1952

Comparisons of some organic compounds containing group IV-B elements

Tse Cheng Wu
Iowa State College

NOTE TO USERS

COMPARISONS OF SOME ORGANIC COMPOUNDS CONTAINING GROUP IV-B ELEMENTS

by

Tse Cheng Wu

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

Major Subject: Organic Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State College
1952

TABLE OF CONTENTS

Page

Page

Page

I. INTRODUCTION

Since the discoveries of organic compounds of silicon, germanium, tin, and lead in the last half of the nineteenth century, much information about the relationships of analogous compounds has appeared in the chemical literature. As a classical example, Mendeléeff[1] predicted, in 1871, that the hitherto missing element "eka-silicon"--germanium--would form a tetraethyl derivative boiling at 160° with a density of 0.96 based on the properties of analogous compounds of its neighboring elements. The synthesis of tetraethylgermane in 1887 verified his prediction in a surprising way.[2] However, soon after enough knowledge of these compounds had been accumulated, it was realized that the similarities among them are limited to a certain extent and in some cases are only superficial. Scattered information about the comparisons of certain specific types of organic compounds of Group IV-B elements (silicon, germanium, tin, and lead) is abundant but no comprehensive work has been found in this field.

---

[1] Mendeléeff, Ann., Suppl. 8, 196 (1871).

[2] C. Winkler, J. prakt. Chem. [2] 36, 204 (1887).

It has been the chief purpose of this work to generalize the properties of some types of organic compounds containing Group IV-B elements and to extend the studies to the unknown analogs in order to fill some of the gaps of missing information concerning the chemistry of these compounds.

In the historical part of this thesis an effort has been made to summarize the organic compounds containing Group IV-B elements with the viewpoint of comparing the similarities and differences in properties among the analogous types of compounds. These are discussed under various sections according to the nature of groups attached to the central Group IV-B elements. Important types are emphasized with examples of some individual compounds so that a general picture of this important branch of organic chemistry may be given.

During the course of this investigation, a method for the synthesis of a highly versatile organosilicon-metallic compound, triphenylsilylpotassium, has been developed. Subsequent studies have shown that compounds of this and related types are unusually good for the preparation of some difficultly obtainable organosilicon compounds. Also, it has been shown that triphenylsilylpotassium adds to ethylenic linkages in the same way as some very reactive organometallic compounds. A number of hexasubstituted disilanes were made for the studies of the possibility of dissociation. Several new water-soluble organotin compounds were prepared as a

result of the studies of introducing water-solubilizing groups into organotin compounds.

II. HISTORICAL

While organic compounds containing Group IV-A elements[3] (Ti, Zr, Hf, and Th) are relatively little known,[4] there is a tremendous amount of work reported on the organic compounds containing Group IV-B elements.[5] Silicon, as a second element of Group IV of the periodic table, belongs more definitely to the B-subgroup than to the A-subgroup since the inert gas structure (with two s-electrons and six p-electrons in the outermost shell of an atom) is satisfied by the atoms of the B-subgroup elements in their tetracovalent state but not by those of the A-subgroup elements. Many known organosilicon compounds are closely related to the analogous compounds of other elements of this subgroup. It is now known that silicon has an organic chemistry of its own but not one rivaling that of carbon.[6]

---

[3] In some periodic charts subgroups A and B from Group III to Group VII are named in the opposite manner.

[4] See H. Gilman, "Organic Chemistry", 2nd ed., John Wiley and Sons, New York, 1943, p. 557. See, also, R. G. Jones, Doctoral Dissertation, Iowa State College, 1941.

[5] A list of general references is given at the end of the Historical Part.

[6] For a general discussion of the relationships between organosilicon compounds and their carbon analogs see G. E. Dunn, Doctoral Dissertation, Iowa State College, 1951.

In the historical review only compounds containing at least one carbon-silicon, carbon-germanium, carbon-tin, or carbon-lead bond are discussed. Compounds in which all bonds are indirectly connected between carbon and Group IV-B elements such as lead tetraacetate, $Pb(OOCCH_3)_4$, are not included. Compounds classified in this category have the E atoms (E represents any Group IV-B element throughout this thesis) linked to carbon, hydrogen, halogen, oxygen, nitrogen, and other atoms. Due to the large number of compounds which might be included under this classification, it is impossible to discuss all of them in this survey. Therefore, only the important types are presented.

Generally speaking, as the atomic weight of the central element E increases, its bond become weaker. For example, chlorine and bromine attack the carbon-hydrogen bond of tetraalkylsilane rather than the carbon-silicon bond. In tetraalkylgermane they attack one of the carbon-germanium bonds while usually two alkyl groups are removed at once from the corresponding tin and lead compounds. Tetraphenylsilane boils undecomposed above 400°,[7] and can be nitrated, sulfonated, or halogenated, while tetraphenyllead decomposes at 270° and loses all its phenyl groups by heating with glacial acetic acid.[8]

---

[7] R. N. Lewis and A. E. Newkirk, J. Am. Chem. Soc., 69, 701 (1947).

[8] L. W. Jones and L. Werner, ibid., 40, 1257 (1918).

While there is a gradual change of the properties of analogous compounds from silicon to lead, a much greater gap can be found between germanium and tin than anywhere else in this group. Important properties in which the organic compounds of tin and lead differ from those of silicon and germanium are as follows:

(1) The monols R_3EOH (in this thesis R represents any organic radical, alkyl or aryl) and diols $R_2E(OH)_2$ of tin and lead are much less like alcohols. They are definitely basic and form salts with acids.

(2) While the monols of silanes and germanes lose water to form ethers such as hexaphenyldisiloxane, the organotin and organolead hydroxides usually give a mixture of R_2EO and R_4E compounds upon heating.

(3) Organic halides of tin and lead form complexes with ammonia and amines such as $(C_6H_5)_2SnCl_2.2NH_3$. Those of silicon and germanium usually react with these basic substances.

(4) Organotin and organolead halides are much more stable than the corresponding silicon and germanium analogs. Halides of the former group are only partially hydrolyzed by water in the absence of alkali.

(5) Mono- and di-fluorides of organotin and organolead compounds either melt or decompose at a high temperature and are somewhat soluble in water while the analogous compounds

of silicon and germanium are either liquids or low-melting solids insoluble in water.

(6) The E-E bond of organoditin and organodilead compounds gives indications of dissociation. Little is known about germanes, while negative results have been reported for organodisilanes.

It seems desirable to mention briefly the nomenclature of organic compounds of silicon, germanium, tin, and lead before the various types of compounds are discussed. For organosilanes the report by the Committee on Nomenclature, Spelling, and Pronunciation of the American Chemical Society[9] is adopted throughout this work. Post[10] gives a very good discussion on this subject in his book. Organogermanes are named with the same rules as those for the silanes. The shorter form "germ-" and "germyl" are used instead of "german-" and "germanyl", as proposed by O. H. Johnson.[11] Thus, corresponding to "silanol" and "disiloxane", the names "germanol" and "digermoxane" follow. Finally, in conformity with the nomenclature generally adopted for organotin and organolead compounds, the endings "tin" and "lead" are used instead of the older forms "stannane" and "plumbane".

---

[9] E. J. Crane, Chem. Eng. News, 24, 1233 (1946).

[10] H. W. Post, "Silicones and other Organic Silicon Compounds", Reinhold, New York, 1949.

[11] O. H. Johnson, Chem. Revs., 48, 259 (1951).

A. Tetraalkyl and Tetraaryl Compounds

Compounds containing four C-E bonds are included in this section. They are the simplest, most stable, and most common compounds of this series. Numerous simple (only one kind of radical) and mixed (more than one kind of radical)tetraalkyls and tetraaryls are known. The first organic compounds of silicon, germanium, tin, and lead synthesized are all of this type. In 1863 Friedel and Crafts[12] synthesized the first organosilicon compound, tetraethylsilane. Winkler[2], the discoverer of germanium, was also the first chemist who prepared tetraethylgermane. Löwig, in 1853, published an article on the first organotin compounds in the chemical literature.[13] He was also credited as the producer of the first organolead compound in the following year.[14] Since then the list of tetraalkyl and tetraaryl compounds has increased rapidly over a period of about one hundred years.

Tetraalkyl- and tetraaryl-silanes are made by the action of the Grignard reagent on silicon tetrachloride[12] or by the Fittig procedure.[15] The use of the Grignard reagent has the advantage that it allows stepwise introduction of organic

---

[12] C. Friedel and J. M. Crafts, Ann., 127, 28 (1863).

[13] C. Löwig, Ann., 84, 308 (1852).

[14] C. Löwig, J. prakt. Chem., 60, 304 (1853).

[15] A. Polis, Ber., 18, 1540 (1885).

radicals into silicon tetrachloride. By this method, Kipping[16] was able to prepare optically active organosilicon compounds such as benzylethylpropylsilanol.

The germanium analogs can also be prepared by the reaction of the Grignard reagent with germanium tetrahalide. A large excess of Grignard reagent must be used, or the main product would be of the type R_3GeX. Thus, even with 36 moles of phenylmagnesium bromide to 1 mole of germanium tetrabromide only a 40 per cent yield of tetraphenylgermane is obtained.[17] However, if the Grignard reagent is first converted into diphenylzinc before it is treated with germanium tetrabromide, high yields of tetraphenylgermane may be obtained.[17a] Johnson and Nebergall[18] observed that the use of organolithium compounds in the preparation of tetrasubstituted germanes often gives better yields than the Grignard procedure. Johnson and Harris[19] studied the reaction between triphenylgermane and phenyllithium and found that the principal product depended on the order of mixing the reactants. Thus, when dilute triphenylgermane is added to phenyllithium, the principal product is tetraphenylgermane.

---

[16] F. S. Kippling, J. Chem. Soc., 91, 209 (1907).

[17] G. T. Morgan and H.D.K. Drew, ibid., 127, 1760 (1925).

[17a] C. A. Kraus and L. S. Foster, J. Am. Chem. Soc., 49, 457 (1927).

[18] O. H. Johnson and W. H. Nebergall, ibid., 71, 1720 (1949).

[19] O. H. Johnson and D. M. Harris, ibid., 72, 5566 (1950).

When the reverse is carried out, over half of the product is hexaphenyldigermane. In 1931 Schwarz and Levinsohn[20] demonstrated optical activity of organogermanium compounds by preparing bromoethylisopropylgermane and resolving the mixture through the use of D-bromocamphorsulfonate.

Simple tetrasubstituted organotin compounds are made by the action of the Grignard reagent[21] or the organolithium compound[22] on stannic chloride, by the reaction of tin alloys with organic halides,[13] and by other methods.[23] Unsymmetrical compounds are best made from the reaction of the Grignard reagent with an organotin halide.[24]

The tetrasubstituted lead compounds are prepared by the reaction of lead chloride with an organic halide,[25] by the reaction of alkyl halides with sodium-lead alloy,[26] and by other methods.[27] Good yields of tetraalkylleads are obtained from the reaction of alkyllithium with a lead halide

---

[20] R. Schwarz and M. Lewinsohn, Ber., 64, 2352 (1931).

[21] W. J. Pope and S. J. Peachey, Proc. Chem. Soc., 19, 290 (1903).

[22] P. R. Austin, J. Am. Chem. Soc., 54, 3726 (1932).

[23] C. E. Arntzen, Doctoral Dissertation, Iowa State College, 1942.

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

[25] G. Grüttner and E. Krause, Ber., 49, 1415 (1916).

[26] A. Cahours, Ann., 122, 48 (1860).

[27] R. W. Leeper, Doctoral Dissertation, Iowa State College, 1942.

and an alkyl halide.[28]

The tetraalkyl compounds are mostly colorless, stable liquids. Going down the series, the boiling point, density, and refractive index of the tetraalkyl compounds increase from silicon to lead. The tetraphenyl compounds are all colorless solids with a slight decrease in melting point from silicon to lead. The mixed melting point depressions in these compounds are very small. However, the mixed melting point depression of $(C_6H_5)_4Ge + (C_6H_5)_4Sn$ is about three times as great as that of $(C_6H_5)_4Sn + (C_6H_5)_4Pb$.[29]

Among the mixed compounds, the aryl groups are, on the whole, less firmly attached than the alkyl groups. Diethyldiphenylgermane, for example, splits off phenyl groups rather than the ethyl groups on treatment with bromine to form diethyldibromogermane.[30] The firmness of attachment of carbon to tin in the reaction

$$R_2SnR'_2 + 2HCl \longrightarrow R_2SnCl_2 + 2R'H$$

increases in the order:[31]

cyclohexyl > phenyl > 1-naphthyl > p-anisyl > 1-thienyl.

---

[28]H. Gilman and R. G. Jones, J. Am. Chem. Soc., 72, 1760 (1950).

[29]H.D.K. Drew and J. K. Landquist, J. Chem. Soc., 1480 (1935).

[30]E. A. Flood, J. Am. Chem. Soc., 54, 1663 (1932).

[31]T. S. Bobaschinskaja and K. A. Kotscheschkov, J. Gen. Chem. (U.S.S.R.), 8, 1850 (1938), [C.A., 33, 5820 (1939)].

Krause and Schlöttig[32] found the order of decreasing strength of the carbon-lead bond to be:

cyclohexyl > ethyl > methyl > phenyl > p-tolyl > 1-naphthyl.

The reason that the cyclohexyl group is the most stable group in these compounds is by no means due to steric hindrance. The action of excess cyclohexyllithium on silicon tetrachloride gives only tricyclohexylchlorosilane, which does not accept an alkyl, phenyl, or benzyl group from the corresponding alkyllithium. On the other hand, germanium accommodates three cyclohexyl and one alkyl, phenyl, or benzyl group, but not a fourth cyclohexyl group.[18,33] The steric strain of the cyclohexyl group is completely absent in tin; tetracyclohexyltin is a stable compound melting at 263°.[24] The 1-naphthyl group seems to be less sterically hindered than the cyclohexyl group. Three 1-naphthyl groups can be put on silicon[34] and four on germanium.[35]

That steric hindrance alone cannot explain the difficulties of obtaining some organolead compounds is shown by the fact that tetra-1-naphthyltin is known[36] while the lead

---

[32]E. Krause and O. Schlöttig, Ber., 58, 427 (1925).

[33]W. H. Nebergall and O. H. Johnson, J. Am. Chem. Soc., 71, 4022 (1949).

[34]H. Gilman and C. G. Brannen, ibid., 73, 4640 (1951).

[35]R. West, unpublished work through the courtesy of Dr. E. G. Rochow.

[36]C. Quintin, Ing. chim., 14, 205 (1930)/C.A., 26, 2182 (1932)/.

analog is difficult to prepare,[37] although lead is larger than tin. Tri-tert-butyltin compounds are known whereas only organolead compounds containing two tert-butyl groups attached to lead have been synthesized.[39,40] Apparently, other factors such as reaction mechanism must be considered.[41]

Tetrasubstituted compounds of the type R_4E are in general stable to strong bases.[42] Tetra-n-propylsilane, for example, is stable on heating with a strong potassium hydroxide solution.[43] Tetraphenyltin is refluxed with alcoholic sodium hydroxide for three hours without appreciable decomposition.[23] On the other hand, this type of compound is cleaved rather easily by halogens and acids.[44] Tetraphenyllead is cleaved by bromine in pyridine at -50° to give almost quantitative

---

[37]H. Gilman and J. C. Bailie, J. Am. Chem. Soc., 61, 731 (1939).

[38]E. Krause and K. Weinberg, Ber., 63, 381 (1930).

[39]J. Robinson, Doctoral Dissertation, Iowa State College, 1929.

[40]H. Gilman and L. Balassa, Iowa State Coll. J. Sci., 3, 105 (1929).

[41]C. G. Brannen, Doctoral Dissertation, Iowa State College, 1951.

[42]L. S. Miller, Doctoral Dissertation, Iowa State College, 1950.

[43]C. Pape, Ann., 222, 354 (1884).

[44]H. Gilman and F. J. Marshall, J. Am. Chem. Soc., 71, 2066 (1949); see, also, F. J. Marshall, Doctoral Dissertation, Iowa State College, 1948.

yield of triphenyllead bromide.[45] Similarly, tetrasubstituted tins,[46] germanes,[47] and silanes[48] are cleaved by bromine to form the corresponding halides.

The hydrogenation of tetraalkyl and tetraaryl compounds of tin and lead have been studied, among other workers, by Gershbein and Ipatieff.[49] They concluded that the chief products are the hydrocarbons RH derived from the organic radicals with hydrogen and only a trace of the R-R compounds resulting from the coupling reaction.

While the hydrogenation of tetrasubstituted germanes is little known, hydrogenation of symmetrical and unsymmetrical silanes has been investigated by Dolgov and co-workers.[50,51,52] They found that by heating a number of

---

[45]G. Grüttner, Ber., 51, 1298 (1918).

[46]R. W. Post and H. R. Baker, J. Am. Chem. Soc., 55, 1112 (1933).

[47]W. R. Orndorff, D. L. Tabern, and L. M. Dennis, ibid., 49, 2512 (1927).

[48]A. Ladenberg, Ber., 40, 2274 (1907).

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

[50]V. Ipat'ev and B. N. Dolgov, Ber., 62B, 1220 (1929).

[51]B. N. Dolgov and Y. N. Volnov, J. Gen. Chem. (U.S.S.R.), 1, 330 (1931), /C.A., 26, 2168 (1932)/.

[52]B. Dolgov and Y. Volnov, Zhur. Obschei Khim., 1, 91 (1931), /C.A., 25, 4535 (1931)/.

simple and mixed silanes in hydrogen, decomposition and rearrangement take place in such a way that the more symmetrical compounds are produced. This symmetrization reaction is general and proceeds according to the scheme:

$2RSiR'_3 \longrightarrow R_2SiR'_2 + R'_4Si$ and $2RSiR'_3 + H_2 \longrightarrow 2RH + R'_3SiSiR'_3$

As an example, phenyltriethylsilane is hydrogenated to form benzene and hexaethyldisilane. The latter compound is also produced by heating tetraethylsilane at 350° under hydrogen pressure.[50,51]

There is another type of interesting reaction of the tetrasubstituted compounds, namely, the disproportionation reaction.[53] When an equimolecular mixture of tetramethyllead and tetraethyllead is treated with triethyllead chloride or aluminum chloride as a catalyst, a redistribution takes place to yield all of the five possible $R_nPbR'_{4-n}$ compounds, the amount of each product being dependent upon the law of probability. In other words, this is a completely random redistribution.[54] Similar observations have been obtained for organic compounds of tin and silicon.[55]

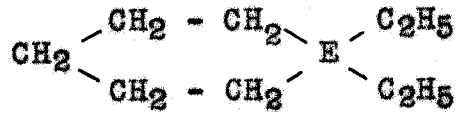
---

[53]For a general discussion see G. Calingaert and H. A. Beatty in H. Gilman's "Organic Chemistry", 2nd ed., John Wiley and Sons, New York, 1943, pp. 1807-1818.

[54]G. Calingaert, H. A. Beatty, and H. Soroos, J. Am. Chem. Soc., 62, 1099 (1940).

[55]G. Calingaert, H. Soroos, and V. Hnizda, ibid., 62, 1107 (1940).

Alicyclic compounds containing a Group IV-B element have been synthesized. Compounds of the type



are known for silicon,[56] Germanium,[57] Tin,[58] and lead.[59] The steric hindrance of these cyclic compounds increases from silicon to lead. When the tin and lead compounds are treated with bromine, the rings are broken with the formation of bromodiethyl-ω-bromopentyl-tin and -lead, respectively.

B. Halogen Compounds

Nearly every type of halogen compound (R_3EX, R_2EX_2, and REX_3) with nearly every element of Group IV-B and every halogen is known. The halogen compounds occupy a position of great importance in the organic chemistry of these elements because during the synthesis of various types of other compounds some halogen compounds are utilized. Very often the use of halogen compounds is the best if not the only way for the synthesis of organic compounds containing Group IV-B elements.

---

[56] A. Bygden, Ber., 48, 1236 (1915).

[57] R. Schwarz and W. Reinhardt, Ber., 65, 1743 (1932).

[58] G. Grüttner, E. Krause, and M. Wiernik, Ber., 50, 1549 (1917).

[59] G. Grüttner and E. Krause, Ber., 49, 2666 (1916).

