treatment of triphenylsilyllithium with tetraphenyllead, and by the treatment of triphenylsilyllithium with lead(II) chloride, followed by triphenylchlorosilane. Indeed, no compound has yet been prepared which contains a lead-silicon bond. Several workers have unsuccessfully tried to synthesize (triphenylsilyl)triphenyllead by the treatment of triphenylsilylpotassium with triphenyllead iodide, and by the treatment of triphenylleadlithium with triphenylchlorosilane (130).

For tetrakis compounds, $(R_3M)_4M'$, where the lateral groups are trimethylsilyl and the central atom is silicon, germanium or tin, only one method of preparation is available at this time. A mixture of trimethylchlorosilane, lithium and germanium tetrachloride in THF stirred at 56-60° for 12 hr. gave, after the usual work-up, a yield of 11% of tetrakis(trimethylsilyl)germane. Under similar reaction conditions, but starting with stannic chloride instead of germanium tetrachloride a yield of 13.3% of tetrakis(trimethylsilyl)tin was obtained. The properties of these two compounds, $(Me_3Si)_4Ge$ and $(Me_3Si)_4Sn$, are very similar to those of $(Me_3Si)_4Si$. These tetrakis compounds are very soluble in most organic solvents and can be purified by sublimation. Their X-ray powder diffraction patterns are isomorphous with that of $(Me_3Si)_4Si$ whose structure has been rigorously established.

Several attempts to prepare tetrakis compounds with trimethyltin as the lateral groups have been unsuccessful.

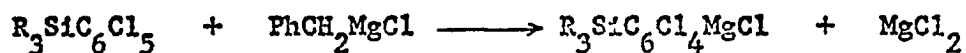
Perhalogenated Phenyl Derivatives of the Group IVB Elements

Pentachlorophenylmagnesium chloride was first reported in 1959 and was prepared by the reaction of a four-fold excess of magnesium turnings with hexachlorobenzene in tetrahydrofuran, using a small crystal of iodine and 2 ml. of ethyl bromide to initiate the reaction. The yield of the Grignard reagent, as characterized by hydrolysis to pentachlorobenzene, was 60% (101). This procedure was modified to a smaller scale, using 0.1 mole or less of hexachlorobenzene for each preparation. Furthermore, only a few drops of ethylene bromide were found necessary to initiate the reaction. When an acid-hydrolyzed aliquot of the Grignard reagent was analyzed by vapor phase chromatography, the spectrum showed a small band followed by a relatively large band. The area ratio of these two peaks was about 1:20. The retention times of the two bands corresponded to 1,2,4,5-tetrachlorobenzene and pentachlorobenzene, respectively. The total base titration of an aliquot from a regular preparation showed a yield of 105%. These observations indicated that about 5% of the reaction mixture was the para-di-Grignard reagent and 95% was the mono-Grignard reagent.

Pentachlorophenylmagnesium chloride was also prepared by halogen-metal exchange between hexachlorobenzene and benzylmagnesium chloride in THF. This method offers no basic advantage over the direct procedure using magnesium turnings. However, it should provide a procedure for

selectively forming a Grignard reagent of a pentachlorophenyl compound.

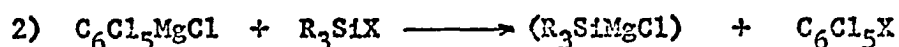
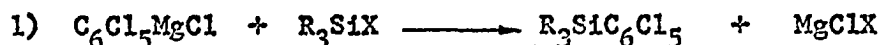
e.g.



The position with which the Grignard reagent will exchange has not yet been determined, but from steric and electronic considerations, exchange with the para-position would be expected.

Pentachlorophenylmagnesium chloride gives a positive Color Test I about 5 minutes after the addition of the iodine solution if a saturated Michler's ketone solution is used.

When pentachlorophenylmagnesium chloride is added to a THF solution of an organo-Group IVB element halide, two kinds of reactions operate simultaneously: 1) halogen-metal coupling, and 2) halogen-metal exchange.



In most cases, it is the halogen-metal coupling reaction that is desirable, and reaction conditions must be adjusted for maximum coupling with minimum exchange.

For the reaction between pentachlorophenylmagnesium chloride and triphenylchlorosilane, a 70% yield of the coupling product, (pentachlorophenyl)triphenylsilane was obtained. Only a trace amount of hexachlorobenzene was isolated. A slow rate of addition of triphenylchlorosilane to the Grignard reagent was crucial in maximizing the yield

of the coupling product.