A simple way of making organohalosilanes is by the treatment of an organic halide with silicon. Thus, when silicon is treated with an alkyl or aryl chloride at high temperature in the presence of a catalyst, a mixture of mono-, di-, and tri-halides is obtained.[60] The action of a limited amount of Grignard reagent on tetrahalosilanes furnishes a convenient way for the synthesis of partially alkylated or arylated halosilanes.[16,61] Direct addition of trichlorosilane to alkynes[62] in the presence of acetyl peroxide or ultraviolet light gives rise to substituted trichlorosilanes. Good yields of triethylsilyl bromide, chloride, and fluoride can be obtained by treating hexaethyldisiloxane with concentrated sulfuric acid and the corresponding sodium or ammonium halide.[63]

The preparations of organogermanium halides are in general similar to those of the silicon analogs.[11] For the preparation of triphenylgermyl bromide by the bromination of tetraphenylgermane, ethylene bromide is a better solvent than carbon tetrachloride.[47] With hydrogen bromide in the presence of aluminum bromide, one of the alkyl or aryl groups of

---

[60] E. G. Rochow, J. Am. Chem. Soc., 67, 963 (1945).

[61] W. F. Gilliam, H. A. Liebhafsky, and A. F. Winslow, ibid., 63, 801 (1941).

[62] E. W. Pietrusza, L. H. Sommer, and F. C. Whitmore, ibid., 70, 484 (1948).

[63] E. A. Flood, ibid., 55, 1735 (1933).

tetrasubstituted germane is replaced by bromine.[64] Dihalides of organogermanes are made by heating an organic halide with germanium in the presence of copper,[65] or by the action of bromine on dialkyldiarylgermane in which the aryl and not the alkyl groups are displaced.[30] Two phenyl groups of tetraphenylgermane can be substituted by bromine with ease, while diethyldibromogermane is obtained by bromination of tetraethylgermane in very low yield.[66] The dibromide and difluoride can be made by converting the dichloride to its oxide and treating with hydrobromic or hydrofluoric acid.[65] Organogermyl trichlorides are made by the action of alkyl or aryl halides on the cesium germanium chloride complex $Cs(GeCl_3)$.[67] Thus, ethyl iodide at 110° reacts with this complex to give a 60 per cent yield of ethyltrichlorogermane, and iodobenzene similarly reacts at 250° to give 80 per cent of phenyltrichlorogermane. Recently, Anderson developed a method of changing a chloride into an iodide.[68] Ethyltrichlorogermane is treated with diethylamine to give

---

[64]L. M. Dennis and W. I. Patnode, ibid., 52, 2779 (1930).

[65]E. G. Rochow, ibid., 69, 1729 (1947).

[66]C. A. Kraus and C. L. Brown, ibid., 52, 3690 (1930).

[67]A. Tchakarian and M. Lewinsohn, Compt. rend., 201, 835 (1935).

[68]H. H. Anderson, J. Am. Chem. Soc., 74, 1421 (1952).

ethyl-tri(diethylamino)-germane followed by conversion into ethyltriiodogermane using hydrogen iodide.

One of the most convenient methods for the preparation of organotin halides involves the heating of a mixture of tetraalkyl- or tetraaryl-tin with stannic halide.[69,70] By varying the ratio of these reactants, good yields of R_3SnX, R_2SnX_2, and $RSnX_3$ can be obtained. Another general method of preparation is to cleave tetrasubstituted tin compounds with halogens. Due to the ease of replacing two organic radicals at once by halogen, chlorine is seldom used for the preparation of a monohalide by this method. When bromine is used, the reaction must be carried out at a low temperature in order to minimize the formation of the dibromide. Iodine is preferable for less of the dihalide results. Organotin fluorides can be made by treating an alcoholic solution of either an R_3SnOH or R_3SnX compound with potassium fluoride. The organotin fluorides are so insoluble that R_3SnOH or R_3SnX compounds would precipitate the fluoride ions of potassium fluoride quantitatively.[71,72] Organotin dihalides can be made by treating the R_4Sn compound with halogens[24,36] or halogen acids,[31] by heating equivalent

---

[69]K. A. Kocheshkov, Ber., 66, 1661 (1933).

[70]K. A. Kocheshkov, J. Gen. Chem. (U.S.S.R.), 4, 1359 (1934), [C.A., 29, 3650 (1935)].

[71]E. Krause, Ber., 51, 1447 (1918).

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

amounts of tetrasubstituted tin with stannic halide,[69] or by reacting R_2SnO with halogen acids[13,24] or phosphorous pentachloride.[73] The trihalides are made by the action of hydrogen chloride on an alkylstannonic* acid,[74] by the action of alkyl iodides on $KSnCl_3$,[75] or by heating a mixture of R_4Sn or R_2SnX_2 with a stannic halide.[69]

The lead compounds, likewise, can be prepared from the reaction of an organolead compound with halogen or hydrogen halide. From the studies of Calingeart et al.,[76] a purer product of R_3PbCl can be obtained from the cleavage of R_4Pb compound with HCl gas in hexane than in ether or cleavage with aqueous hydrochloric acid. The preparation of monohalides from the tetraaryls are difficult to control because halogens convert these dirdetly into the dihalides. Even at -75° bromine cleaves tetraaryllead in ether to the dibromide though tetraalkyllead gives the monobromide under these conditions. However, when the activity of the halogen is

---

[73]A. Cahours, Ann., 114, 354 (1860).

[74]J.G.F. Druce, J. Chem. Soc., 119, 758 (1921).

[75]A. Tchakirian, M. Lesbre, and M. Lewinsohn, Compt. rend., 202, 138 (1936).

[76]G. Calingeart, F. J. Dykstra, and H. Shapiro, J. Am. Chem. Soc., 67, 190 (1945).

*In this thesis compounds of the type "-EOOH" are called "-nonic" acids in accordance with the Chemical Abstracts. However, an alternative form "-oic" has been proposed by Johnson (see footnote 11).

diminished by solvation, the monohalide can be obtained in good yields.[45] Organolead halides, similar to those of the tin compounds, can also be made by heating the tetrasubstituted compound with a dihalide.[77] Action of halogens on diarylleads furnishes a method of making organolead dihalides.[78] No aromatic trihalides of lead have been reported, though a few alkyl trihalides are known.[79] Organolead trihalides are less stable than the mono- and dihalides since the most stable inorganic and organic compounds of lead are the di- and the tetra-valent compounds; for the tetravalent lead compounds, therefore, the stability decreases with increasing number of inorganic groups.

With the exceptions of fluorides of tin and lead, all of the halides of this group are liquids or low-melting solids more soluble in organic solvents than in water. Organic fluorides of tin and lead are peculiar. They are nonvolatile, salt-like compounds with high decomposition temperatures without melting, and are somewhat soluble in water.

Organotin and organolead halides tend to form complexes, especially the tin compounds. Typical examples are

---

[77]P. R. Austin, ibid., 54, 3289 (1932).

[78]G. Calingeart, Chem. Revs., 2, 43 (1925).

[79]M. Lesbre, Compt. rend., 206, 1481 (1938).

$(CH_3)_3SnBr.NH_3$,[80] $CH_3PbI_3.2C_5H_5N$,[79] and $(C_2H_5)_2SnO.(C_2H_5)_2SnCl_2$.[81]

The analogous germanium[82] and silicon[83] halides react with ammonia or amines without the formation of complexes.

Organic halides of this group are hydrolyzed with water to the hydroxy compounds or derivatives of polymers derived from them. The lighter the central element E, the more easily the compound hydrolyzes. The halides react with a large variety of organometallic compounds to form simple and mixed tetrasubstituted compounds. Compounds of the type R_3EM (M is a Group I-A metal) have been reported for all Group IV-B elements. They can be made from the corresponding halides of the type R_3EX. These will be discussed in a later section.

C. Oxygen Compounds

Organic compounds containing at least one E-O bond are classified under this section. There are two important types

---

[80] C. A. Kraus and F. C. Schmidt, J. Am. Chem. Soc., 56, 2297 (1934).

[81] P. Pfeiffer and O. Brach, Z. anorg. allgem. Chem., 87, 229 (1914).

[82] C. A. Kraus and E. A. Flood, J. Am. Chem. Soc., 54, 1635 (1932).

[83] R. O. Sauer and R. H. Hasek, ibid., 68, 241 (1946).

of oxygen-containing compounds, namely, the alcoholic type (with an E-OH linkage), and the ethereal type (with either an E-O-R or an E-O-E linkage).

All three types of hydroxy compounds, R_3EOH, $R_2E(OH)_2$, and $RE(OH)_3$, occur, theoretically at least, with the Group IV-B elements. However, two hydroxyl groups on the same E atom always tend to lose water similar to those of the carbon analogs. Unlike the latter compounds they polymerize immediately to form polymeric "omofams" (an abbreviation of "organometallic oxides of Group Four-A metals"; silicones are the typical examples although silicon is considered by some to be a non-metal). The polymeric oxides have no resemblance to the ketones other than the empirical formulas. The trihydroxy compounds, likewise, lose water at once to give compounds of the type, REOOH, which are highly polymerized and they bear no resemblance to the carboxylic acids except for a feeble acidity.

The monols of silicon and germanium undergo molecular condensation with great ease and in some cases the uncondensed monols are difficult to isolate. Trimethylsilanol, for example, condenses so rapidly that it can be isolated only by a special procedure.[84,85] It forms a sodium salt even

---

[84] R. O. Sauer, ibid., 66, 1707 (1944).

[85] L. H. Sommer, E. W. Pietrusza, and F. C. Whitmore, ibid., 68, 2282 (1946).

with an aqueous sodium hydroxide solution.[85] Hydrolyses of triethylbromogermane and triphenylbromogermane do not yield the germanols. Instead, hexaethyldigermoxane[82] and hexaphenyldigermoxane[86] are isolated as the products of hydrolysis. Triphenylgermanol can be made by treating a benzene solution of sodium triphenylgermanolate with water.[86]

Monohydroxy compounds of tin and lead, unlike those of silicon and germanium, have no resemblance to alcohols. They behave like the alkalies and form salts with acids. The low molecular weight compounds are soluble in water. Unlike silanols and germanols, they do not give ether-like oxides on heating. Instead, they disproportionate to give a mixture of oxides and tetrasubstituted compounds. Thus, when triphenyltin hydroxide is heated, a mixture of tetraphenyltin, diphenyltin oxide, and water is obtained.[87] Similar results are observed with trimethyltin hydroxide,[88] while the thermal decomposition of triethyltin hydroxide splits off a molecule of ethane to give diethyltin oxide and diethyltin.[89] Few organolead hydroxides have been described.

---

[86] C. A. Kraus and L. S. Foster, ibid., 49, 457 (1927).

[87] R. F. Chambers and P. C. Scherer, ibid., 48, 1054 (1926).

[88] C. A. Kraus and R. H. Bullard, ibid., 51, 3605 (1929).

[89] T. Harada, Sci. Papers Inst. Phys. Chem. Research (Tokyo), 36, 497 (1939) [C.A., 34, 3674 (1940)].

They are made by treating the halides with potassium hydroxide or silver oxide.[90,91] They are basic and absorb carbon dioxide gas from the air to form a carbonate.[91]

Dialkylsilane diols lose water and polymerize to form polysiloxanes.[92] Diarylsilane diols are more stable although on heating they also lose water to give polymers such as $\left[(C_6H_5)_2SiO\right]_3$. The latter compound has been isolated from the hydrolysis of diphenyldichlorosilane.[93]

Hydrolysis of dimethyldichlorogermane presumably gives dimethylgermanium dihydroxide, but the reaction is reversible which makes it difficult to isolate the hydroxide or oxide.[94] Diethyldibromogermane is converted by alkalies into polymeric forms of diethylgermanium oxide;[30] a similar transformation occurs with the phenyl analog.[17,66]

---

[90] E. Krause and E. Pohland, Ber., 55, 1283 (1922).

[91] O. H. Browne and E. E. Reid, J. Am. Chem. Soc., 49, 830 (1927).

[92] E. G. Rochow, "An Introduction to the Chemistry of the Silicones", 2nd ed., John Wiley and Sons, New York, 1951.

[93] J. F. Hyde and R. C. DeLong, J. Am. Chem. Soc., 63, 1194 (1941).

[94] E. G. Rochow, ibid., 70, 1801 (1948).

In the tin series, all dihydroxy compounds lose water at once to form polymers with the exception of the tertiary alkyl compounds. The di-tertiary alkyl compounds such as di-tert-butyltin dihydroxide can be isolated as such.[38] They are feebly basic like those of the mono-hydroxy compounds though they are weaker. Dialkyllead dihydroxides are unknown though a few of their salts have been prepared. For example, diethyllead dinitrate can be prepared by the action of nitric acid on tetraethyllead in chloroform.[95] Diaryllead dihydroxides are also unknown as such but the dehydrated compounds, diaryllead oxides, can be isolated. These, too, form salts with acids like those of the tin analogs.[96]

The triols of organosilanes are presumably produced from the hydrolysis of the alkyl- or aryl-trihalosilanes but they at once dehydrate and polymerize like the diols.[92] However, the hydrolysis and subsequent condensation of methyltrichlorogermane is found to be reversible like that of dimethyldichlorogermane. Methylgermanetriol has not been isolated but there is evidence for its existence.[11] Hydrolysis of phenyltribromogermane gives an amorphous product soluble in alkaline solutions. The product seems to be a mixture of the acid, C_6H_5GeOOH, and the anhydride, $(C_6H_5GeO)_2O$.[17] A

---

[95]C. D. Hurd and P. R. Austin, ibid., 53, 1543 (1931).

[96]A. Polis, Ber., 20, 3332 (1887).

number of arylgermanonic anhydrides have been prepared by the action of diarylmercury on germanium tetrachloride.[47] Alkylgermanonic anhydrides are prepared from the hydrolysis of alkyltrihalogermane.[97] These substances are amorphous polymers with no definite melting points and are soluble in alkaline solution.

The dehydration products of the organotin trihydroxides, like CH_3SnOOH, can be made from the hydrolysis of the trihalide.[98,99,100] They are amphoteric in character. They form salts with inorganic hydroxides[74,101,102] and form organotin halides with halogen acids.[74,101,102] On heating with aqueous alkali the oxide is formed,[103] while heating with halogen acids[104] splits off the hydrocarbon. Lambourne[98,105] studied

---

[97] E. A. Flood, J. Am. Chem. Soc., 55, 4935 (1933).

[98] H. Lambourne, J. Chem. Soc., 121, 2533 (1922).

[99] K. A, Kotscheschkov, Ber., 62, 996 (1929).

[100] K. A. Kotscheschkov and A. N. Nesmejanov, Ber., 64, 628 (1931).

[101] M. Lesbre and G. Glotz, Compt. rend., 198, 1426 (1934).

[102] J.G.F. Druce, J. Chem. Soc., 121, 1859 (1922).

[103] W. J. Pope and S. J. Peachey, Proc. Roy. Soc., 72, 7 (1903).

[104] E. I. Pikina, T. V. Talalena, and K. A. Kocheshkov, J. Gen. Chem. (U.S.S.R.), 8, 1844 (1938), [C.A., 33, 5839 (1939)].

[105] H. Lambourne, J. Chem. Soc., 125, 2013 (1924).

the structure of methanestannonic acid, CH_3SnOOH, and concluded that it is probably a cyclic trimer. Alkylplumbonic acids (derived from the trihydroxides) can be made by the action of an alkyl iodide on sodium plumbite.[106,107] They are unstable and decompose in moist air or by heating.

Compounds of the type R_3EOR' are known for all Group IV-B elements. The silicon derivatives are prepared from the reaction of the chlorosilanes with alcohols,[84] or from the action of the Grignard reagent or dialkylzinc[108] on the orthosilicates. The alkoxysilanes behave like the halosilanes in that they hydrolyze easily to form the silanols and their dehydration products. The dialkyldialkoxysilanes are satisfactory intermediates for the manufacture of silicone polymers.[92]

Only a few alkoxygermanes and a phenoxygermane have been prepared. Unlike the silicon compounds, neither germanium tetrabromide nor the chloride react with alcohols to form the alkoxygermanes.[109] Tetraethoxygermane and tetraphenoxygermane are made from the reaction of germanium tetrahalide with

---

[106] M. Lesbre, Compt. rend., 200, 559 (1935).

[107] M. Lesbre, ibid., 210, 535 (1940).

[108] A. Ladenburg, Ann., 173, 148 (1874).

[109] D. L. Tabern, W. W. Orndorff, and L. M. Dennis, J. Am. Chem. Soc., 47, 2039 (1925).

sodium ethoxide[110,111] and sodium phenoxide[57], respectively. Germanium tetraisocyanate reacts with alcohols to give alkoxy compounds.[112]

Alkoxytin compounds are also made from the reaction of organotin halides with a sodium alcoholate.[113] Like their silicon and germanium analogs, they are hydrolyzed easily. Very little is known about the lead compounds. Browne and Reid[91] attempted to make triethylalkoxylead from the action of triethyllead chloride with sodium alkoxide but obtained only a small quantity of oil which could not be purified. A number of trialkylphenoxyleads have been made by reacting tetraalkyllead with phenols at about 150° in the presence of silica gel.[114]

Another ethereal type of compound, $R_3EOER'_3$, is also known in this group. Hexasubstituted disiloxanes are made from the dehydration of trisubstituted silanols. The unsymmetrical disiloxanes are conveniently made from the reaction of sodium silanolate with a chlorosilane.[115]

---

[110] N. V. Sidgwick and A. W. Laubengayer, ibid., 54, 948 (1932).

[111] A. W. Laubengayer and P. L. Brandt, ibid., 54, 549 (1932).

[112] H. H. Anderson, ibid., 71, 1799 (1949).

[113] A. Ladenburg, Ber., 3, 353 (1870).

[114] U. S. Pat. 2,008,003; [C.A., 29, 5863 (1935)].

[115] H. N. Benedict, M. S. Thesis, Iowa State College, 1950.

Hexasubstituted digermoxanes are prepared from the hydrolysis of the halogermane.[17] The $(R_3Sn)_2O$ compounds are prepared from the corresponding hydroxides by the removal of a molecule of water,[24,73] or by the oxidation of hexasubstituted ditin compounds.[88,116] The $(R_3Pb)_2O$ compounds are ill-defined solids and are very little mentioned. Triphenyllead oxide is obtained by adding an excess of alcoholic potash to the bromide and is described as being soluble in alcoholic alkalies.[45]

D. Nitrogen Compounds

The amino compounds are the most common type of this series. Like other compounds mentioned before, the stability of the amino compounds decreases with increasing atomic weight of the central E atoms. Trimethylanilinosilane[117] is a stable compound while the anilinogermanes decompose readily.[68] The instability of the germanium compounds is not due to steric hindrance because germanium is larger than silicon. (Germanium forms tetra-1-naphthyl compounds[35] while silicon only forms tri-1-naphthyl derivatives.[34]) This instability may be explained by the acidity or basicity of the elements

---

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

[117] H. H. Anderson, ibid., 73, 5802 (1951).

in this group.[68]

The aminosilanes are prepared from the reaction of halosilanes with ammonia and amines.[83] Organic groups on either the halosilane or the amine hinder the multiple substitution of the hydrogen of the amines. Thus, while two trimethylsilyl[83,84] or two triethylsilyl groups[118] can be introduced into ammonia to give the hexasubstituted disilazanes, only one hydrogen atom in ethylamine is displaced by triethylsilyl group to form the triethylethylaminosilane.[118] With methylamine, however, two trimethylsilyl groups can be introduced to form heptamethyldisilazane.[83] Also, the tertiary amine, $[(CH_3)_3Si]_3N$[83] is not formed from trimethylchlorosilane while $(H_3Si)_3N$ can be made with great ease.[119] Brewer and Haber[120] prepared a number of polysilazanes and found that they have a greater tendency to form small ring compounds than the corresponding siloxanes.[121] Trialkylaminosilanes and hexaalkyldisilazanes are easily hydrolyzed to form the silanols or disiloxanes.[83,84] Trialkylaminosilanes can be converted to

---

[118] C. A. Kraus and W. K. Nelson, ibid., 56, 195 (1934).

[119] A. Stock and K. Somieski, Ber., 54, 740 (1921).

[120] S. D. Brewer and C. P. Haber, J. Am. Chem. Soc., 70, 3888 (1948).