When pentachlorophenylmagnesium chloride was treated with diphenyldichlorosilane, the yield of the coupling product, bis(pentachlorophenyl)diphenylsilane, was decreased to 35%. With phenyltrichlorosilane, no coupling product was isolated, a polymeric oil and hexachlorobenzene being obtained.

When silicon tetrachloride was added very slowly to pentachlorophenylmagnesium chloride, the major product was the exchange product, hexachlorobenzene (15%). A small quantity (0.8 g., 3% yield) of white crystals melting at 402-404° was also isolated. The compound was too insoluble to allow determination of its molecular weight osmotically in benzene. The mass spectrum showed the molecular ion at 954 indicating that the compound has two chlorine atoms less than required for tetrakis(pentachlorophenyl)silane. In order to avoid the halogen-metal exchange reaction, pentachlorophenylmagnesium chloride was treated with tetraethoxysilane instead of silicon tetrachloride. However, no tetrakis(pentachlorophenyl)silane was obtained.

Thus, from the above reactions of pentachlorophenylmagnesium chloride with four different chlorosilanes, it can be seen that the coupling products decrease as the number of chlorine atoms in the silane increase.

This general behavior has also been observed for the tin series. With triphenyltin chloride, the coupling product, (pentachlorophenyl)triphenyltin, was obtained in a 67% yield. However, for the bis and the tetrakis derivatives, the yields were 19% and 4%, respectively. Several

attempts to prepare tris(pentachlorophenyl)phenyltin have not been successful.

Some of the pentachlorophenyl derivatives of silicon and tin prepared, together with their m.p. and yields, are listed in Table 15.

Table 15. Pentachlorophenyl derivatives of Si and Sn

| Compound | M.p. | Percentage yield | Si or Sn cont. | | Mol. weight | |
|---|--------------------|------------------|----------------|----------------|-------------|----------------------|
| | | | Calcd. | Found | Calcd. | Found |
| $\text{Ph}_3\text{Si}(\text{C}_6\text{Cl}_5)$ | 217-220° | 70.0 | 5.51 | 5.67 5.47 | 508 | 518 |
| $\text{Ph}_2\text{Si}(\text{C}_6\text{Cl}_5)_2$ | 239-240° | 35.8 | 4.13 | 4.00 3.94 | 681 | 687 |
| $\text{MeSi}(\text{C}_6\text{Cl}_5)_3$ | 271-273° | 8.5 | 3.14 | 3.33 3.35 | 792 | 811 |
| $\text{Si}(\text{C}_6\text{Cl}_5)_4$ | 402-404° | 3.0 | 2.73 | 2.69 3.19 | 1016 | 954 ^a |
| $\text{Ph}_3\text{Sn}(\text{C}_6\text{Cl}_5)$ | 170-172° | 67.3 | 19.82 | 19.80 20.18 | 599 | 580 |
| $\text{Ph}_2\text{Sn}(\text{C}_6\text{Cl}_5)_2$ | 237-240° | 39.2 | 15.25 | 14.95 14.88 | 722 | 841 |
| $\text{Sn}(\text{C}_6\text{Cl}_5)_4$ | 446-449° (dec.) | 3.9 | 10.62 | 10.76 | 1106 | 1100±10 ^b |

^aThe mass spectrum gave the molecular ion at 954 which is two chlorine atoms less than the required number for $\text{Si}(\text{C}_6\text{Cl}_5)_4$.

^bThe uncertainty is due to the upper limit of the usability of the machine. Confirmatory evidence is provided by a fragment ion cluster at about 858 which corresponds to the loss of one pentachlorophenyl group.

The ultraviolet properties of these compounds are listed in Table 16. All showed absorption maxima at about 220 $m\mu$ with extraordinarily high molar absorptivities. It is noted that as the number of pentachlorophenyl groups in these compounds is increased, the molar absorptivity is increased in the same order. Furthermore, the tin compounds

Table 16. Ultraviolet properties of some pentachlorophenyl derivatives of Si and Sn^a

| Compound | Band position max. ¹ ($m\mu$) | Molar absorptivity ϵ |
|---|---|----------------------------------|
| $\text{Ph}_3\text{Si}(\text{C}_6\text{Cl}_5)$ | 218 | 64,930 |
| $\text{Ph}_2\text{Si}(\text{C}_6\text{Cl}_5)_2$ | 221 | 100,000 |
| $\text{MeSi}(\text{C}_6\text{Cl}_5)_3$ | 223 | 153,800 |
| $\text{Si}(\text{C}_6\text{Cl}_5)_4$ | 220 | 134,000 |
| $\text{Ph}_3\text{Sn}(\text{C}_6\text{Cl}_5)$ | 218 | 85,830 |
| $\text{Ph}_2\text{Sn}(\text{C}_6\text{Cl}_5)_2$ | 219 | 116,900 |
| $\text{Sn}(\text{C}_6\text{Cl}_5)_5^b$ | — | — |

^aSpectrograde cyclohexane was used as solvent.