[121] W. Patnode and D. F. Wilcock, ibid., 68, 358 (1946).

the halosilanes by the treatment with hydrogen halides or halogen acids.[122]

Organoaminogermanes can also be prepared by the reaction of ammonia or amines with an organohalogermane. However, the stability of the aminogermane is even less than that of the aminosilane. In addition to the ease of hydrolysis of the organoaminogermanes, they lose ammonia easily with the formation of secondary amines and even tertiary amines.[123] Dihalogermanes react with ammonia to give polymeric imines such as $(EtGeNH)_n$.[66] When a trihalogermane is treated with ammonia a nitride, RGeN, is formed.[97] These are amorphous substances readily hydrolyzed by water.

Organosilyl isocyanates and isothiocyanates are formed through the reaction of the silver salts with halosilanes.[124,125,126] Organoisocyanates of germanium are similarly prepared by heating germanium tetrachloride with silver isocyanate in benzene.[127] These pseudo halides of organosilanes and organogermanes behave like the

---

[122]D. L. Bailey, L. H. Sommer, and F. C. Whitmore, ibid., 70, 435 (1948).

[123]C. A. Kraus and C. B. Wooster, ibid., 52, 372 (1930).

[124]H. H. Anderson, ibid., 70, 1220 (1948).

[125]G. S. Forbes and H. H. Anderson, ibid., 70, 1222 (1948).

[126]H. H. Anderson, ibid., 72, 193 (1950).

[127]A. W. Laubengayer and L. Reggel, ibid., 65, 1783 (1943).

corresponding halides in that they hydrolyze easily to form the hydroxy compounds. Anderson[124] found that the ease of hydrolysis of the isothiocyanates increases with increasing number of isothiocyanate groups.

Organotin halides combine so easily with ammonia and amines that the preparation merely involves the mixing of the two compounds.[128] Complexes containing as many as four molecules of ammonia have been reported.[129] They have no sharp melting point and are decomposed by heating.

Very few organolead compounds containing a Pb-N bond have been made. Saunders[130] prepared a number of compounds of the type, $RSO_2NR'PbR''_3$ and Heap and Saunders[131] made the phthalimide ($R_3PbN<^{CO}_{CO}>C_6H_4$) compounds. They found that these organolead compounds possess powerful sternutatory properties. Organolead nitrates are made by the treatment of the hydroxides with nitric acid.[27]

In this Laboratory, some methiodides and methosulfates of p-dimethylaminophenyl compounds of silicon,[6] tin,[132] and

---

[128]C. A. Kraus and W. N. Greer, ibid., 45, 3078 (1923).

[129]P. Pfeiffer, Z. anorg. allgem. Chem., 133, 91 (1924).

[130]B. C. Saunders, J. Chem. Soc., 684 (1950).

[131]R. Heap and B. C. Saunders, ibid., 2983 (1949).

[132]See the Experimental Part of this thesis.

lead[133] have been made. Some of these compounds are appreciably soluble in water.

E. Hydrogen Compounds

Compounds containing one or more E-H bonds and at least one C-E bond are included in this section. In general, the hydrogen compounds are rather unstable; the heavier the central element E is, the less stable is the hydride. All three types (R_3EH, R_2EH_2, and REH_3) of hydrides are known with silicon, germanium, and tin, but no organolead hydrides have been reported.

The organosilicon hydrides (or simply organosilanes) are made by the action of the Grignard reagent on halosilanes such as trichlorosilane and by the reduction of organosilicon halides with lithium aluminum hydride.[134] The silicon-hydrogen bond of the organosilanes is easily attacked by oxygen and halogens. The stability of the silanes increases with increasing number of organic radicals attached to silicon. The hydrogen atoms in organosilanes behave very much like the halogen atoms in organohalosilane.

---

[133] L. Summers, Doctoral Dissertation, Iowa State College, 1950.

[134] A. E. Finholt, A. C. Bond, Jr., K. E. Wilzbach, and H. I. Schlesinger, J. Am. Chem. Soc., 69, 2692 (1947).

For example, they react with organolithium compounds to form tetrasubstituted silanes.[135,136,137,138]

Organogermanium hydrides are likewise prepared from the reduction of the halides[134] or by the reaction of ammonium halide with organogermanium-metallic compounds such as triethylgermylsodium.[86] The germanols and digermoxanes can also be reduced by lithium aluminum hydride to the germanes.[18] Organogermanium hydrides react readily with the halogens or halogen acids to form the halides. When triphenylgermane is heated, it disproportionates to form a mixture of tetraphenylgermane, diphenylgermane, and some unchanged triphenylgermane.[19]

Organotin hydrides are made by treating organotinsodium with ammonium bromide or by the reduction of a halide with lithium aluminum hydride.[134] They react rapidly with halogen, oxygen, and the alkali metals.[139] Triphenyltin hydride is oxidized readily in air to form hexaphenylditin.[87] Diphenyltin dihydride is so unstable that it changes to diphenyltin immediately after its preparation.[87]

---

[135] H. Gilman and S. P. Massie, Jr., ibid., 68, 1128 (1946).

[136] R. N. Meals, ibid., 68, 1880 (1946).

[137] H. Gilman and H. W. Melvin, Jr., ibid., 71, 4050 (1949).

[138] W. H. Nebergall, ibid., 72, 4702 (1950).

[139] C. A. Kraus and W. N. Greer, ibid., 44, 2629 (1922).

F. Alkali Compounds

Alkali compounds of all Group IV-B elements are known. They are usually made by the action of an alkali metal on either a halide or a hexasubstituted dimer in the presence of a suitable solvent. These compounds are seldom isolated as such but they are important intermediates for the synthesis of a large number of organic compounds containing Group IV-B elements.

Alkali compounds of silicon are less known than those of any other Group IV-B elements. Kraus and Eatough[140] reported the preparation of triphenylsilyllithium and triphenylsilylsodium in 1933, and Kraus and Nelson[141] made triethylsilylsodium in the following year. In 1951, Benkeser and Severson[142] prepared triphenylsilylpotassium from phenylisopropyltriphenylsilane. Almost at the same time it was observed that hexaphenyldisilane was cleaved with sodium-potassium alloy to give triphenylsilylpotassium.[143] However, some of the early work by Kraus and co-workers could not be repeated in this and other laboratories.[144]

---

[140] C. A. Kraus and H. Eatough, ibid., 55, 5008 (1933).

[141] C. A. Kraus and W. K. Nelson, ibid., 56, 195 (1934).

[142] R. A. Benkeser and R. G. Severson, ibid., 73, 1424 (1951).

[143] H. Gilman and T. C. Wu, ibid., 73, 4031 (1951).

[144] See the Experimental Part and the Discussion Part of this thesis.

In this Laboratory, it has been found that the organosilicon-metallic compounds, R_3SiM, can be prepared by the reaction of alkali metals or their alloys with compounds of the type R_3SiY, where R in this case is an aryl group, and Y may be an alkyl, aryl, alkoxy, trisyl*, halogen, oxygen, hydrogen, and possibly nitrogen.[144] Ether is usually used as the solvent.

Triphenylgermylsodium is prepared by cleaving tetraphenylgermane with sodium in liquid ammonia. An excess of sodium may react further to yield the disodio derivatives.[86,145] Like the silicon analog, hexaphenyldigermane can be cleaved by sodium to give triphenylgermylsodium.[86] Hexaphenyldigermoxane[123] and hexaethyldigermoxane[82] are also cleaved by sodium in liquid ammonia or by lithium in ethylamine to yield the corresponding organogermanium-metallic compounds.

Organotin-alkali compounds are made in the same way. Either a hexasubstituted ditin or a tetrasubstituted tin is treated with sodium in liquid ammonia to give the alkali compounds.[116] Organotin halides and dihalides are also converted to the mono- or di-sodio derivatives by sodium in

---

[145] C. A. Kraus and C. L. Brown, J. Am. Chem. Soc., 52, 4031 (1930).

*An abbreviation of "triphenylsilyl".

liquid ammonia.[146,147] Organotin hydrides, such as triphenyltin hydride, react similarly to form the sodium compounds.[87] The phenoxy group of trimethylphenoxytin can be displaced by sodium.[148] Polytin compounds containing more than one Sn-Na bond have been prepared. For example, hexamethyltritin-1,3-disodium, $(CH_3)_2Sn(Na)Sn(CH_3)_2Sn(Na)(CH_3)_2$ is prepared from the reaction of dimethyltin dibromide with dimethyltin-disodium.[149]

Organolead-metallic compounds of the type R_3PbM are similarly prepared from R_3PbX, R_4Pb, or R_6Pb_2 with alkali metals in liquid ammonia. For example, hexacyclohexyldilead is cleaved by sodium to form tricyclohexyllead-sodium.[150] The yields of R_3PbM compounds from the cleavage of hexaphenyldilead decrease with an increase in the atomic weight of M.[27] It has been observed that the Group II-A metals behave like the monovalent metals in liquid ammonia reactions.[27] Diphenyllead dibromide reacts with lithium to give diphenyllead-dilithium.[151]

---

[146] R. H. Bullard and W. B. Robinson, ibid., 49, 1368 (1927).

[147] R. H. Bullard and F. R. Holden, ibid., 53, 3150 (1931).

[148] C. A. Kraus and A. M. Neal, ibid., 51, 2403 (1929).

[149] C. A. Kraus and W. N. Greer, ibid., 47, 2568 (1925).

[150] F. Hein and E. Nebe, Ber., 75, 1744 (1942).

[151] L. D. Apperson, Doctoral Dissertation, Iowa State College, 1940.

In this Laboratory, it has been shown that lead chloride reacts with three equivalents of phenyllithium to form triphenyllead-lithium.[133] Stannous chloride likewise reacts with phenyllithium to give triphenyltin-lithium.[152] The reaction of germanium diiodide with phenyllithium has been studied, but the identity of triphenylgermyllithium has not been definitely established.[153]

The organometallic compounds of the type R_3EM are quite reactive. They react with a number of R'X compounds to form R_3ER'. They are usually colored compounds ranging from yellow to deep red with the intensity increasing from lead to silicon. The R_3EM compounds are ammonolyzed and hydrolyzed easily. For example, triethylgermyllithium ammonolyzes to give triethylgermane.[82] Triphenylsilylpotassium hydrolyzes to give triphenylsilane which undergoes further hydrolysis to yield triphenylsilanol.[144]

Carbonation of triphenylsilylpotassium gives the expected acid, $(C_6H_5)_3SiCOOH$, which loses carbon monoxide easily to give triphenylsilanol.[142] When triphenyllead-lithium is carbonated and hydrolyzed, benzoic acid is obtained. An equilibrium reaction

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

---

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

[153] H. Gilman, L. Summers, and S. D. Rosenberg, in press.

has been proposed[133] to account for the formation of benzoic acid. However, this is not observed with triphenyltin-lithium.[152]

G. Di-Compounds

Organic compounds containing one E-E' bond (E may or may not equal to E') are included in this section. The stability of the E-E bond also decreases with increasing atomic weight of E. The E-E bond of all elements in the group can be broken by chlorine or bromine, and by alkali metals.

Hexasubstituted disilanes are made by treating the hexahalodisilane with dialkylzinc,[154] Grignard reagents,[155] or a mixture of an organic halide and sodium.[156,157] However, the yields obtained by these methods are low and tetrasubstituted silanes are formed presumably due to the cleavage of the silicon-silicon bond under the experimental conditions. These disilanes can be prepared by coupling a

---

[154] C. Friedel and A. Ladenburg, Ann., 203, 251 (1880).

[155] W. C. Schumb and C. M. Saffer, Jr., J. Am. Chem. Soc., 61, 363 (1939).

[156] W. C. Schumb, J. Ackerman, Jr., and C. M. Saffer, Jr., ibid., 60, 2487 (1938).

[157] W. C. Schumb and C. M. Saffer, Jr., ibid., 63, 93 (1941).

trisubstituted halosilane with sodium in boiling xylene.[158,159] Hexaethyldisilane is formed by heating tetraethylsilane with hydrogen under high pressure.[51]

Hexaphenyldigermane, like the silicon analog, may be prepared by treating triphenylbromogermane with sodium in boiling xylene.[17] However, the reaction of germanium tetrachloride with the Grignard reagent may give either tetraphenylgermane or hexaphenyldigermane, depending on the experimental conditions.[160] Also, the reaction of triphenylgermane with phenyllithium yields either tetraphenylgermane or hexaphenyldigermane as the chief product, depending on the order of mixing these reagents.[19] The coupling reaction of a halogermane with sodium cannot be carried out in liquid ammonia because it ammonolyzes easily. However, using a weak ammonolyzing solvent and a weak hydrolyzing halide, Kraus and Flood[82] were able to obtain hexaethyldigermane by treating triethylfluorogermane with lithium in ethylamine.

Symmetrical hexasubstituted ditins are prepared conveniently by the coupling of trisubstituted tin halides with sodium in liquid ammonia.[116] Hexaphenylditin can be obtained

---

[158] W. Schlenk, J. Renning, and G. Racky, Ber., 44, 1178 (1911).

[159] H. Gilman and G. E. Dunn, J. Am. Chem. Soc., 73, 5077 (1951).

[160] O. H. Johnson and D. M. Harris, ibid., 72, 5564 (1950).

by heating diphenyltin.[72] Unsymmetrical ditins are prepared by the reaction of R_3SnX compounds with R_3SnNa compounds.[161]

Organodilead compounds are made by the reaction of lead chloride with an organolithium compound,[22] or by the elimination of halogen from the halide with sodium in liquid ammonia.[37]

Several mixed di-compounds have been made by the coupling reaction of the R_3EM compounds with the $R_3E'X$ compounds. These include $(C_2H_5)_3SiGe(C_6H_5)_3$,[118] $(C_6H_5)_3SiSn(C_6H_5)_3$,[152] $(C_6H_5)_3SiSn(CH_3)_3$,[140] and $(C_6H_5)_3GeSn(CH_3)_3$.[86] Mixed di-compounds containing a Pb-E' (E' may be Si, Ge, or Sn) bond such as $(CH_3)_3SnPb(C_2H_5)_3$[116] have not been successfully made.

As it has been mentioned previously the strength of the E-E bond of the di-compounds increases with decreasing atomic weight of the central E atom, it might be expected that the silicon-silicon bond is the most stable in this series. That this is the case is shown by the reports that the silicon-silicon bonds of some hexasubstituted disilanes are not cleaved by sodium in liquid ammonia.[118] lithium in ethylamine,[118] iodine,[159] oxygen,[158] concentrated sulfuric acid,[162] or alkali.[162] However, in this Laboratory, it has

---

[161] C. A. Kraus and R. H. Bullard, ibid., 48, 2131 (1926).

[162] F. S. Kipping, J. Chem. Soc., 119, 647 (1921).

been shown that the silicon-silicon bond of hexaphenyldisilane can be cleaved by bromine, sodium in liquid ammonia, or potassium in hot di-n-butyl ether[132] although the cleavage of the silicon-silicon bond is slower than that of other E-E bonds under similar conditions.

Hexasubstituted digermanes react with sodium in liquid ammonia, lithium in ethylamine, or bromine.[82] Like its silicon analog, hexaphenyldigermane gives no sign of dissociation into triphenylgermyl radicals either in dilute benzene solution[17,163] or in the solid state.[163]

The Sn-Sn bond in hexasubstituted ditin is weaker than the Ge-Ge bond and the Si-Si bond of the corresponding germanium and silicon analogs. Thus, the Sn-Sn bond of an organoditin is not only cleaved by sodium in liquid ammonia or by halogen, but also by the halogens of other halogen-containing compounds. For example, hexaethylditin reacts with mercuric chloride to form triethyltin chloride and mercury.[164] Hexaethylditin can also be cleaved by organometallic compounds like phenylmercuric chloride[164] or by an alkyl halide such as ethyl iodide.[165] Hexamethylditin reacts with oxygen or sulfur to form the oxide or sulfide,

---

[163] P. W. Selwood, J. Am. Chem. Soc., 61, 3168 (1939).

[164] A. N. Nesmeyanov, K. A. Kocheshkov, and V. P. Puzyreva, J. Gen. Chem (U.S.S.R.), 7, 118 (1937), [C.A., 31, 4290 (1937)].

[165] A. Ladenburg, Ber., 4, 19 (1871).

respectively.[116]

The Pb-Pb bond in organodileads is even less stable than the Sn-Sn bond in organoditins. Thus, hexaphenylditin melts at 237° while hexaphenyldilead decomposes at 155°. Hexa-substituted dileads are cleaved by iodine[166] as well as bromine. In the latter case a dibromide can be obtained.[167] Hexaaryldileads can be oxidized by potassium permanganate to the triaryllead hydroxides while the tetraarylleads do not react under similar conditions.[168]

The observations on the degree of dissociation of organoditins and organodileads reported in the literature are quite discordant. Molecular weight determinations by boiling- and melting-point measurements indicate that they are appreciably dissociated in dilute solutions and less so in concentrated solutions,[24,116,169,170,171,172] while magnetic susceptibility measurements show that the degree

---

[166] E. Krause and G. G. Reissaus, Ber., 55, 888 (1922).

[167] P. R. Austin, J. Am. Chem. Soc., 53, 1548 (1931).

[168] P. R. Austin, ibid., 53, 3514 (1931).

[169] T. Midgley, Jr., C. A. Hochwalt, and G. Calingaert, ibid., 45, 1821 (1923).

[170] E. Krause, Ber., 54, 2060 (1921).

[171] E. Krause, Ber., 54, 2060 (1921).

[172] E. Krause and G. G. Reissaus, Ber., 55, 897 (1922).

of dissociation is very small.[173,174,175] Until the whole problem has been re-examined carefully all one can say now is that the qualitative indications point to some dissociation of these compounds, especially those of the aryl series and those of the lead compounds. However, the quantitative results obtained so far appear to be of doubtful value.

H. Poly-Compounds

The poly-compounds consist of an E-E chain of three or more E atoms. Like the di-compounds, the heavier the atom E is the less stable is the poly compound.

Organopolysilanes of the type $(R_2Si)_n$, in which n equals to 4, 6, or 8, have been prepared by the reaction of diaryldichlorosilane with sodium.[176,177,178] According to these authors, two types of compounds are obtained, a cyclic type and a linear one. Polydimethylsilanes are prepared by the reaction of dimethyldichlorosilane with sodium in a

---

[173] R. Preckel and P. W. Selwood, J. Am. Chem. Soc., 62, 2765 (1940).

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

[175] H. Morris, W. Byerly, and P. W. Selwood, ibid., 64, 1727 (1942).

[176] F. S. Kipping and J. E. Sands, J. Chem. Soc., 119, 830, 848 (1921).

[177] F. S. Kipping, ibid., 123, 2590, 2598 (1923).

[178] F. S. Kipping, ibid., 125, 2291 (1924).

similar way.[179] Octaphenyltrisilane can be made from triphenylsilylpotassium[180] although it has not been made by the reaction of octachlorotrisilane with the Grignard reagent.[155]

Octaphenyltrigermane is made on treatment of diphenyldichlorogermane with triphenylgermylsodium as is the case with the silicon analog.[145] When diphenyldichlorogermane is treated with sodium in xylene, a product of the composition $[(C_6H_5)_2Ge]_4$ is formed.[145] Similarly, when phenyltrichlorogermane is treated with sodium or potassium a product of the composition $(C_6H_5Ge)_6$ is obtained. Also, a linear and a cyclic structure have been proposed.[20]

A few polytin compounds have been reported. Decamethyltetratin[148] and dodecamethylpentatin[149] are prepared from the reaction of dimethyltin dibromide, sodium, and trimethyltin bromide in liquid ammonia. The reaction of phenylmagnesium bromide with stannous chloride gives dodecaphenylpentatin as a side reaction product.[181] A series of compounds of the formula R_2Sn have been made by the reaction of the Grignard reagent with stannous chloride[24,72] or by the reaction of an R_2SnX_2 compound with sodium in

---

[179] C. A. Burkhard, J. Am. Chem. Soc., 71, 963 (1949).

[180] H. Gilman, T. C. Wu, H. A. Hartzfeld, G. A. Guter, A. G. Smith, J. J. Goodman, and S. H. Eidt, ibid., 74, 561 (1952).

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

liquid ammonia.[87,149] These compounds are yellow solids and their molecular weights depend on the method of preparation and their age.[24] Apparently, they are polymers. The structure of $(C_6H_5)_2Sn$ has been studied by Jensen and Clauso-Kaas.[182]

The diarylleads, likewise, are prepared by the reaction of the Grignard reagent with lead chloride.[166] They are unstable in the air or light and form colored solutions.

I. General References

1. Organic compounds containing Group IV-B elements

A. E. Goddard and D. Goddard in J. N. Friend's "A Text-Book of Inorganic Chemistry", Vol. XI, Charles Griffin and Co., London, 1928, pp. 246-253.

E. Krause and A. von Grosse, "Die Chemie der Metallorganischen Verbindungen", Borntraeger, Berlin, 1937, pp. 254-429.

N. V. Sidgwick, "The Chemical Elements and Their Compounds", Vol. I, Clarendon Press, Oxford, 1950, pp. 555-598.

2. Organosilicon compounds

K. A. Andrianov, A. A. Zhdanov, S. A. Golubtsov, and M. V. Sobolevskii, Uspekhi Khim., 18, 145 (1949), [C.A., 44, 1404 (1950)].

C. Burkhard, E. G. Rochow, H. S. Booth, and J. Hartt, Chem. Revs., 41, 97 (1947).

---

[182] V.K.A. Jensen and N. Clauson-Kaas, Z. anorg. allgem. Chem., 250, 277 (1943).

R. Haul, Angew. Chem., A60, 225 (1948), [C.A., 43, 561 (1949)].

M. Marchland, Chem. Tech., 2, 139 (1950), [C.A., 44, 7580 (1950)].

H. W. Post, "Silicones and Other Organic Silicon Compounds", Reinhold, New York, 1949.

E. G. Rochow, "Introduction to the Chemistry of the Silicones", 2nd ed., John Wiley and Sons, New York, 1951.

3. Organogermanium compounds

O. H. Johnson, Chem. Revs., 48, 259 (1951).

K. A. Kocheshkov, Uspekhi Khim., 3, 83 (1934), [C.A., 28, 5402 (1934)].

4. Organotin compounds

C. E. Arntzen, Doctoral Dissertation, Iowa State College, 1942.

K. A. Kocheshkov, Uspekhi Khim., 3, 83 (1934), [C.A., 28, 5402 (1934)].

5. Organolead compounds

G. Calingeart, Chem. Revs., 2, 43 (1925).

R. W. Leeper, Doctoral Dissertation, Iowa State College, 1942.

L. Summers, Doctoral Dissertation, Iowa State College, 1950.

III. EXPERIMENTAL

All reactions involving organometallic, organosilicon-metallic, or organotin-metallic compounds were carried out in essentially the same manner. It consisted of a three-necked flask with standard taper ground glass joints, equipped with a glass-blade stirrer, a graduated dropping funnel, and a Friedrich condenser. (For the preparation and reactions involving triphenylsilylpotassium the condenser was replaced by a ground glass gas-inlet tube.) The apparatus was carefully cleaned and dried in an electric oven at 110° for at least 2 hours and, while it was still hot, flushed well with dry, oxygen-free nitrogen passed through a train containing alkaline pyrogallol, concentrated sulfuric acid, anhydrous calcium chloride, and soda lime, in that order. A small positive pressure of nitrogen was always maintained above the reaction mixture during the reaction period with an oil trap connected in parallel with the reaction system. Ether and other solvents were dried over sodium wire until the surface of freshly cut sodium remained bright in the solvent.

Analyses for chlorine, bromine, and iodine were made by the macro Parr bomb method. Organotin and organosilicon compounds were analyzed by decomposing a sample in concentrated sulfuric acid, followed by ignition of the residue

to the corresponding oxide. In the case of some organosilicon compounds, glacial acetic acid was added to wet the sample prior to the addition of sulfuric acid.

The boiling points and melting points reported herein were uncorrected. For compounds melting below 250° determination was made in a silicone-oil bath with a 250° thermometer (one degree divisions). For high-melting compounds a copper block equipped with a 520° thermometer (two degree divisions) was employed.

A. Organosilicon Compounds

1. Triphenylsilylpotassium

a. Preparation and handling of sodium-potassium alloy. During the course of this investigation sodium-potassium alloy was used frequently. The preparation and handling of the extremely reactive alloy warrant special precautions.

The alloy was easily made by heating 1 part of sodium with 5 parts (by weight) of potassium in xylene until both metals melted. The molten metals were fused together to a big globule by using a glass rod in an atmosphere of nitrogen. After the alloy had been cooled to room temperature,[183] it was transferred to a well-protected container with a dry, clean pipet. It was advisable always to cover the alloy with

[183]This alloy is a liquid at room temperature.

a layer of dry xylene in the pipet as well as in the container in order to protect it from the air. A 50-ml. test tube surrounded by a jar filled with soda ash was found satisfactory as the alloy container.

In cases where the alloy had to be disposed of, this was always carried out in a nitrogen atmosphere because the alloy reacted mildly even with water or alcohol in nitrogen if they were added slowly. In the presence of air the alloy may inflame spontaneously. Accordingly, no large amount of volatile inflammable liquids should be placed in the vicinity of the alloy unless they are well protected.

Very often there was a small film of alloy attached to the inner wall of the pipet after it had been used to transfer the sodium-potassium alloy. This was removed conveniently by putting it in a 15-ml. test tube and adding just 2 or 3 drops of ethanol from the top of the pipet and closing it with the forefinger. As the ethanol flowed down inside the pipet, it reacted with the trace of alloy and evolved hydrogen, which forced the alloy down to the bottom of the test tube and thereby reacted with the solvent smoothly. It must be pointed out, however, that this operation is not recommended for an inexperienced handler unless he is closely watched by someone. For further information one may look up "Precautions in the Preparation and Handling of Sodium-Potassium Alloy and Compounds Prepared from It" compiled by

the Organic Group of the Chemistry Department, Iowa State College.

By exercising proper precautions with the use of sodium-potassium alloy, the author has not experienced any accident caused by the use of the alloy in more than one hundred experiments. Sodium-potassium alloy has been found to be one of the most useful reagents for the preparation of triarylsilicon-metallic compounds.

b. Triphenylsilylpotassium from hexaphenyldisilane and sodium-potassium alloy. Triphenylsilylpotassium was made conveniently by the reaction of hexaphenyldisilane with sodium-potassium alloy. A typical preparation is described below:

In a 250-ml. three-necked flask fitted with a glass stirrer, a stopper, and a gas-inlet tube, was placed 4.0 g. (0.0077 mole) of hexaphenyldisilane after the flask had been swept with nitrogen. One ml. of sodium-potassium alloy was added all at once onto the disilane against a stream of nitrogen. About 5 ml. of anhydrous ether was added to form a paste. The reaction mixture was then stirred slowly. In most cases a greenish yellow coloration was developed right after the stirring motor had been started. This indicated that the triphenylsilylpotassium began to form. After about 30 minutes a brown paste was obtained. To this was added

50 ml. of anhydrous ether[184] and the reaction mixture was stirred at room temperature for 24 hours. It should be pointed out that if too much ether was used at the early stage of the reaction, the alloy became coated and it did not initiate any reaction at all. However, as soon as the reaction had started, the alloy cleaned itself so that the reaction went smoothly even in a heterogeneous system. Usually, the reaction was practically complete in a day.

While the triphenylsilylpotassium suspension was being stirred, 15 to 20 g. of pure mercury was added slowly to amalgamate the excess alloy in the system. The amalgamation was an exothermic reaction and, therefore, was carried out very cautiously. The amalgam was stirred in the system for 1 or 2 hours until a viscous, semi-liquid amalgam was insured. Then the suspension was decanted from the sticky amalgam into a dropping funnel in an atmosphere of nitrogen. Traces of solids remaining in the flask were rinsed with a small amount of ether and decanted into the funnel. Ordinarily, one washing was sufficient to bring everything but the amalgam into the dropping funnel. Due to the lack of a suitable method for analyzing the amount of triphenylsilylpotassium, it was assumed that the cleavage reaction was complete, as in most cases it was nearly so. A qualitative test for the completion of the reaction involved

---

[184]The color of the reaction mixture faded out somewhat during the addition of ether.

the removal of a sample and the hydrolysis of it. Appearance of white solids in the interface indicated an incomplete reaction. Color Test I[185] for the triphenylsilylpotassium suspension was positive, the organic layer being bluish-green and the aqueous layer being violet.

c. Triphenylsilylpotassium from hexaphenyldisilane and potassium. A mixture of 2.0 g. (0.0039 mole) of hexaphenyldisilane, 0.6 g. of potassium, and 50 ml. of n-butyl ether was stirred at 80-90° for 30 hours. To the light brown suspension was added 1.0 g. (0.0092 mole) of trimethylchlorosilane dissolved in 20 ml. of ether after the triphenylsilylpotassium suspension had been cooled to room temperature. The color of the reaction mixture changed to light gray at the conclusion of the addition. After 45 minutes water was added carefully to destroy the excess potassium. The hydrolyzed mixture was filtered to give 0.4 g. (20 per cent) of recovered hexaphenyldisilane melting at 360-362°. The ethereal solution from the filtrate was dried over sodium sulfate, filtered, and distilled to give 1.8 g. (70 per cent) of colorless crystals melting at 97-102°. Two recrystallizations from 95 per cent ethanol yielded 1.2 g. (47 per cent) of pure 1,1,1-triphenyl-2,2,2-trimethyldisilane melting at 107-108°.

---

[185]H. Gilman and F. Schultz, J. Am. Chem. Soc., 47, 2002 (1925).

d. Triphenylsilylpotassium from triphenylchlorosilane and sodium-potassium alloy. A solution of 4.5 g. (0.015 mole) of triphenylchlorosilane in 80 ml. of anhydrous ether was added rapidly to a stirred mixture of 2 ml. of sodium-potassium alloy in 20 ml. of ether. On stirring the reaction mixture became bluish-gray, and some black precipitate was gradually formed. After 36 hours a solution of 2.0 g. (0.018 mole) of trimethylchlorosilane in 20 ml. of ether was added rapidly to the reaction mixture. Fifteen minutes later water was added carefully to get rid of the excess alloy. Following the removal of the solvent from the sodium sulfate-dried ethereal solution there was obtained 4.9 g. (97 per cent) of pale yellow crystals melting at 95-101°. Two recrystallizations from 95 per cent ethanol gave 3.4 g. (67 per cent) of colorless crystals of 1,1,1-triphenyl-2,2,2-trimethyldisilane melting at 107-108°.

e. Triphenylsilylpotassium from triphenylethoxysilane and sodium-potassium alloy. A solution of 3.0 g. (0.01 mole) of triphenylethoxysilane and 1.2 ml. of sodium-potassium alloy in 100 ml. of ether was stirred at room temperature for 18 hours to give a dark suspension. Then 3.5 g. (0.022 mole) of bromobenzene in 15 ml. of ether was added rapidly to the reaction mixture, and the latter was stirred for 15 minutes. The excess alloy was destroyed carefully by adding dilute hydrochloric acid. From the

hydrolyzed mixture 1.6 g. (48 per cent) of tetraphenylsilane melting at 218-231° was obtained by filtration. After two recrystallizations from benzene, 0.8 g. (24 per cent) of pure crystals melting at 233-235° was obtained; a mixed melting point with an authentic sample showed no depression.

f. Triphenylsilylpotassium from tetraphenylsilane and sodium-potassium alloy. A mixture of 3.4 g. (0.01 mole) of tetraphenylsilane and 2 ml. of sodium-potassium alloy in 50 ml. of ether was stirred 24 hours at room temperature. Mercury was added cautiously to the dark tan mixture for amalgamating the excess alloy. The suspension was decanted from the amalgam to a dropping funnel from which it was added to 11.8 g. (0.04 mole) of triphenylchlorosilane dissolved in ether. Some heat was evolved, and the reaction mixture changed to light gray rapidly. After 20 minutes of stirring water was added, and the mixture was filtered to separate 7.5 g. of insoluble solid residue. This was boiled with benzene and filtered again. There was obtained 4.3 g. (83 per cent) of solid residue melting at 350-355°. One recrystallization from dioxane gave 3.6 g. (70 per cent) of hexaphenyldisilane (mixed melting point) melting at 360-362°. From the ethereal solution there was obtained 2.1 g. (0.008 mole) of pure triphenylsilanol melting at 149-150°. This was supposedly the hydrolysis product of the unused triphenylchlorosilane.

g. Hydrolysis of triphenylsilylpotassium. A triphenylsilylpotassium suspension (0.01 mole) prepared in accordance with the method described on page 52 was hydrolyzed with water. Two colorless liquid layers were formed. The ethereal solution was separated, dried over sodium sulfate, filtered, and distilled to give some colorless oily crystals. Petroleum ether (b.p. 28-40°) was added to the solid and filtered to give 1.4 g. (50 per cent) of colorless crystalline residue melting at 150-152°; a mixed melting point with triphenylsilanol showed no depression. From the evaporation of the filtrate followed by a recrystallization an additional 0.2 g. of triphenylsilanol was obtained. The total yield of pure triphenylsilanol thus obtained was 1.6 g. (58 per cent). Further evaporation of the mother liquor resulted in an oil from which no solid separated on standing.

2. Organosilanes prepared from triphenylsilylpotassium

a. Tetraphenylsilane.

(1) From bromobenzene. A mixture of 1.6 g. (0.0031 mole) of hexaphenyldisilane, 1 ml. of sodium-potassium alloy, and 50 ml. of ether was stirred at room temperature for 16 hours. One g. (0.0064 mole) of bromobenzene dissolved in 20 ml. of ether was added rapidly to the resulting dark brown mixture. Some heat was evolved. Fifteen minutes later water was added to destroy the excess alloy. The

colorless solid thus formed was filtered and dried to give 2.0 g. (96 per cent) of crude product melting at 228-231°. One recrystallization from benzene raised the melting point to 233-235°; no depression of melting point resulted from admixture with an authentic specimen of tetraphenylsilane.

(ii) From chlorobenzene. A triphenylsilylpotassium suspension (from 8.0 g. of hexaphenyldisilane) was prepared according to the procedure described on page 52. This was added rapidly to 3.5 g. (0.031 mole) of chlorobenzene dissolved in 30 ml. of ether. Some heat was evolved. Color Test I at the end of 15 minutes was positive; at the end of 30 minutes it became negative. After 1 hour of stirring, the reaction mixture was poured into a dry ice-ether slurry in order to see if any carbonation product could be obtained. Following the attainment of room temperature, the carbonated mixture was acidified with dilute hydrochloric acid and filtered. The ethereal solution was separated and extracted three times with dilute aqueous alkaline solution. However, no organic acid separated upon the acidification of the alkaline extract. The ether-insoluble solid from the reaction mixture was filtered and dried to give 7.6 g. of white solid melting at 230° to form a turbid liquid. The crude product was boiled with benzene and filtered hot. The insoluble solid was recrystallized from dioxane to give 0.8 g. (10 per cent) of hexaphenyldisilane (mixed melting point) melting at 360-362°. The benzene solution

was evaporated to a small volume and cooled to give 5.6 g. (53 per cent) of colorless crystals melting at 230-232°; a mixed melting point with tetraphenylsilane was not depressed.

(iii) From fluorobenzene. A triphenylsilylpotassium suspension (from 4.0 g. of hexaphenyldisilane) prepared as before (page 52) was added rapidly to 1.5 g. (0.016 mole) of fluorobenzene dissolved in 25 ml. of ether. There was no color change or heat effect. Six hours later there still seemed to be no apparent change. Another 1.5 g. of fluorobenzene was added to the reaction mixture, and it was stirred at room temperature for 70 hours. At the end of this period Color Test I was still strongly positive. Water was added to the reaction mixture. Some heat was evolved while the reaction mixture turned bright yellow and then gradually gave way to a gray suspension. The hydrolyzed mixture was filtered to give 0.1 g. (3 per cent) of impure hexaphenyldisilane melting at 350-356°. The ethereal solution was separated from the filtrate, dried over anhydrous sodium sulfate, filtered, and distilled. The oily residue, on cooling, solidified. This solid was washed with a small amount of cold petroleum ether (b.p. 60-70°) and filtered in order to remove the oily material. The solid residue thus obtained was boiled with ethanol and filtered to separate 0.6 g. (12 per cent) of colorless crystals melting at 231-233°; a mixed melting point with

tetraphenylsilane was not depressed. Ethanol was distilled from the filtrate. The residue was recrystallized from petroleum ether (b.p. 60-70°) to give 1.3 g. (31 per cent) of triphenylsilanol (mixed melting point) melting at 149-151°.

b. Triphenylbenzylsilane. A triphenylsilylpotassium suspension was prepared from 4.0 g. of hexaphenyldisilane as previously described (page 52). This was added fairly rapidly to 2 g. (0.016 mole) of benzyl chloride in 20 ml. of ether. Heat was evolved, and Color Test I became negative immediately after the addition. Five minutes later the reaction mixture was hydrolyzed with water and filtered to remove 0.2 g. (5 per cent) of impure hexaphenyldisilane melting at 340-348°. The ethereal solution was dried over anhydrous sodium sulfate, filtered, and distilled to yield 4.6 g. of gummy solids. The crude product was dissolved in 50 ml. of petroleum ether, filtered hot, and cooled to give 0.7 g. (17 per cent) of colorless shining plates melting at 215-220°. This was shown to be hexaphenyldisiloxane by a mixed melting point. Evaporation of the mother liquor deposited a second crop of solids melting from 90-170°. Further evaporation of the mother liquor to a very small volume gave 1.8 g. (33 per cent) of big transparent crystals melting at 85-92°. This was recrystallized from 5 ml. of petroleum ether (b.p. 60-70°), yielding 1.2 g. (22 per cent)

of pure triphenylbenzylsilane (mixed melting point) melting at 98-99°.

c. Triphenyl-p-tolylsilane. A mixture of 2.0 g. (0.0039 mole) of hexaphenyldisilane, 1 ml. of sodium-potassium alloy, and 75 ml. of ether was stirred at room temperature for 24 hours. To this was added 2.0 g. (0.0092 mole) of p-iodotoluene dissolved in 20 ml. of ether. Some heat was evolved. Ten minutes later the reaction mixture was hydrolyzed with water and filtered to collect 0.12 g. (6 per cent) of recovered hexaphenyldisilane melting at 345-353°. From the ethereal solution there was obtained 2.7 g. of solid melting at 125-135°. The crude product was dissolved in 25 ml. of petroleum ether (b.p. 60-70°), filtered, and cooled to give 1.7 g. (63 per cent) of practically colorless crystals melting at 138-140°; a mixed melting point with an authentic sample of triphenyl-p-tolylsilane was the same. From the mother liquor there was obtained 0.5 g. (19 per cent) of impure product melting at 132-136°.

d. Triphenyl-o-tolylsilane. A triphenylsilylpotassium suspension prepared from 4.0 g. of hexaphenyldisilane according to the procedure described previously (page 52) was added rapidly to 3.0 g. (0.018 mole) of o-bromotoluene dissolved in 20 ml. of ether. Heat was evolved from the resulting light reddish brown suspension. Color Test I after 15 minutes was negative. After 4 hours of stirring the reaction

mixture was filtered by suction. The solid residue after the evaporation of ether was washed with some cold petroleum ether (b.p. 60-70°) to dissolve the gummy material, and then it was filtered to give 3.1 g. of light tan powder melting at 155-170°. This was dissolved in 50 ml. of hot benzene, filtered hot, and cooled. There was obtained 0.3 g. of needles melting at 224-227°. A mixed melting point showed that this was hexaphenyldisiloxane. The mother liquor was concentrated to a small volume and chilled to give 1.7 g. of crystals melting at 185-190°. One recrystallization from a solvent of benzene and ethanol yielded 1.3 g. (24 per cent) of pure triphenyl-o-tolylsilane melting at 188-190°.

e. Triphenyl-p-carboxyphenylsilane (attempted). A batch of triphenylsilylpotassium suspension was made from 4.0 g. (0.0077 mole) of hexaphenyldisilane by the procedure described before (page 52). This alloy-free suspension was added rapidly to 4 g. (0.014 mole) of potassium p-iodobenzoate suspended in 20 ml. of ether. There was no apparent change during the addition, so the reaction mixture was stirred 90 hours at room temperature. At the end of this period there seemed to be no change. Color Test I was positive. Aqueous ammonium chloride solution was added to the reaction mixture, the mixture was filtered. The solid residue was boiled with glacial acetic acid and filtered to give 0.4 g. of colorless shining plates melting at

264-267°; a mixed melting point with p-iodobenzoic acid was not depressed. From the ethereal solution 0.6 g. of triphenylsilanol was obtained. The aqueous solution was acidified with dilute acid to give 2.8 g. of solid which, after one recrystallization from a mixed solvent of benzene and alcohol, yielded 2.1 g. of p-iodobenzoic acid melting at 266-268°. Since there was 3.2 g. (0.013 mole, 92 per cent) of p-iodobenzoic acid accounted for, there seemed to have been no reaction between triphenylsilylpotassium and potassium p-iodobenzoate under the experimental conditions.