^bThe compound was too insoluble in cyclohexane.

have higher molar absorptivities than the corresponding silicon compounds. At this time the following are possible explanations for these unusual results. 1) The effect of availability of d-orbitals of silicon and tin to interact with the π -electrons of the phenyl ring. (This effect is significant if one considers the high electronegativity of the chlorine atoms in the phenyl ring.) 2) The possibility of the unshared electron pairs of the ortho-chlorine atoms interacting with the empty d-orbitals of silicon or tin to form a five or more co-ordinated silicon or tin atom.

When (pentachlorophenyl)triphenylsilane was treated with magnesium in THF, a Grignard reagent was formed as evidenced by a positive Color Test I. This Grignard reagent was derivatized with trimethylchlorosilane and a compound melting at 171-172° was obtained. The NMR spectrum of the compound showed only methyl and phenyl protons directly attached to the silicon atoms. The calculated proton ratio for the compound, $\text{Ph}_3\text{SiC}_6\text{Cl}_4\text{SiMe}_3$, was 15 aromatic protons to 9 aliphatic protons (1.67:1) and the observed value was 1.71:1. The position in the benzene ring of the magnesium atom of the Grignard reagent has not yet been determined and work is presently directed on this line.

Suggestion for Further Research

During the course of this investigation, there have been numerous occasions to use Ph_3MLi reagents ($M = \text{Si, Ge, Sn, and Pb}$) to couple with an alkyl halide, polyhaloalkane, and Group IVB element halide and polyhalide. The usefulness of this coupling reaction was found to be

seriously complicated by the halogen-metal exchange reaction operating simultaneously. Therefore, a new synthetic route or modified reaction conditions to avoid the halogen-metal exchange reaction is needed. Recently, it has been found in These Laboratories¹ that Ph_3SiNa reacts with chlorosilanes to give improved yields of coupling products over those of Ph_3SiLi . A study could be made on the relative reactivities of these two classes of reagents, i.e., the Ar_3MLi and Ar_3MNa (where $\text{M} = \text{Si}, \text{Ge}, \text{Sn}, \text{and Pb}$). Trialkyl phosphate has been used to alkylate Ph_3MLi reagents to give good yields of coupling products, this method having an advantage over the method using alkyl halide which gives coupling as well as exchange products. A study could be made replacing the halides of Group IVB elements with some other functional groups, e.g., tetravinyltin, tetraethoxysilane, lead tetracetate, in reactions with Ph_3MLi reagents.

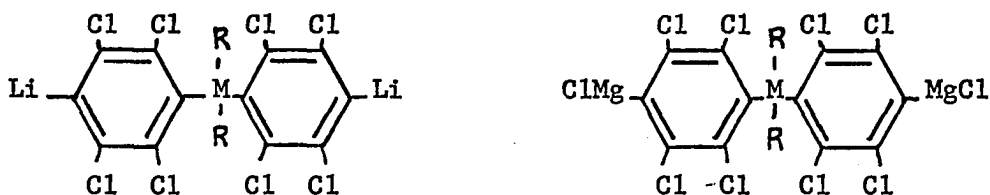
Attempts to prepare $(\text{Ph}_3\text{Si})_4\text{Si}$ by the interaction of Ph_3SiLi with SiCl_4 have not been successful and the only product isolated was hexaphenyldisilane, a halogen-metal exchange product. Since $(\text{Ph}_3\text{Pb})_4\text{C}$, in which four relatively large Ph_3Pb groups were bound to the relatively small central carbon atom has been reported, steric hindrance could not be the cause of the unsuccessful preparation of $(\text{Ph}_3\text{Si})_4\text{Si}$ as the Ph_3Si group is smaller than the Ph_3Pb group. If halogen-metal exchange reactions such as those with Ph_3SiLi and SiCl_4 could be overcome, the

¹H. Gilman, F. W. G. Fearon and R. L. Harrell, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. In the formation on triphenylsilylsodium. Private communication. 1966.