3. Organodisilanes prepared from triphenylsilylpotassium

a. 1,1,1-Triphenyl-2,2,2-trimethyldisilane. It has been shown previously that this compound was made in a 47 per cent yield from hexaphenyldisilane and potassium (page 54) and in a 67 per cent yield from triphenylchlorosilane and sodium-potassium alloy (page 55). It was found that a better yield of 1,1,1-triphenyl-2,2,2-trimethyldisilane could be obtained from the triphenylsilylpotassium prepared from hexaphenyldisilane and sodium-potassium alloy.

A mixture of 3.0 g. (0.0058 mole) of hexaphenyldisilane, 1.5 ml. of sodium-potassium alloy, and 70 ml. of ether was stirred 20 hours at room temperature. Then 1.6 g. (0.015 mole) of trimethylchlorosilane dissolved in 20 ml. of ether was added rapidly to the reaction mixture. The colorless suspension was hydrolyzed carefully with water. Following

drying and distillation of the ethereal solution there was obtained 3.3 g. (86 per cent) of crystals melting at 101-104°. One recrystallization from 95 per cent ethanol gave 2.9 g. (75 per cent of colorless needles melting at 107-108°. Since the melting point was a few degrees higher than that reported in the literature,[186] analysis was made on this compound.

Anal. Calcd. for $C_{21}H_{24}Si_2$: Si,16.88. Found: Si, 16.69, 16.70.

b. 1,1,1-Triphenyl-2,2,2-triethyldisilane. A mixture of 3.0 g. (0.01 mole) of triphenylchlorosilane, 1 ml. of sodium-potassium alloy, and 50 ml. of ether was stirred at room temperature for 24 hours. To the resulting dark suspension was added 1.8 g. (0.012 mole) of redistilled triethylchlorosilane dissolved in 20 ml. of ether. The brownish tinge of the reaction mixture faded out, and a bluish-gray coloration appeared. Fifteen minutes later water was added slowly to destroy the unreacted alloy. There was obtained 0.13 g. (5 per cent) of hexaphenyldisilane melting at 354-359°. From the ethereal solution 3.5 g. (92 per cent) of colorless crystals melting at 80-85° was collected. Two

---

[186]Benkeser and Severson (see footnote 142) reported the melting points of 1,1,1-triphenyl-2,2,2-trimethyldisilane and 1,1,1-triphenyl-2,2,2-triethyldisilane to be 103-104° and 92.5-93.5°, respectively. Later, they reported the corrected melting point of the former compound to be 107-108° and that of the latter compound to be 96.5-97° in a recent article [R. A. Benkeser, H. Landesman, and D. J. Foster, J. Am. Chem. Soc., 74, 648 (1952)].

recrystallizations from 95 per cent ethanol gave 2.3 g. (60 per cent) of colorless granular crystals melting at 98-99°. Analysis for silicon was made because the melting point was a few degrees higher than that reported in the literature.[186]

Anal. Calcd. for $C_{24}H_{30}Si_2$: Si, 14.98. Found: Si, 14.85, 14.93.

c. Pentaphenylchlorodisilane. A triphenylsilylpotassium suspension prepared from 4.0 g. of hexaphenyldisilane according to the previously described procedure (page 52) was added fairly rapidly to 4.0 g. (0.016 mole) of diphenyldichlorosilane dissolved in 20 ml. of ether. The resulting gray suspension was stirred 1 hour at room temperature and was then filtered. The solvent was distilled from the filtrate to give 7.1 g. of colorless solids melting at 120-140°. Two recrystallizations from petroleum ether (b.p. 60-70°) gave colorless granular crystals melting at 154-155°. The yield of the pure product was 3.7 g. (50 per cent).

Anal. Calcd. for $C_{30}H_{25}Si_2Cl$: Si, 11.79; Cl, 7.43. Found: Si, 11.76, 11.81; Cl, 7.42, 7.43.

d. 1,1,1,2-Tetraphenyl-2,2-dichlorodisilane. A mixture of 10 g. (0.019 mole) of hexaphenyldisilane, 2 ml. of sodium-potassium alloy, and 75 ml. of ether was stirred 48 hours at room temperature. Then 25 g. of mercury was added slowly to amalgamate the unused alloy. The triphenylsilylpotassium suspension was decanted into a dropping funnel

from which it was added slowly to 8.0 g. (0.038 mole) of phenyltrichlorosilane dissolved in 30 ml. of ether during a period of 30 minutes. Some heat was evolved, and the reaction mixture turned gray. After 1.5 hours of stirring at room temperature the reaction mixture was filtered. The insoluble gray solid residue was extracted twice with hot benzene to give 1.6 g. (16 per cent) of hexaphenyldisilane melting at 360-362°. The ethereal solution was distilled to give 13.5 g. of gummy residue which solidified on standing. This solid was very soluble in benzene, acetone, and chloroform and was partially soluble in ethanol and petroleum ether. An attempt to crystallize this solid was unsuccessful, so it was crushed to a powder, washed with cold petroleum ether (b.p. 28-40°) and filtered. The solid residue after such treatment melted at 98-101°. The yield of this partially purified product was 5.6 g. (34 per cent).

Anal. Calcd. for $C_{24}H_{20}Si_2Cl_2$: Si, 12.89. Found: Si, 13.35, 13.42.

e. 1,1,1-Triphenyl-2,2,2-trichlorodisilane. A batch of triphenylsilylpotassium of the same size (10.0 g. of hexaphenyldisilane) was prepared in the same way as that described in the previous section. The suspension thus made was added, over a period of 10 minutes, to 6.5 g. (0.038 mole) of silicon tetrachloride dissolved in 25 ml. of ether. At the end of the addition Color Test I of the greenish-gray mixture was negative. After 2 hours of stirring the

reaction mixture was filtered by suction. The insoluble solid was shaken with dilute alcohol in order to dissolve the inorganic substances. There was obtained 3.7 g. (37 per cent) of hexaphenyldisilane melting at 360-362°. The ethereal solution was distilled to give a solid residue melting at 140-145°. The crude yield was 9.0 g. (59 per cent). It was soluble in ether, benzene, acetone, and chloroform. One crystallization from 40 ml. of petroleum ether (b.p. 60-70°) gave 4.1 g. (27 per cent) of crystals melting at 143-145°. From the mother liquor a second crop melting at 140-143° was recovered. It was noticed that the compound was not very stable. On standing the melting point was lowered.

Anal. Calcd. for $C_{18}H_{15}Si_2Cl_3$: Si, 14.25. Found: 14.38, 14.41.

4. Organopolysilanes prepared from triphenylsilylpotassium.

a. Octaphenyltrisilane. A triphenylsilylpotassium suspension was prepared from 4.0 g. (0.0077 mole) of hexaphenyldisilane according to the previously described procedure (page 52). This was added fairly rapidly to 1.5 g. (0.0059 mole) of diphenyldichlorosilane dissolved in 20 ml. of anhydrous ether. The reaction mixture was stirred 9 hours at room temperature. At the end of this period Color Test I was positive, probably due to the slight excess of triphenylsilylpotassium present. The reaction mixture was

filtered by suction. The gray residue was boiled 30 minutes with 50 ml. of dry benzene and filtered hot. On standing, a small amount of white precipitate was formed which was removed by filtration. It melted at about 270° to form a turbid liquid which became clear at about 320°. This was believed to be impure hexaphenyldisilane from the starting material. The benzene extract was concentrated to about 10 ml., and to this was added 20 ml. of petroleum ether (b.p. 60-70°). On cooling to room temperature 2.2 g. (53 per cent) of white solid melting at 238-244° was obtained by filtration. Three recrystallizations from a mixed solvent of ethanol and benzene gave 1.2 g. (29 per cent) of colorless needles melting at 260-262° to form a somewhat gelatinous mass which became clear at 266°.

Anal. Calcd. for $C_{48}H_{40}Si_3$: Si, 12.00. Found: Si, 11.98, 11.84.

This preparation was checked by Guter and Smith in this Laboratory. It was found that a product melting at 302-303° was obtained by the same procedure. Analysis showed that it, too, had the composition of octaphenyltrisilane. Also, the melting point of this product seemed to vary according to the state of subdivision of the sample. From molecular models studies it was suspected that this inconsistency in the melting points might possibly be due to the existence of isomeric forms.

b. Decaphenyltetrasilane. A mixture of 1.0 g. (0.0021 mole) of pentaphenylchlorodisilane, 0.4 g. of sodium, and 30 ml. of dry xylene was refluxed for 4 hours. The resulting violet suspension was cooled to room temperature and filtered. Ethanol was added to the solid residue to react with the unused sodium, and the mixture was filtered to separate the insoluble solid residue which melted at 320-330°. A small amount of white solid was separated from the xylene solution. The combined yield of crude decaphenyltetrasilane was 0.5 g. (57 per cent). It was recrystallized twice from a mixed solvent of ethanol and benzene to give shining white crystals which melted at 335° when heated rapidly.

Later, Hartzfeld[187] repeated this preparation using 14.3 g. (0.03 mole) of pentaphenylchlorodisilane (24 hours of reflux time) and obtained a product melting at 320-340°. After several recrystallizations a 44 per cent yield of crystals melting at 359-362° was obtained. A sample was heated at 110° for 2 hours and was analyzed to give 12.88 per cent and 12.98 per cent of silicon. (Theoretical value for decaphenyltetrasilane is 12.71 per cent.)

5. Organodisilanes containing phenyl and p-tolyl groups.

a. Hexaphenyldisilane. This compound was made

---

[187]H. A. Hartzfeld, unpublished studies.

essentially according to a published procedure.[159] It was very frequently used as the starting material for the preparation of triphenylsilylpotassium. The success of this preparation depends on the purity of triphenylchlorosilane, the manner of mixing, and the absence of moisture in the system. Under proper conditions, yields of 90-94 per cent could be obtained in very high purity. The product obtained from this preparation was a very finely divided crystalline substance which needed no purification for the preparation of triphenylsilylpotassium.

In connection with the studies of coupling reactions of triarylsilylpotassium with triarylsilyl halides, triphenylsilylpotassium was treated with triphenylchlorosilane to form hexaphenyldisilane. In contrast with the coupling reaction of triphenylsilylpotassium with trimethylchlorosilane to form 1,1,1-triphenyl-2,2,2-trimethyldisilane, the reaction of the triphenylsilylpotassium with triphenylchlorosilane is a rather slow reaction.

A triphenylsilylpotassium suspension was prepared from 4.0 g. (0.0077 mole) of hexaphenyldisilane in accordance with the procedure given on page 52. This suspension was added rapidly to 4.6 g. (0.016 mole) of triphenylchlorosilane dissolved in 20 ml. of ether. No appreciable amount of heat was evolved. The color of the resulting mixture was only a little lighter than that of triphenylsilylpotassium before it was mixed. Color Test I after 2 hours was

positive. The reaction mixture was stirred 24 hours at room temperature and was filtered to give 7.3 g. of solids. Dilute aqueous ethanol solution was added to the residue in order to dissolve the inorganic salts formed from the coupling reaction. It was noticed that some heat was evolved, probably due to the hydrolysis of the unused triphenylchlorosilane. The solid after such treatment was filtered and dried to give 6.2 g. (77 per cent) of crude hexaphenyldisilane melting at 345-353°. One recrystallization gave 5.3 g. (66 per cent) of crystals melting at 360-362°.

In another experiment the reaction mixture containing triphenylsilylpotassium and triphenylchlorosilane was stirred 4 hours at room temperature to give only 30 per cent of pure hexaphenyldisilane and a large amount of hexaphenyldisiloxane as a by-product.

b. Pentaphenyl-p-tolyldisilane.

(i) From pentaphenylchlorodisilane and p-tolyllithium. An ethereal solution containing 0.011 mole of freshly prepared p-tolyllithium was added rapidly to 4.8 g. (0.01 mole) of pentaphenylchlorodisilane. The reaction mixture became more and more turbid, but very little heat was evolved. After 16 hours of stirring water was added, and the mixture was filtered to give 2.8 g. (53 per cent) of white powder melting at 270° to form a turbid liquid.

Two recrystallizations from benzene yielded small, needle-like crystals melting at 283-285°. They weighed 1.5 g. (28 per cent).

Anal. Calcd. for $C_{37}H_{32}Si_2$: Si, 10.54. Found: Si, 10.50, 10.47.

(ii) From triphenylsilylpotassium and diphenyl-p-tolylchlorosilane. A triphenylsilylpotassium suspension prepared from 5.2 g. (0.01 mole) of hexaphenyldisilane in accordance with the procedure given before (page 52) was added rapidly to 6.2 g. (0.02 mole) of diphenyl-p-tolylchlorosilane (prepared from diphenyldichlorosilane and p-tolyllithium in 81 per cent yield according to the procedure of G. E. Dunn[6]) dissolved in 30 ml. of ether. The reaction mixture became light greenish-gray, and some heat was evolved. Color Test I after 1 hour was weakly positive, becoming negative at the end of 5 hours. Water was then added, and the mixture was filtered to give 8.7 g. (82 per cent) of white powder melting at 276-282°. One recrystallization from benzene gave 8.2 g. (77 per cent) of fine, needle-like crystals melting at 283-285°. A mixed melting point with the product prepared by the reaction of pentaphenylchlorodisilane with p-tolyllithium was the same.

c. 1,1,2,2-Tetraphenyl-1,2-di-p-tolyldisilane. A mixture of 22.4 g. (0.0725 mole) of freshly distilled diphenyl-p-tolylchlorosilane, 4.8 g. (0.21 g. atom) of sodium, and 50 ml. of dry xylene was heated until the sodium melted.

Then the reaction mixture was stirred vigorously at the refluxing temperature. Immediately some deeply violet precipitate appeared, and a dark suspension was formed on further stirring. After 6 hours of refluxing the reaction mixture was allowed to cool to room temperature. A large amount of white precipitate separated from the dark violet reaction mixture. Some benzene was added in order to make it possible to pour the slurry out easily. The insoluble solid was obtained by suction filtration. The filtrate was practically colorless. The violet residue containing some finely divided sodium was transferred into a 600-ml. beaker and was treated with 50 ml. of 95 per cent ethanol for the removal of unused sodium. The colorless solid thus obtained was washed first with water, then with 20 per cent ethanol, and filtered. There was obtained 16.6 g. (84 per cent) of colorless solid melting at 250-252°. Two recrystallizations from benzene yielded 12.3 g. (62 per cent) of colorless solid melting at 252-253°. From the mother liquor 1.9 g. (10 per cent) of impure product melting at 248-250° was recovered. Also, from the xylene solution of the original reaction mixture 1.2 g. of solid melting at 180-210° was obtained by evaporation. No purification work was done on these impure products.

Anal. Calcd. for $C_{38}H_{34}Si_2$: Si, 10.27. Found: Si, 10.26, 10.28.

d. 1,1,1,2-Tetraphenyl-2,2-di-p-tolyldisilane.

(i) From 1,1,1,2-tetraphenyl-2,2-dichlorodisilane and p-tolyllithium. A solution containing 4.0 g. (0.0092 mole) of 1,1,1,2-tetraphenyl-2,2-dichlorodisilane in 40 ml. of ether was added, over a period of 10 minutes, to 0.0205 mole of freshly prepared p-tolyllithium in ether. A small amount of heat was evolved during the addition. The reaction mixture after the addition was pale yellow and a little cloudy. On stirring more and more white precipitate was formed. Color Test I after 5 hours was still positive, so the reaction mixture was stirred at room temperature overnight. After 16 hours a large amount of white precipitate was formed, and Color Test I became negative. The reaction mixture was filtered by suction. The solid residue was extracted twice with hot benzene. The benzene extract was evaporated to give 1.2 g. of white solid melting at 217-222°. Two recrystallizations from petroleum ether (b.p. 60-70°) gave colorless fine needles melting at 229-230°. Yield: 0.7 g. (14 per cent). From the ethereal solution of the reaction mixture a large amount of gummy residue was obtained from which a small amount of the desired product could be isolated.

Anal. Calcd. for $C_{38}H_{34}Si_2$: Si, 10.27. Found: Si, 10.31, 10.33.

(ii) From triphenylsilylpotassium and phenyldi-p-tolylchlorosilane. A suspension of 0.02 mole of

triphenylsilylpotassium was prepared in accordance with the procedure described on page 52. This was added rapidly to 6.4 g. (0.02 mole) of phenyldi-p-tolylchlorosilane (prepared in 92 per cent yield from phenyltrichlorosilane and p-tolyllithium by the modified procedure of G. E. Dunn[6]) dissolved in 60 ml. of ether. A yellowish-gray suspension was formed with evolution of a small amount of heat. Color Test I after 30 minutes was negative. Four hours later this gray pasty suspension was hydrolyzed with water and filtered to give 8.1 g. of white powder melting at 228°. From the ethereal solution 3.2 g. of gummy solid residue was obtained. It was washed with petroleum ether to dissolve the tarry material and filtered to give 1.2 g. of white solid melting at 226°. The combined crude yield was 9.3 g. (85 per cent). One crystallization from a solution of benzene and petroleum ether (b.p. 60-70°) gave 7.9 g. (72 per cent) of pure product melting at 229-230°; a mixed melting point with the product prepared from 1,1,1,2-tetraphenyl-2,2-dichlorodisilane was the same.

e. 1,1,1-Triphenyl-2,2,2-tri-p-tolyldisilane.

(i) From tri-p-tolylsilylpotassium and triphenylchlorosilane. A tri-p-tolylsilylpotassium suspension was prepared from 4.0 g. (0.0066 mole) of hexa-p-tolyldisilane and 1 ml. of sodium-potassium alloy by the same method as that for triphenylsilylpotassium. After amalgamation

the alloy-free organosilicon-metallic compound was added rapidly to 3.9 g. (0.013 mole) of triphenylchlorosilane dissolved in 40 ml. of ether. The reaction mixture changed slowly from tan to white with the evolution of a small amount of heat. One hour later Color Test I was negative. Water was added, and the mixture was filtered to give 3.6 g. of white solid melting at 258-262°. The ethereal solution was separated, dried over sodium sulfate, filtered, and distilled. The residue was boiled with petroleum ether and filtered to separate 0.3 g. of insoluble solid residue melting at 255-260°. The total crude yield was 3.9 g. (53 per cent). The crude product was dissolved in a benzene-petroleum ether (b.p. 75-115°) solution and cooled to give 0.7 g. of colorless crystals melting at 260-350°. Evaporation of the mother liquor deposited 0.3 g. of colorless crystals melting at 240-340°. These two batches of solids appeared to be a mixture of 1,1,1-triphenyl-2,2,2-tri-p-tolyldisilane and hexa-p-tolyldisilane, the latter coming from the uncleaved starting material. Further evaporation of the mother liquor yielded 1.9 g. (26 per cent) of colorless fine needles melting at 262-264°. The remaining mother liquor was evaporated to almost dryness, and some petroleum ether was added to the residue and filtered to give 0.5 g. of impure product melting at 240-248°. One recrystallization raised the melting point to 262-264°.

Anal. Calcd. for $C_{39}H_{36}Si_2$: Si, 10.01. Found: Si, 9.94, 9.94.

From the ethereal solution of the reaction mixture, after the removal of 0.3 g. of solids melting at 255-260° described above, there was obtained 0.5 g. of triphenylsilanol (mixed melting point) melting at 145-148°. Evaporation of the mother liquor deposited some colorless plates melting at 151°. These were recrystallized from petroleum ether (b.p. 60-70°) to give colorless granular crystals melting at 156-160°; mixed melting point with 1,1,1-triphenyl-3,3,3-tri-p-tolyldisiloxane prepared by Benedict[115] showed no depression.