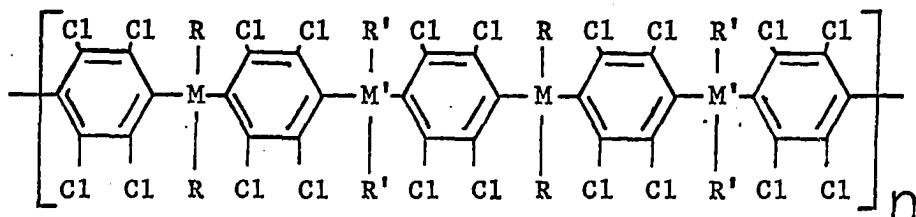
so far unknown $(Ph_3M)_4M'$ could be prepared.

Pentachlorophenyl derivatives of germanium and lead could be synthesized and it would be of interest to compare their properties with those of the silicon and tin derivatives.

It has been found that (pentachlorophenyl)triphenylsilane reacts with magnesium to give a Grignard reagent which, in turn, couples with trimethylchlorosilane to produce $Ph_3Si-C_6Cl_4-SiMe_3$. The position of the trimethylsilyl group has not yet been determined. Thus, further investigations could be conducted on $R_2M(C_6Cl_5)_2$ ($M = Si, Ge, Sn, \text{ and } Pb$) which might form bifunctional monomers such as



These bifunctional monomers could copolymerize with $R'M'Cl_2$ to form polymers such as



Finally, any intermediates of pentachlorophenyl and pentafluorophenyl derivatives such as $(C_6Cl_5)_3MCl$, $(C_6Cl_5)_3MBr$, $(C_6Cl_5)_3MI$ and

$(C_6Cl_5)_3MH$ which would serve as starting materials for the formation of $(C_6F_5)_3MLi$ and $(C_6Cl_5)_3MLi$ could be investigated.

SUMMARY

Homogenous solutions of triphenyltinlithium and triphenylleadlithium have been prepared from the corresponding chloride and lithium in tetrahydrofuran in good yields. Hexaphenylditin has also been cleaved to give the tinlithium derivative. When this triphenyltinlithium reagent was hydrolyzed and carbonated, only hexaphenylditin was obtained. In contrast to a previous report that tetraphenyltin was isolated from the hydrolysis and carbonation of triphenyltinlithium prepared from phenyllithium and stannous chloride, no tetraphenyltin was obtained. Reactions of this triphenyltinlithium reagent with alkyl halides and trialkyl phosphates gave good yields of alkyltriphenyltin derivatives. In contrast to the carbonation of triphenylleadlithium prepared from lead(II) chloride and phenyllithium in ether which gives benzoic acid, carbonation of triphenylleadlithium prepared from the corresponding chloride and lithium in tetrahydrofuran, gave no acid. Thus, if triphenylleadlithium in tetrahydrofuran disproportionates to diphenyllead and phenyllithium at all, the equilibrium is displaced principally toward the triphenylleadlithium.

A method for the quantitative analysis of triorganosilyl-, triorganogermyl-, triorganotinlithium compounds involving a double titration procedure using allyl bromide, ethylene bromide and several other reactive organic halides, has been investigated and compared with the n-butyl bromide-Volhard procedure. The allyl bromide double titration is considered to be more accurate and convenient than previous methods. A gravimetric method involving the quantitative reaction of triphenyltin

chloride with phenyllithium, serves as a comparison with the double titration procedure. The allyl bromide double titration procedure was found to be unsatisfactory for the analysis of triphenylleadlithium.

Several highly symmetrical catenated compounds of mixed atoms, such as Si-Ge, Ge-Sn, etc., in the neopentane structure have been prepared. Their structures have been determined, wherever possible, by elemental analyses, molecular weight determinations and X-ray powder diffraction patterns. It was found that the preparations of these compounds were complicated by halogen-metal interconversion operating simultaneously.

A modified preparation of pentachlorophenylmagnesium chloride in tetrahydrofuran giving an improved yield was developed. Reactions involving this Grignard reagent with several chlorosilanes and tin chlorides to form pentachlorophenyl derivatives of silicon and tin were investigated. The ultraviolet spectra of these compounds were determined and all found to possess an absorption band at about $220\text{ m}\mu$ with unusually high molar absorptivities.

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