(ii) From 1,1,1-triphenyl-2,2,2-trichlorodisilane and p-tolyllithium. Freshly prepared p-tolyllithium solution (0.022 mole) in ether was added rapidly to 2.0 g. (0.0051 mole) of impure 1,1,1-triphenyl-2,2,2-trichlorodisilane (page 66) dissolved in 40 ml. of ether. Some heat was evolved, and white solids were formed. After 6 hours of stirring at room temperature the light yellow suspension was hydrolyzed with water. Two practically clear liquid layers were formed. The aqueous layer was extracted once with ether. The combined ethereal solution was dried over sodium sulfate, filtered, and distilled to give a glassy residue weighing 2.7 g. This was dissolved in a solution containing 50 ml. of petroleum ether (b.p. 60-70°) and 10

ml. of benzene. On cooling only 0.3 g. (11 per cent) of colorless crystals melting at 260-264° separated; a mixed melting point with the 1,1,1-triphenyl-2,2,2-tri-p-tolyldisilane prepared from tri-p- tolylsilylpotassium and triphenylchlorosilane was not depressed.

f. 1,1,2-Triphenyl-1,2,2-tri-p-tolyldisilane. A mixture of 4.6 g. (0.0082 mole) of 1,1,2,2-tetraphenyl-1,2-di-p-tolyldisilane, 1 ml. of sodium-potassium alloy, and 10 ml. of ether was stirred at room temperature. About 1 minute later a yellow color appeared; 15 minutes later a deep yellow suspension was formed. Another 40 ml. of ether was added all at once to the reaction mixture the color of which faded out somewhat during the addition. An hour after the addition of the second batch of ether a bright orange-colored suspension was formed. The diphenyl-p-tolylsilylpotassium suspension thus made appeared to be somewhat different from triphenylsilypotassium in that the former was a pasty suspension which did not precipitate down readily on standing while the latter did. Also, their colors were different as mentioned above.

After 40 hours of stirring the excess alloy was amalgamated with 15 g. of mercury. The alloy-free organosilicon-metallic suspension was decanted into a dropping funnel. It was observed that it dissolved in benzene or petroleum ether (b.p. 60-70°) to give a slightly turbid solution.

Color Test I of the suspension was positive.

The diphenyl-p-tolylsilylpotassium suspension was added rapidly to 5.2 g. (0.016 mole) of phenyldi-p-tolylchlorosilane dissolved in 40 ml. of ether. There was very little heat evolved during the addition. After 2 hours of stirring at room temperature the gray suspension was hydrolyzed with water and filtered to remove a trace of gray precipitate. The ethereal solution was washed twice with water, separated, and dried over sodium sulfate. Distillation of the solution gave 8.3 g. (92 per cent) of colorless sticky solids melting at 215-225°. The crude product was recrystallized from 120 ml. of benzene-ethanol (1:1) solution to give 4.6 g. of lustrous crystals melting at 222-225°. The mother liquor was concentrated to give 1 g. of crystals melting at 190° which, after one recrystallization, melted at 221-224°. The combined crude product was recrystallized from benzene-ethanol to yield 4.7 g. (52 per cent) of shining, fluffy crystals melting at 226-227°.

Anal. Calcd. for $C_{39}H_{36}Si_2$: Si, 10.01. Found: Si, 9.92, 9.95.

g. 1,2-Diphenyl-1,1,2,2-tetra-p-tolyldisilane. A mixture of 10.7 g. (0.033 mole) of phenyldi-p-tolylchlorosilane, 1.5 g. (0.065 g. atom) of sodium, and 50 ml. of dry xylene was stirred at the refluxing temperature for 15 hours. The dark violet suspension was cooled to room temperature and

filtered by suction. The solid residue was placed in a beaker containing 200 ml. of 95 per cent ethanol until all excess sodium had reacted. The resulting white solid was filtered, washed with 20 per cent ethanol, and dried to give 5.9 g. of crude product melting at 232-236°. From the distillation of the xylene solution a considerable amount of somewhat oily solid was obtained. This was washed with 50 ml. of cold petroleum ether (b.p. 60-70°) and filtered to separate 2.3 g. of crude product melting at 217-225°. A mixed melting point showed that these two batches of products were the same. The combined yield of the crude material was 8.2 g. (86 per cent). Two recrystallizations from a benzene-petroleum ether (b.p. 60-70°) solution gave 6.7 g. (71 per cent) of shining granular crystals melting at 240-241°.

Anal. Calcd. for $C_{40}H_{38}Si_2$: Si, 9.77. Found: Si, 9.69, 9.76.

h. 1,1-Diphenyl-1,2,2,2-tetra-p-tolyldisilane. A suspension of tri-p-tolylsilylpotassium in ether was prepared from the cleavage of 4.8 g. (0.008 mole) of hexa-p-tolyldisilane with sodium-potassium alloy in the same way as for triphenylsilylpotassium. After amalgamation, the alloy-free organosilicon-metallic mixture was added rapidly to 4.9 g. (0.016 mole) of diphenyl-p-tolylchlorosilane dissolved in 40 ml. of ether. Some heat was evolved during the addition. Water was added to the tan mixture after it had been

stirred for 20 hours at room temperature. The colorless mixture was filtered to give 3.2 g. of white solid melting at 226-233°. The ethereal solution was separated, dried, and distilled to give 6.0 g. of colorless fluffy solid melting at 200-220°. The 9.2 g. of combined crude product was recrystallized once from benzene-petroleum ether (b.p. 60-70°) and once from acetone to give 5.2 g. (57 per cent) of fine, colorless needles melting at 240-241°.

Anal. Calcd. for $C_{40}H_{38}Si_2$: Si, 9.77. Found: Si, 9.64, 9.65.

It was observed that a mixed melting point of 1,1-diphenyl-1,2,2,2-tetra-p-tolyldisilane and 1,2-diphenyl-1,1,2,2-tetra-p-tolyldisilane was the same, 240-241°.

1. Phenylpenta-p-tolyldisilane. A tri-p-tolylsilylpotassium suspension was prepared from 3.0 g. (0.005 mole) of hexa-p-tolyldisilane and sodium-potassium alloy. The alloy-free suspension was added rapidly to 3.2 g. (0.01 mole) of phenyldi-p-tolylchlorosilane dissolved in ether. Some heat was evolved. After 16 hours of stirring the reaction mixture was hydrolyzed with water and filtered. There was obtained 2.4 g. of white solid melting at 284-288°. From the ethereal solution 0.3 g. of white solid melting at 270-280° was isolated. The combined crude product was recrystallized twice to yield 1.1 g. (19 per cent) of shining plates melting at 288-290°.

Anal. Calcd. for $C_{41}H_{40}Si_2$: Si, 9.53. Found: Si, 9.49, 9.50.

j. Hexa-p-tolyldisilane. An ethereal solution containing 0.078 mole of p-tolyllithium was added to 2.6 g. (0.01 mole) of hexachlorodisilane dissolved in 50 ml. of ether over a period of 10 minutes. Heat was evolved from the orange-colored suspension. The reaction mixture was stirred 20 hours at room temperature. At the end of this period Color Test I was positive. Following the hydrolysis of the reaction mixture 3.6 g. of colorless solid was collected by filtration. It melted at about 230-330°. The crude product was dissolved in 100 ml. of hot toluene and cooled slowly to room temperature. There was obtained 1.8 g. (30 per cent) of hexa-p-tolyldisilane (mixed melting point) melting at 354-356°. Evaporation of the filtrate yielded a second crop of colorless crystals melting at 228-300°. Further concentration of the mother liquor gave 1.2 g. (31 per cent based on the assumption that one mole of hexachlorodisilane produced one mole of tetra-p-tolylsilane) of tetra-p-tolylsilane melting at 228-230°. This compound was also identified by a mixed melting point with an authentic sample.

In a second experiment a 10 per cent excess of p-tolyllithium was added to hexachlorodisilane dissolved in dry benzene at 0° over a period of 1 hour followed by 16 hours of stirring of the reaction mixture at room

temperature. There was obtained a 28 per cent yield of hexa-p-tolyldisilane and a 32 per cent yield of tetra-p-tolylsilane.

In a third experiment a 20 per cent excess of p-tolyllithium was added to hexachlorodisilane dissolved in ether at -65° over a period of 1 hour followed by stirring 16 hours at room temperature and was worked up as usual to give a 27 per cent yield of hexa-p-tolyldisilane and a 29 per cent yield of tetra-p-tolylsilane.

In a fourth experiment, instead of adding the organolithium compound to hexachlorodisilane the reverse order of addition was employed. Thus, 0.36 mole of freshly prepared p-tolyllithium solution was placed in a three-necked flask immersed in an ice bath. To this there was added 15 g. (0.056 mole) of hexachlorodisilane dissolved in 40 ml. of ether over a period of one hour. It was observed that a vigorous reaction occurred when each drop of the hexachlorodisilane solution hit the p-tolyllithium solution. After the addition had been completed, the reaction mixture was stirred at room temperature for 16 hours and then was hydrolyzed. There was obtained 15.3 g. of insoluble solid which melted at 180° to form a turbid liquid. This crude product was boiled in 100 ml. of toluene and filtered hot. The insoluble residue did not melt below 450°, whereas it burned with a yellow flame. It weighed 0.4 g. The toluene

solution was concentrated to a small volume and was cooled to give 12 g. of colorless granular crystals melting at 180-190°. Two recrystallizations from toluene yielded 9.2 g. (42 per cent) of tetra-p-tolylsilane (mixed melting point) melting at 228-230°. No hexa-p-tolyldisilane was isolated from this experiment. From the ethereal solution of the reaction mixture only a molasses-like residue was obtained after the removal of the sodium sulfate-dried ether solution. No pure product could be obtained from this residue.

6. Cleavage of the silicon-silicon bond of hexasubstituted disilanes

a. Hexaphenyldisilane.

(i) By potassium. The cleavage reaction of hexaphenyldisilane with potassium in di-n-butyl ether was described on page 54.

(ii) By sodium-potassium alloy. This reaction has been described on page 52, and elsewhere in the Experimental Part.

(iii) By sodium in liquid ammonia. This will be described on page 97.

(iv) By 40 per cent sodium amalgam (attempted). A mixture of 2.0 g. (0.0039 mole) of hexaphenyldisilane, 0.4 ml. of 40 per cent sodium amalgam, and 50 ml. of ether was stirred at room temperature for 68 hours. There was no

evidence of reaction though the reaction mixture became light gray at the end of this period. In order to find out if triphenylsilylsodium had formed, a solution containing 5.4 g. (0.035 mole) of ethyl iodide in 20 ml. of ether was added rapidly to the reaction mixture. There was no heat effect or color change during and after the addition. After the reaction mixture had been stirred 2 hours at room temperature, water was added carefully to destroy the unchanged sodium amalgam. The resulting mixture was decanted from the mercury and filtered. The recovered hexaphenyldisilane (mixed melting point) melting at 359-361° weighed 2.0 g. (100 per cent).

In another experiment a mixture containing 2.0 g. (0.0039 mole) of hexaphenyldisilane, 8.5 equivalents of 40 per cent sodium amalgam, and 100 ml. of ether was stirred 48 hours at room temperature. Then 1.7 g. of trimethylchlorosilane in 20 ml. of ether was added to the reaction mixture followed by 20 minutes of stirring after the addition. There was recovered 1.9 g. (95 per cent) of hexaphenyldisilane (melting point and mixed melting point) from the hydrolysis of the reaction mixture.

(v) By sodium dispersion in xylene (attempted). A mixture of 2.86 g. (0.0055 mole) of hexaphenyldisilane and 0.72 g. (0.011 g. atom) of a 35 per cent sodium dispersion in tetrahydronaphthalene (Ethyl Corporation) was stirred

vigorously in 70 ml. of dry xylene at the refluxing temperature for 5 hours. Then 3.4 g. (0.022 mole) of ethyl iodide dissolved in 10 ml. of xylene was added to the reaction mixture, and it was refluxed for another 5 hours. The mixture was hydrolyzed carefully and filtered to give 2.75 g. (96 per cent) of recovered hexaphenyldisilane.

(vi) By sodium dispersion in dioxane (attempted). A mixture of 2.4 g. (0.0046 mole) of hexaphenyldisilane and 1.2 g. (0.018 g. atom) of a 35 per cent sodium dispersion in tetrahydronaphthalene (Ethyl Corporation) was refluxed in 70 ml. of pure dioxane for 66 hours. There was no evidence of reaction. A solution of 2.9 g. (0.019 mole) of ethyl iodide in 15 ml. of dioxane was then added, and the reaction mixture was refluxed for another 7 hours. Following hydrolysis 2.1 g. (88 per cent) of hexaphenyldisilane melting at 357-360° was recovered.

(vii) By lithium aluminum hydride (attempted). A suspension containing 3.0 g. (0.0078 mole) of hexaphenyldisilane, 0.17 g. (0.0044 mole) of lithium aluminum hydride, and 50 ml. of ether was stirred at the refluxing temperature for 48 hours. There was no apparent change in the reaction mixture. The unchanged lithium aluminum hydride was destroyed by first adding water, then dilute hydrochloric acid solution. There was obtained 2.9 g. (97 per cent) of unchanged hexaphenyldisilane melting at 362-364°.

(viii) By 30 per cent hydrogen peroxide (attempted). Seven g. of 30 per cent hydrogen peroxide was added to 5.2 g. (0.01 mole) of hexaphenyldisilane suspended in 50 ml. of glacial acetic acid. The reaction mixture was refluxed for 24 hours. Water was added to the suspension, and the mixture was filtered. The recovery of the unchanged hexaphenyldisilane was quantitative.

(ix) By chromic acid. Chromic acid solution was prepared by dissolving 5.0 g. of chromium trioxide in 5 ml. of water followed by the addition of 10 ml. of glacial acetic acid. This solution was added to 3.0 g. of hexaphenyldisilane, and the mixture was heated at 80-90° for 2 hours with occasional shaking. The resulting dark green mixture was diluted with 100 ml. of water. Solid sodium carbonate was added to neutralize the reaction mixture until the addition of a small amount of sodium carbonate did not cause evolution of gases. Following filtration of the neutralized mixture there was obtained 2.7 g. (90 per cent) of impure hexaphenyldisilane melting at 356-360°. It was boiled with petroleum ether (b.p. 60-70°) and filtered hot to separate 2.5 g. (83 per cent) of pure hexaphenyldisilane melting at 362°. Only a trace of brown solid remained from the distillation of the filtrate.

In a second experiment, double the amount of chromic acid was used, and the reaction mixture containing chromic

acid and hexaphenyldisilane was refluxed 48 hours. In this run, only 48 per cent of hexaphenyldisilane could be recovered. The aqueous solution was extracted with ether, from which a syrupy residue was obtained. Purification of this by-product was unsuccessful.

(x) By bromine. Ten g. (0.019 mole) of hexaphenyldisilane suspended in 250 ml. of refluxing carbon tetrachloride containing 3.4 g. (0.021 mole) of bromine was stirred 42 hours. The solvent and the unchanged bromine were removed by distillation to leave a solid residue (10.8 g.) melting at about 100° to form a turbid liquid. This crude product was boiled in 200 ml. of petroleum ether (b.p. 60-70°), filtered hot, and cooled. The insoluble solid, melting point 346-354°, weighing 4.1 g. was recrystallized from dioxane to give 3.6 g. (36 per cent) of pure hexaphenyldisilane (mixed melting point). The petroleum ether extract was concentrated twice to collect 6.2 g. (47 per cent) of crude triphenylbromosilane melting at 115-118°. Two recrystallizations from petroleum ether (b.p. 60-70°) raised the melting point to 118-120°; a mixed melting point with an anthentic specimen of triphenylbromosilane was the same. The yield of the pure product was 4.3 g. (33 per cent).

In a second experiment hexaphenyldisilane was allowed to react with bromine in refluxing carbon tetrachloride for 6 days. The reaction mixture was worked up according to

the procedure described in the previous paragraph to give a 19 per cent recovery of hexaphenyldisilane and a 65 per cent yield of crude, or a 55 per cent yield of pure triphenylbromosilane.

b. Hexa-p-tolyldisilane. A mixture of 1.0 g. (0.0017 mole) of hexa-p-tolyldisilane, 0.6 ml. of sodium-potassium alloy, and 5 ml. of ether was stirred at room temperature. Three hours later another 30 ml. of ether was added to the brown slurry. The color of the reaction mixture became yellow after this addition, but it resumed a brown coloration on stirring. After 24 hours of stirring 0.6 g. (0.0035 mole) of p-bromotoluene dissolved in 20 ml. of ether was added. The reaction mixture changed to greenish-brown, then greenish-gray, and finally a gray suspension was formed. Meanwhile, some heat was evolved. Ten minutes later water was added to destroy the excess alloy. Two liquid layers with some white solid at the interface were formed. This solid was removed by filtration. It melted at 220-226° (0.5 g.). The ethereal solution was separated, dried over sodium sulfate, filtered, and distilled. There was obtained 0.6 g. of white solid melting at 216-222°. A mixed melting point showed that this product was identical with that obtained by the filtration of the hydrolyzed reaction mixture. The total crude yield was, therefore, 1.1 g. (85 per cent). The combined crude product was

recrystallized twice from a benzene-ethanol solution to give 0.6 g. (46 per cent) of colorless crystals melting at 232-234°. There was no depression in mixed melting point with an authentic sample of tetra-p-tolylsilane.

c. 1,1,1-Triphenyl-2,2,2-trimethyldisilane. A mixture of 2.0 g. (0.006 mole) of 1,1,1-triphenyl-2,2,2-trimethyldisilane, 1.5 ml. of sodium-potassium alloy, and 100 ml. of ether was stirred at room temperature. Immediately after mixing a yellow color developed from the reaction mixture. About 2 hours later a large amount of yellow precipitate was formed in the dark green mixture. After 21 hours of stirring a solution containing 1.4 g. (0.009 mole) of bromobenzene dissolved in 20 ml. of ether was added rapidly. Heat was evolved during the addition while the reaction mixture became a light tan suspension containing some white precipitate. Fifteen minutes later water was added to destroy the excess alloy. The hydrolyzed mixture was filtered by suction to give 1.0 g. (50 per cent) of tetraphenylsilane melting at 230-232°. The ethereal solution was separated and distilled to leave a small amount of brown liquid containing some white solid. The solid was filtered and washed with a small amount of petroleum ether (b.p. 60-70°). This was shown to be tetraphenylsilane by a mixed melting point. It weighed 0.2 g. (10 per cent) and melted at 217-226°. No attempt was made to distill the small amount

of supposed phenyltrimethylsilane from the brown oil.

d. 1,1,2,2-Tetraphenyl-1,2-di-p-tolyldisilane.

(i) By sodium-potassium alloy. This organodisilane was cleaved readily by sodium-potassium alloy in ether. The procedure has been given on page 78.

(ii) By iodine (attempted). Ten drops of a dilute solution of iodine in chloroform was added to 0.50 g. of 1,1,2,2-tetraphenyl-1,2-di-p-tolyldisilane dissolved in 30 ml. of chloroform. The solution was refluxed for 24 hours. There was no evidence of reaction. The purple color of the solution seemed to be the same as that at the beginning. Chloroform and iodine were removed by distillation to recover 0.46 g. (92 per cent) of starting material melting at 250-252°.

(iii) By oxygen (attempted). Dry oxygen gas was bubbled through a solution containing 0.50 g. of 1,1,2,2-tetraphenyl-1,2-di-p-tolyldisilane dissolved in 30 ml. of refluxing benzene for 24 hours. The benzene was then distilled to recover 0.48 g. (96 per cent) of starting material melting at 250-252°.

e. 1,1,2-Triphenyl-1,2,2-tri-p-tolyldisilane.

(i) By iodine (attempted). A solution containing 25 ml. of chloroform and 0.5 g. of 1,1,2-triphenyl-1,2,2-tri-p-tolyldisilane was heated with 4 drops of a 1 per cent solution of iodine in chloroform at the refluxing temperature for 16 hours. After the solvent had been removed by

distillation, 0.47 g. (94 per cent) of unchanged starting material was recovered.

(ii) By oxygen (attempted). Oxygen gas was bubbled through 0.50 g. of 1,1,2-triphenyl-1,2,2-tri-p-tolyldisilane dissolved in 25 ml. of benzene at the refluxing temperature for 18 hours. A 98 per cent recovery of starting material was obtained.

7. Preparation of other organosilicon-metallic compounds

a. Triphenylsilyllithium.

(i) From triphenylchlorosilane (attempted). Triphenylchlorosilane, 2.9 g. (0.01 mole), was dissolved in 50 ml. of ethylamine at 10°. To this there was added 0.14 g. (0.02 g. atom) of lithium. The latter dissolved slowly to form a deep red solution. Then 1.8 g. of bromobenzene was added to the solution. The deep red color of the solution changed to light yellow after the addition. The solution was stirred for 1 hour at room temperature, and the solvent was evaporated slowly at room temperature by a stream of nitrogen. Ether was added to extract the deep brown residue and filtered to separate 0.8 g. of insoluble material which did not melt below 250° and was soluble in water (presumably inorganic). The ethereal solution was distilled to give a deep brown oil. No tetraphenylsilane or any pure product could be isolated.

In a second run, the solution containing lithium and

triphenylchlorosilane (same size) was cooled to -30°, and to it there was added another portion of triphenylchlorosilane. The deep red color gave way to light yellow as before, and the reaction mixture was stirred 2 hours at -30°. Then the mixture was warmed to room temperature to remove the solvent. The gelatinous residue was extracted with ether. From the ether extract an oily residue was obtained which was vacuum-distilled to give 4.0 g. of colorless liquid boiling at 186-188° at 1.1 mm. pressure. On standing, it solidified, m.p. 48-51°. This solid product appeared to be triphenylethylaminosilane. No hexaphenyldisilane was isolated.

In a third attempt one equivalent of lithium was added to triphenylchlorosilane in ethylamine in order to try to make the so-called "Triphenylsilicyl Ethylamine" prepared by Kraus and Eatough.[140] The reaction mixture was stirred 2 hours at -50°, and then it was warmed to remove the solvent. The residue was vacuum-distilled to give a colorless liquid boiling at 176-178° at 0.6 mm. pressure, m.p. 51-54°. A mixed melting point with the product obtained from the second run was not depressed. A sample of this product was boiled in ether for 2 hours, but no hexaphenyldisilane resulted. When this product was treated with dilute hydrochloric acid, triphenylsilanol separated. Apparently the only product which could be isolated was triphenylethylaminosilane.

In a fourth experiment it was planned to find out whether or not triphenylchlorosilane alone reacted with ethylamine. A solution of 5.9 g. (0.02 mole) of triphenylchlorosilane in ethylamine was stirred 2 hours at -20°. After evaporation of the solvent 7.1 g. of light tan solid melting at 50-53° was obtained. This did not depress the melting point of the product formed when lithium was added. Apparently triphenylchlorosilane reacted with the solvent, ethylamine, with or without the presence of lithium to give triphenylethylaminosilane.

(ii) From triphenylbromosilane (attempted). Triphenylbromosilane was prepared in 98 per cent yield from the bromination of triphenylsilane with bromine in refluxing carbon tetrachloride.

In the first attempt 3.4 g. (0.01 mole) of triphenylbromosilane was dissolved in ethylamine at -40°. Lithium wire, 0.14 g. (0.02 mole) was dissolved in this solution in about 30 minutes to form a deep red solution. Then the reaction mixture was warmed to remove ethylamine, and about 30 ml. of liquid ammonia was condensed on the oily residue after the latter had been cooled to -40°. No apparent change was observed after the addition of 1.9 g. of bromobenzene. The reaction mixture was stirred at -40° for 5 hours, and the solvent was evaporated as it was allowed to warm to room temperature. The gummy brown residue was

extracted with ether from which a brown oil was obtained. This appeared to be triphenylethylaminosilane. No tetraphenylsilane was isolated.

(iii) From triphenylsilane (attempted). A preliminary experiment was designed for the purpose of finding out if triphenylsilane reacted with ethylamine the same way triphenylchlorosilane did. Triphenylsilane was stirred in ethylamine at 0° for 4 hours. After the solvent had been evaporated, there was recovered 94 per cent of unchanged triphenylsilane. This showed that triphenylsilane alone did not react with ethylamine.

In a second experiment 4.0 g. (0.015 mole) of triphenylsilane was dissolved in ethylamine at -30°. Then 0.22 g. (0.031 g. atom) of lithium wire was added to form a deep red solution. Two hours later 6.3 g. (0.031 mole) of iodobenzene was added in one portion. There was no appreciable change during the addition. The solvent was evaporated slowly by a stream of nitrogen while it was allowed to warm to room temperature. A deep brown gummy residue was remained. An attempt to purify the residue was unsuccessful.

(iv) From hexaphenyldisilane and phenyllithium (attempted). A mixture containing 5.2 g. (0.01 mole) of hexaphenyldisilane and 0.02 mole of phenyllithium in 50 ml. of ether was stirred 60 hours at room temperature. No apparent reaction was observed. The ether was distilled,

and 50 ml. of xylene was added to the residue. The reaction mixture was heated at the refluxing temperature for another 30 hours. It was noticed that a brownish-orange color was developed when the reaction mixture was heated. On cooling the color faded somewhat. On re-heating the color became intense again. Finally, the suspension was cooled and filtered by suction to give 4.7 g. (90 per cent) of recovered hexaphenyldisilane melting at 362-364°. From the filtrate a small amount of gummy solid melting at 210-240° was separated. The quantity was too small to be purified conveniently. This reaction had also been studied by Dunn[6] in this Laboratory with similar results.

b. Triphenylsilylsodium.

(i) From triphenylsilane (attempted). A solution of 2.85 g. (0.011 mole) of triphenylsilane in 50 ml. of ether was stirred at room temperature for 5 hours with 0.5 g. of 35 per cent sodium dispersion in tetrahydronaphthalene (Ethyl Corporation). Then 3.5 g. (0.022 mole) of ethyl iodide was added to the reaction mixture and was stirred for another 4 hours. The excess sodium was treated with a few ml. of ethanol, followed by about 50 ml. of water. The organic layer was separated, dried over sodium sulfate, and distilled. Petroleum ether (b.p. 60-70°) was added to the residue and filtered. One g. of triphenylsilanol was obtained as the insoluble residue. The filtrate was

evaporated to leave an oil which solidified on standing. There was obtained 1 g. of triphenylethoxysilane (mixed melting point) melting at 62-64°. No triphenylethylsilane was isolated.

(ii) From triphenylbenzylsilane (attempted). A mixture containing 1.4 g. of 35 per cent sodium dispersion in tetrahydronaphthalene (Ethyl Corporation), 3.8 g. (0.011 mole) of triphenylbenzylsilane, and 75 ml. of ether was refluxed for 8 hours. No change was observed except that part of the sodium dispersion coalesced to form small lumps. To this there was added 6.8 g. (0.044 mole) of ethyl iodide, and the reaction mixture was then stirred 18 hours at room temperature. Some deep blue precipitate was formed, probably due to the formation of sodium iodide. A small amount of methanol was added to react with the unused sodium in the system. The mixture was distilled to remove volatile solvents. Water and ether were added to extract the residue. From the ethereal solution 3.8 g. (100 per cent) of impure starting material melting at 90-93° was recovered. One recrystallization from petroleum ether (b. p. 60-70°) yielded 2.4 g. (68 per cent) of colorless transparent crystals melting at 98-99°. From the mother liquor only some impure triphenylbenzylsilane was obtained.

(iii) From hexaphenyldisilane and sodium in liquid ammonia. Although hexaphenyldisilane did not react

with sodium in xylene or dioxane, it was cleaved by sodium in liquid ammonia smoothly to give presumably triphenylsilylsodium.

Sodium, 0.35 g. (0.015 g. atom), was cut into small pieces and dropped into about 50 ml. of liquid ammonia at -50°. To this deep blue solution was added 2.6 g. (0.005 mole) of hexaphenyldisilane in one portion. The reaction mixture was stirred 6 hours at -50°. It was observed that some brown precipitate had formed although the color was masked by the deep blue color due to the excess of sodium in liquid ammonia. The cooling bath was then removed so that ammonia was evaporated as it was warmed up. A small amount of ethanol was added to the dead white residue to destroy the excess sodium. Water was then added, and the mixture was filtered to give 1.6 g. of solid which softened at 120° but did not melt completely until 360°. This was boiled with a solution of benzene and ethanol and filtered hot. There was obtained, as the insoluble residue, 0.1 g. (4 per cent) of hexaphenyldisilane melting at 360-362°. The filtrate was cooled to give 0.8 g. of solid melting at 150-200°. This was shaken with cold ethanol and filtered to separate 0.4 g. of solid melting at 230-234°. One recrystallization from benzene raised the melting point to 233-235°; a mixed melting point with tetraphenylsilane was the same. The yield was 0.3 g. (9 per cent). The

ethanolic solution was evaporated to dryness, and the residue was recrystallized from petroleum ether (b. p. 60-70°) to give 0.4 g. (11 per cent) of triphenylsilanol melting at 151-152°.

From the mother liquor after the removal of 0.8 g. of solid melting at 150-200°, evaporation of solvent resulted in 0.12 g. of colorless crystals melting at 163-167°. It appeared to be impure hexaphenyldisilazane (lit.[188] m.p. 175°).

c. Pentaphenyldisilanyllithium (attempted). A mixture of 2.0 g. of pentaphenylchlorodisilane, 0.25 g. of lithium, and 30 ml. of ether was stirred 7 hours at room temperature and then refluxed 10 hours. No reaction was observed. The ether was evaporated, and 30 ml. of di-n-butyl ether was added. The reaction mixture was refluxed 12 hours. There was no indication of any reaction. Color Test I at the end of this period was negative.

d. Trimethylsilylpotassium (attempted). A mixture of 2.4 g. of trimethylethoxysilane, 2 ml. of sodium-potassium alloy, and 20 ml. of ether was stirred vigorously at room temperature for 24 hours. There was no indication of reaction. The colorless suspension gave a negative Color Test I.

In another experiment 2.5 g. of trimethylchlorosilane

---

[188] H. H. Reynolds, L. A. Bigelow, and C. A. Kraus, J. Am. Chem. Soc., 51, 3067 (1929).

was stirred with 2 ml. of sodium-potassium alloy for 70 hours at room temperature. Then 5.9 g. (0.02 mole) of triphenylchlorosilane was added and stirred for 30 minutes. Water was added to destroy the excess alloy, and the mixture was filtered to remove traces of solid melting at 330°. From the ethereal solution 5.4 g. of impure triphenylsilanol melting at 126-142° was obtained, presumably from the hydrolysis of triphenylchlorosilane. One recrystallization from petroleum ether (b. p. 60-70°) gave 3.8 g. of pure triphenylsilanol melting at 150°.

3. Diphenylsilyldipotassium (attempted). A solution of 5.1 g. (0.02 mole) of diphenyldichlorosilane in 50 ml. of ether was added to 5 ml. of sodium-potassium alloy. The reaction mixture was stirred 70 hours at room temperature to form a bluish-gray suspension. As much as 60 g. of mercury was necessary to amalgamate the unchanged alloy to form a sticky mass. The suspension was decanted from the amalgam into a dropping funnel from which it was added to 7.1 g. (0.05 mole) of methyl iodide. After 24 hours water was added, and the mixture was filtered to remove a small amount of solid melting at about 300°. From the ethereal solution a very sticky gummy solid residue was formed. Purification of this residue was not successful.

In another experiment 2.5 g. of diphenyldichlorosilane was stirred with 2.4 ml. of sodium-potassium alloy in 60 ml.

of ether for 86 hours. The excess alloy was amalgamated, and the suspension was decanted into a dropping funnel from which it was added to 5.9 g. (0.02 mole) of triphenylchlorosilane suspended in a small amount of ether. There was no apparent change during this addition. The reaction mixture was then stirred 44 hours. Water was added to the bluish-gray suspension, and it was filtered by suction. The solid residue was extracted with benzene and filtered hot to give 1.1 g. of solid melting at 170-270°. Further recrystallization from benzene yielded 0.7 g. of white powder melting at 180-230°. Subsequent recrystallizations did not yield a pure product. From the ethereal solution 3.0 g. of impure triphenylsilanol melting at 142-146° was obtained. There was no indication of the formation of diphenylsilyldipotassium.

8. Addition of triphenylsilylpotassium to the carbon-carbon double bond

a. Triphenyl-α,β-diphenylethylsilane. A triphenylsilylpotassium suspension prepared from 5.2 g. (0.01 mole) of hexaphenyldisilane according to the procedure described previously on page 52 was added rapidly to 3.6 g. (0.02 mole) of trans-stilbene dissolved in 50 ml. of dry benzene. The reaction mixture turned brownish-red rapidly during the addition without much change in temperature. After 24

hours of stirring the reaction mixture was hydrolyzed with water. Some heat was evolved during the hydrolysis, and the mixture changed momentarily to deep violet, then light green and finally a light gray, turbid liquid resulted. The hydrolyzed mixture was filtered to remove traces of solids. The organic layer was separated from the filtrate, dried over sodium sulfate, filtered, and distilled to give 8.8 g. of colorless viscous oil. This oil was boiled with ethanol, filtered hot, and cooled. On standing, 0.36 g. (5 per cent) of tetraphenylsilane (mixed melting point) melting at 230-232° was obtained. The mother liquor was concentrated to give 4.7 g. (53 per cent) of colorless crystals melting at 129-134°. Two recrystallizations from a mixed solvent of ethanol and petroleum ether (b. p. 60-70°) gave 3.4 g. (39 per cent) of large, transparent crystals melting at 135-136°.

Anal. Calcd. for $C_{32}H_{28}Si$: Si, 6.37. Found: Si, 6.40, 6.41.

b. Carbonation of β-triphenylsilyl-α,β-diphenylethylpotassium. A triphenylsilylpotassium suspension was prepared from 5.2 g. (0.01 mole) of hexaphenyldisilane in accordance with the procedure described on page 52. This suspension was added rapidly to 3.6 g. (0.02 mole) of trans-stilbene dissolved in 50 ml. of dry benzene. The brownish-red mixture was stirred 18 hours at room temperature and then was poured into a dry ice-ether slurry with stirring. The carbonation mixture was allowed to stand until it

reached room temperature. It was hydrolyzed with dilute hydrochloric acid and was filtered to remove 3.0 g. of solid melting at 295° with evolution of gases. This product was insoluble in chloroform, xylene, ethanol, or alcoholic potash, but it was very soluble in hot dioxane. Three recrystallizations from dioxane gave 1.7 g. of white crystals melting at 298-300° with evolution of gases at the melting temperature.

From the ethereal solution of the reaction mixture, 0.4 g. of tetraphenylsilane (mixed melting point) was isolated from 6.1 g. of the gummy resinous residue. Attempts to isolate other pure products from the mother liquor were unsuccessful.

The silicon content of the carbonation product was analyzed. Results showed that it contained 6.12 per cent and 6.18 per cent of silicon. The calculated value for β-triphenylsilyl-α,β-diphenylpropionic acid, $(C_6H_5)_3SiCH(C_6H_5)CH(C_6H_5)COOH$, is 5.79, while that for di-(β-triphenylsilyl-α,β-diphenylethyl) ketone, $[(C_6H_5)_3SiCH(C_6H_5)CH(C_6H_5)]_2CO$, is 6.19. Infrared spectra[189] showed that this product seemed to be the former compound, namely, the acid. Further identification work and related investigations are underway.

---

[189]The author thanks Mr. M. Margoshes for the infrared spectra studies of this and other compounds.

B. Organotin Compounds

1. Organotin chlorides

a. Triphenyltin chloride. This compound was prepared by the reaction of tetraphenyltin with stannic chloride according to the procedure given by Dr. Bullard of Eastman Kodak Company. The yield varied somewhat with the ratio of the two reagents. An excess of stannic chloride is necessary in order to obtain good yields of triphenyltin chloride.

In one experiment 61.0 g. (0.143 mole) of dry tetraphenyltin and 12.4 g. (0.0476 mole) of stannic chloride were placed in a 1000-ml. flask equipped with an air condenser topped with a drying tube. The mixture was heated in a wax bath to 220° in a period of 30 minutes. The liquid was maintained at this temperature for 2 hours with occasional shaking. The reaction mixture was cooled and then it was boiled with petroleum ether (b. p. 75-115°) and filtered hot to remove 10.2 g. (17 per cent) of unconverted tetraphenyltin. The filtrate was concentrated and cooled to give 50.4 g. (69 per cent) of triphenyltin chloride melting at 98-103°. Two recrystallizations from petroleum ether (b. p. 75-115°) raised the melting point to 105-107°).

In another run 128 g. (0.30 mole) of tetraphenyltin and 36.5 g. (0.14 mole) of stannic chloride were fused together and worked up the same way described above to give 71 per

cent of triphenyltin chloride and 1 per cent recovery of tetraphenyltin. Rosenberg[190] ran the reaction with 118.0 g. (0.276 mole) of tetraphenyltin and 33.4 g. (0.128 mole) of stannic chloride and obtained 92.8 g. (65.5 per cent) of triphenyltin chloride melting at 104-106°.

b. Diphenyltin dichloride. A mixture containing 85.4 g. (0.2 mole) of tetraphenyltin and 52.1 g. (0.2 mole) of stannic chloride was heated slowly to 180° and then maintained at that temperature for 2 hours with occasional shaking. The light yellow liquid solidified on cooling. The crude product was boiled with active carbon in 250 ml. of petroleum ether (b. p. 28-40°), filtered hot, and cooled to yield 119 g. (87 per cent) of colorless crystals melting at 40-44°. One recrystallization from 300 ml. of petroleum ether (b. p. 60-70°) raised the melting point to 43°. Yield: 105 g. (76 per cent).

c. Phenyltin trichloride. A mixture containing 21.4 g. (0.05 mole) of tetraphenyltin and 39.1 g. (0.15 mole) of stannic chloride was heated at 150° for 3 hours. The resulting liquid was distilled in vacuo. There was obtained 50.7 g. (84 per cent) of colorless liquid boiling at 96° at 1.4 mm. pressure.

---

[190]Unpublished studies of S. D. Rosenberg.

2. Organotin compounds containing substituted phenyl groups

a. Triphenyl-p-bromophenyltin. Triphenyl-p-bromophenyltin was prepared by Krause and Weinberg[191] from the reaction of p-dibromobenzene, magnesium, and triphenylbromotin. No yield was given in this paper. Besides, the melting point of this compound was reported to be 224°, which seemed to be abnormally high for compounds of this type. Accordingly, the preparation of triphenyl-p-bromophenyltin was re-investigated. Triphenyltin chloride was used as starting material because of its availability. Also, the use of an organolithium compound was employed.

(i) From p-bromophenyllithium (attempted). Several attempts were made to prepare triphenyl-p-bromophenyltin essentially using a published procedure[192] for the preparation of the silicon analog.

In the first experiment 0.10 mole of freshly prepared n-butyllithium was added, over a period of 10 minutes, to 25.8 g. (0.11 mole) of p-dibromobenzene suspended in 50 ml. of ether at 0°. A negative Color Test II-A[193] was obtained immediately after the addition. Then 34.7 g. (0.09 mole) of triphenyltin chloride dissolved in ether was added to the

---

[191] E. Krause and K. Weinberg, Ber., 62, 2235 (1929).

[192] H. Gilman and H. W. Melvin, Jr., J. Am. Chem. Soc. 72, 995 (1950).

[193] H. Gilman and J. Swiss, ibid., 62, 1847 (1940).

organolithium compound thus formed. The reaction mixture was warmed by the heat of reaction while a large amount of white precipitate was formed. After two hours of refluxing the reaction mixture was hydrolyzed with ammonium chloride solution and filtered by suction. There was obtained, as the insoluble solid, 20.5 g. of white solid melting at 190-212°. Two recrystallizations from benzene yielded 15.2 g. of tetraphenyltin (mixed melting point) melting at 223-225°. The ethereal solution of the reaction mixture was separated, dried over sodium sulfate, filtered, and distilled to give a pleasant-smelling, yellow gummy residue. This was treated with hot 95 per cent ethanol, cooled, and filtered to separate 19.9 g. of cream-colored, sticky solid melting at 103-110°. Two recrystallizations from a solution of benzene and ethanol raised the melting point to 117-119°. This compound contained halogen and tin. It contained 18.9 per cent of bromine and 22.8 per cent of tin by analysis. The structure of this compound was not investigated.

In a second experiment, 0.11 mole of n-butyllithium was added to 27.2 g. (0.02 mole) of p-dibromobenzene dissolved in 100 ml. of ether. After 5 minutes, 36.5 g. (0.095 mole) of triphenyltin chloride dissolved in 100 ml. of benzene was added rapidly to the organolithium compound which was cooled in an ice bath. Ten minutes later the reaction mixture was poured onto a dry ice-ether slurry with stirring. Following

attainment of room temperature the carbonation mixture was hydrolyzed with dilute hydrochloric acid (1:3) and filtered to separate 18.6 g. of tetraphenyltin melting at 219-222°. The ether solution was extracted twice with 400 ml. of 7 per cent sodium hydroxide solution. Upon acidification of the alkaline extract some solid precipitated. The organic acid was extracted with ether, from which 1.2 g. of p-bromobenzoic acid (mixed melting point) melting at 248-252° was obtained. From the ethereal solution after the alkaline extraction some oily solid was formed. This was washed with a small amount of cold ethanol and filtered. The colorless solid residue (23.5 g.) melted at 105-110°. Two recrystallizations from ethanol raised the melting point to 117-119°. A mixed melting point showed that this was the same compound as that obtained in the first run.

In a third attempt, the reaction was run at -20° and worked up as usual. Again, the only products obtained were tetraphenyltin and the unidentified compound melting at 117-119°. In these attempts no triphenyl-p-bromophenyltin was formed.

(ii) From p-bromophenylmagnesium iodide. A magnesium iodide solution in ether was prepared by treating an excess of magnesium with iodine in anhydrous ether followed by filtration through glass wool to remove the excess magnesium. To 11.8 g. (0.05 mole) of p-dibromobenzene was added 0.05 mole of n-butyllithium at 0°. Ten minutes later

0.05 mole of magnesium iodide dissolved in ether was added rapidly to the reaction mixture and was stirred 10 minutes; meanwhile, the reaction mixture was cooled to -20°. Then 19.3 g. (0.05 mole) of triphenyltin chloride dissolved in 75 ml. of dry benzene was added rapidly to the reaction mixture. Color Test I at the end of the addition was negative. Three minutes later the reaction mixture was hydrolyzed with cold, aqueous ammonium chloride solution. The ethereal solution was separated, dried over sodium sulfate, filtered, and distilled to give 21.7 g. (86 per cent) of white solid melting at 132-134°. One recrystallization from a solution containing 150 ml. of ethanol and 50 ml. of benzene gave 18.1 g. (72 per cent) of colorless crystals melting at 133-135°. Subsequent recrystallizations from a solution of ethanol and benzene or from ethanol alone did not change the melting point. Since the melting point found was very different from that described in the literature[191], the compound was analyzed.

Anal. Calcd. for $C_{24}H_{19}BrSn$: Sn, 23.46; Br, 15.79. Found: Sn, 23.58, 23.64; Br, 15.64, 15.70.

b. Triphenyl-p-dibromomethylphenyltin (attempted). Attempt was made to prepare triphenyl-p-dibromomethylphenyltin by the bromination of triphenyl-p-tolyltin with N-bromosuccinimide following essentially the method of preparation of the silicon analog by C. G. Brannen.[41]

Thirteen and two-tenths g. (0.03 mole) of

triphenyl-p-tolyltin, 11.8 g. (0.06 mole) of 96 per cent N-bromosuccinimide, and 300 ml. of carbon tetrachloride were refluxed 12 hours under the irradiation of a mercury-vapor lamp. Four and one-half g. of tan powder melting with decomposition at 120° was obtained by filtration. From the distillation of the filtrate, 1.5 g. of light brown solid decomposing at 180° and 13.2 g. of light brown sticky solid were obtained. They gave a positive Beilstein Test for halogen. No pure compound was isolated from this reaction.

This experiment was repeated in benzene solution, from which a small amount of solid decomposing at 260° and a large amount of gummy solid were obtained. They, again, seemed to be a bad mixture which could not be separated.

3. Organotin compounds containing water-solubilizing groups

a. Triphenyl-p-dimethylaminophenyltin. An ether solution containing 0.14 mole of p-dimethylaminophenyllithium was added to a suspension of 52.1 g. (0.14 mole) of triphenyltin chloride in 150 ml. of ether over a period of 15 minutes. Some heat was evolved. The grayish-yellow suspension was stirred 1 hour at room temperature and then hydrolyzed with aqueous ammonium chloride solution. The somewhat pasty solid formed was filtered and dried. Then it was boiled with charcoal in petroleum ether (b. p. 75-115°) and filtered hot. On cooling a white solid melting

at 127-130° was separated. Yield, 45.5 g. (72 per cent). Two recrystallizations from petroleum ether (b. p. 75-115°) raised the melting point to 132-134°.

(i) Triphenyl-p-dimethylaminophenyltin methiodide. A mixture containing 4.7 g. (0.01 mole) of triphenyl-p-dimethylaminophenyltin, 14.2 g. (0.10 mole) of freshly distilled methyl iodide, and 25 ml. of methanol was refluxed for 4 hours. The reaction mixture was cooled in an ice-water bath and was filtered by suction. There was obtained 5.8 g. (95 per cent) of colorless solid which melted at 167-169° with evolution of gases when it was heated at the rate of 6° per minute in a capillary tube. When it was heated at the rate of 2° per minute it melted at 164°. Recrystallization from methanol did not change the melting point. On exposure to light the compound turned yellow. In the absence of light it remained colorless. This compound is slightly soluble in hot water and is very soluble in hot methanol and ethanol.

Anal. Calcd. for $C_{27}H_{28}INSn$: Sn, 19.39; I, 20.73. Found: Sn, 19.60, 19.59; I, 20.71, 20.43.

(ii) Triphenyl-p-dimethylaminophenyltin methosulfate. Two and one-half g. (0.02 mole) of redistilled dimethyl sulfate was added to 4.7 g. (0.01 mole) of triphenyl-p-dimethylaminophenyltin dissolved in 20 ml. of dry benzene. There was very little heat effect while some white solid

appeared slowly. The reaction mixture was heated in a hot water bath for 2 hours. On cooling, 5.1 g. (86 per cent) of white solid melting at 229-233° with evolution of gas was obtained. This was recrystallized from methanol. It was found that the melting point of this purified product also varied with the rate of heating. When a sample was heated in a capillary tube at the rate of 3° per minute, it melted at 240-243°. When it was heated twice as fast, it melted at 244-246°. This compound is insoluble in water and is soluble in hot methanol, hot chloroform and ethylene glycol.

Anal. Calcd. for $C_{28}H_{31}NO_4SSn$: Sn, 19.91. Found: Sn, 20.14, 20.09.

b. Diphenyldi-(p-dimethylaminophenyl)-tin. A solution of 0.085 mole of p-dimethylaminophenyllithium in 86 ml. of ether was added, over a period of 10 minutes, to 14.4 g. (0.042 mole) of diphenyltin dichloride dissolved in 20 ml. of dry ether. Heat was evolved, and a dark green color developed. The reaction mixture was stirred 1 hour at room temperature, and the ether was distilled. The greenish oily residue was extracted with hot benzene. After the benzene had been evaporated from the extract, a light brown resinous residue resulted. It weighed 18.7 g. (87 per cent). Attempts to purify the crude product were unsuccessful. It was soluble in most organic solvents except cold ethanol and cold petroleum ether (b. p. 60-70°). This crude product

was used for the preparation of the following two derivatives without further purification.

(i) Diphenyldi-(p-dimethylaminophenyl)-tin dimethiodide. To 5.1 g. (0.01 mole) of this crude diphenyldi-(p-dimethylaminophenyl)-tin was added 14.2 g. (0.10 mole) of methyl iodide (the excess methyl iodide being used as the solvent). The reaction mixture was allowed to stand at room temperature for 3 hours during which time a white solid was formed. This was crushed, washed with petroleum ether (b. p. 28-40°), and filtered. Light tan solid weighing 7.8 g. (98 per cent) was obtained. When it was heated at the rate of 4° per minute, it melted at 164-168°. It was insoluble in water and most organic solvents except alcohols and glycols. Recrystallization of the crude product from methanol did not change the melting point, which varied with the rate of heating.

Anal. Calcd. for $C_{30}H_{36}I_2N_2Sn$: I, 31.84; Sn, 14.89. Found: I, 32.32, 31.76; Sn, 14.63, 14.69.

(ii) Diphenyldi-(p-dimethylaminophenyl)-tin dimethosulfate (attempted). Ten g. (0.08 mole) of dimethyl sulfate was added to 5.1 g. (0.01 mole) of crude diphenyldi-(p-dimethylaminophenyl)-tin dissolved in 30 ml. of methanol. The solution turned green with evolution of heat. After 2 hours of refluxing a brown solution resulted. Ether was added to the cold solution; two layers were formed. No solid

separated. Then the solution was distilled, and the residue was taken up with water. An excess of acetone was added to precipitate 0.9 g. of fine white powder decomposing at 125°. Purification of this product was unsuccessful. Further addition of acetone to the mother liquor resulted in an oil. This oil was insoluble in most organic solvents except methanol. Also, it was slightly soluble in water.

c. Phenyltri-(p-dimethylaminophenyl)-tin (attempted). A solution containing 0.12 mole of p-dimethylaminophenyllithium in 75 ml. of ether was added to 11.8 g. (0.039 mole) of phenyltin trichloride dissolved in 20 ml. of ether. Color Test I was negative until all of the aryllithium compound had been added. After 2 hours the reaction mixture was hydrolyzed and worked up as usual. About 20 g. of oily, grayish-violet solid was obtained from the ether solution. Attempts to purify the crude product were unsuccessful. It separated as an oil in benzene, carbon tetrachloride, acetone, and solvent pairs.

d. Tetrakis-(p-dimethylaminophenyl)-tin. A solution containing 0.12 mole of p-dimethylaminophenyllithium in ether was added to 7.8 g. (0.03 mole) of stannic chloride dissolved in 25 ml. of benzene. Heat was evolved while the reaction mixture became grayish-green. After 1 hour of stirring the pasty mixture was poured into iced water. There was obtained 14.8 g. (82 per cent) of light brown solid melting at 163-200°. Recrystallization from a solution of ethanol and

benzene gave white needles melting at 196-198°.

(i) Tetrakis-(p-dimethylaminophenyl)-tin tetramethiodide. Three g. (0.005 mole) of tetrakis-(p-dimethylaminophenyl)-tin, 12 ml. of methyl iodide, and 50 ml. of methanol were refluxed gently on a water bath for 4 hours. Light brown solid (5.4 g., 93 per cent) was obtained by filtration. It melted with decomposition at 190°. The crude product could be recrystallized from water to give colorless needles, but the melting point was not affected. This compound is soluble in hot water and slightly soluble in hot methanol.

Anal. Calcd. for $C_{36}H_{52}I_4N_4Sn$: Sn, 10.17; I, 43.50. Found: Sn, 10.19, 10.03; I, 42.73, 42.79.

(ii) Tetrakis-(p-dimethylaminophenyl)-tin tetramethosulfate (attempted). A mixture containing 3.0 g. (0.005 mole) of tetrakis-(p-dimethylaminophenyl)-tin, 10.4 g. (0.082 mole) of dimethyl sulfate, and 20 ml. of methanol was refluxed on a water bath for 1.5 hours. On cooling, a light violet precipitate was formed. This crude product was too sticky to be placed in a capillary tube for melting point determination. It was soluble in water and hot methanol, but insoluble in most other organic solvents. It was partially purified by dissolving in hot methanol and then precipitated by a large amount of ether. The pale reddish-brown solid so formed was dried in a desiccator. It softened

at 180°, then gas bubbles evolved and finally turned dark at 195°. The weight was 3.1 g. Analysis showed that it contained 13.5 per cent of sulfur and 13.1 per cent tin. No reasonable product had this composition. It appeared to be a mixture.

e. Triphenyl-γ-diethylaminopropyltin. In a 1000-ml. three-necked flask fitted with a glass stirrer, a dropping funnel, and a nitrogen gas-inlet tube was placed 6.6 g. (0.035 mole) of finely ground anhydrous stannous chloride suspended in 300 ml. of ether. While this suspension was kept at -10°, 0.105 mole of phenyllithium was added dropwise, over a period of 1.5 hours, to the stannous chloride. The reaction mixture changed from yellow to deep red and finally to tan. Freshly distilled γ-diethylaminopropyl chloride, 5.8 g. (0.039 mole), was added over a period of 15 minutes to the triphenyltin-lithium suspension at -10°. After the addition, the reaction mixture was allowed to warm to room temperature and then was refluxed for 2 hours. The gray suspension was hydrolyzed with cold water and filtered. Seven-tenths g. of solid melting at 215-220° was obtained, which, after one recrystallization, was identified as tetraphenyltin by mixed melting point. Following separation, drying, and distillation of the ethereal solution from the filtrate an oily residue weighing 14.5 g. was obtained. It solidified upon cooling in a dry ice-acetone bath. However, attempts to purify the crude product by low

temperature crystallization were unsuccessful. The crude product was used as such for the preparation of the following derivatives.

(i) Triphenyl-γ-diethylaminopropyltin methiodide. Crude triphenyl-γ-diethylaminopropyltin, 4.6 g. (0.01 mole), was mixed with 14.2 g. of methyl iodide with stirring. A paste was formed immediately with evolution of heat. After 30 minutes, the excess methyl iodide was evaporated to give a light yellow paste which was then washed with petroleum ether (b. p. 28-40°) and filtered. Six g. of solid melting at 153-158° was obtained. Two recrystallizations from a solution of ethanol and petroleum ether (b. p. 60-70°) gave 4.1 g. (68 per cent) of colorless lustrous plates melting at 173-175°. This compound is soluble in ethylene glycol and chloroform and is slightly soluble in hot water.

Anal. Calcd. for $C_{26}H_{34}INSn$: I, 20.94; Sn, 19.58. Found: I, 21.07, 21.37; Sn, 19.64, 19.72.

(ii) Triphenyl-γ-diethylaminopropyltin methosulfate (attempted). Three g. of dimethyl sulfate was added to 3.8 g. (0.0082 mole) of triphenyl-γ-diethylaminopropyltin dissolved in 30 ml. of benzene. A large amount of heat was evolved while the whole mixture solidified. After 1 hour of refluxing on a water bath, two liquid layers were formed. The mixture was placed in a refrigerator. Four g. of white solid melting at 118-132° with evolution of gases

was separated by filtration. This product was very soluble in water, ethanol, methanol, and acetic acid at room temperature. Purification of the crude product was unsuccessful. It either separated as a sticky solid or formed two liquid layers in several solvents.

f. Triphenyl-p-carboxyphenyltin (attempted). This compound has been made by the oxidation of triphenyl-p-hydroxymethylphenyltin with potassium permanganate.[23] In this experiment, an attempt was made to synthesize it by the reaction of triphenyltin chloride and lithium p-lithiobenzoate.

One-tenth mole of n-butyllithium dissolved in 62 ml. of ether was added fairly rapidly to 10.1 g. (0.05 mole) of p-bromobenzoic acid suspended in 50 ml. of ether. Heat was evolved during the addition. The reaction mixture was kept below -10° at all time. Color Test II-A was negative after the addition. Then 19.3 g. (0.05 mole) of triphenyltin chloride was added in one portion to the cold mixture. Color Test I immediately after the addition became negative. The reaction mixture was hydrolyzed with aqueous ammonium chloride solution and was filtered to separate 10.2 g. of white solid melting at 113-118°. Recrystallizations from petroleum ether (b. p. 60-70°) raised the melting point to 125-126°. This compound contained 33.0 per cent of tin by analysis. It seemed to be triphenyltin oxide, $[(C_6H_5)_3Sn]_2O$, the calculated value of which was: Sn,

33.2 per cent. The melting point reported for this compound is 124°. The preparation of triphenyl-p-carboxyphenyltin might be successful if the organolithium compound is first converted to the Grignard reagent and then treated with triphenyltin chloride.

C. Organic Compounds Containing Bonds Between Two Different Group IV-B Elements

1. Triphenylsilyltriphenyltin

A triphenylsilylpotassium suspension prepared from 5.2 g. (0.01 mole) of hexaphenyldisilane was, after amalgamation, added rapidly to 7.7 g. (0.02 mole) of triphenyltin chloride suspended in 50 ml. of ether. Some heat was evolved, and the tan color of the reaction mixture faded away gradually. Color Test I after 4 hours was still positive; 6 hours later it became negative. The light gray suspension thus formed was hydrolyzed with water and filtered. There was obtained 10.5 g. (0.017 mole, 86 per cent) of white solid melting at 280-286°. Upon further heating some gray solid began to form in the molten sample. The crude product was recrystallized once from a mixed solvent of dioxane and benzene (1:1) to give 9.2 g. (76 per cent) of colorless, shinging crystals the melting point of which depended somewhat on the rate of heating. Thus, when a sample was heated fairly rapidly in a capillary tube it melted at 296-298°;

when another sample was heated very slowly it softened at 288° and melted at 292°. In all cases some gray precipitate was formed in the molten sample when it was heated above its melting point. A mixed melting point of this compound with the triphenylsilyltriphenyltin prepared by the reaction of triphenyltin-lithium with triphenylchlorosilane[152] was not depressed.

2. Triphenylsilyltriphenyllead (attempted)

In the first experiment, a suspension of triphenyllead-lithium was prepared by treating 0.09 mole of phenyllithium with 8.4 g. (0.03 mole) of lead chloride suspended in ether according to the procedure described recently.[194] To the cold suspension of triphenyllead-lithium thus prepared, there was added rapidly a solution of 8.9 g. (0.03 mole) of triphenylchlorosilane in 100 ml. of ether. There was no apparent change during the addition. After 15 minutes Color Test I was weakly positive; 1 hour later it became negative. The reaction mixture was stirred at room temperature for 4 hours and then was hydrolyzed with aqueous ammonium chloride solution. The mixture was filtered to separate 9.7 g. of gray solid which did not melt below 360° and was insoluble in benzene, chloroform, or nitrobenzene.

---

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

Upon ignition it burned with a smoky flame, emitting blue and carmine red color. It was suspected to be lead chloride contaminated with some lithium salt and some organic material. A sample was boiled with water and filtered hot. The aqueous solution gave a positive test for lead and chloride ions. From the ethereal solution 7.8 g. of light yellow solid melting at 125-140° was obtained. This was dissolved in a mixed solvent of petroleum ether (b. p. 60-70°) and acetone and was cooled to give 0.3 g. of light yellow solid which turned gray at 140° and black at 210°. The mother liquor was concentrated to yield 5.4 g. of crystals melting at 135-146°. One recrystallization from petroleum ether (b. p. 60-70°) gave 3.8 g. of triphenylsilanol (mixed melting point). This experiment was repeated three times by varying the reaction time and the temperature. In all cases only lead chloride and triphenylsilanol were obtained in good yield; no triphenylsilyltriphenyllead was isolated.

Since there appeared to be no reaction between triphenylchlorosilane and triphenyllead-lithium, it was hoped that it might be possible to synthesize the triphenylsilyltriphenyllead by the reaction of triphenylsilylpotassium with triphenyllead iodide. A triphenylsilylpotassium suspension was prepared by cleaving 2.0 g. (0.0039 mole) of hexaphenyldisilane with sodium-potassium alloy as described previously on page 52. A suspension of 3.9 g. (0.0069 mole)

of triphenyllead iodide in ether was added to the alloy-free triphenylsilylpotassium suspension. The reaction mixture became light brown after the addition, and no appreciable amount of heat was evolved. After 1 hour of stirring a light gray suspension was formed. This was hydrolyzed with water and was filtered. The greenish-gray solid residue was boiled with benzene and was filtered to separate 0.7 g. of greenish-yellow powder which turned gray at about 340° but did not melt below 500°. From the benzene solution 1.1 g. of white solid which turned gray at 155° and melted at 220° was obtained. This seemed to be hexaphenyldilead. From the ethereal solution 1.8 g. of colorless solid was obtained which melted with decomposition at 170°. On standing it changed to a light brown color. This was boiled with petroleum ether (b. p. 60-70°) and filtered hot. From the colorless filtrate there was obtained 0.5 g. of white crystals which turned gray at 165° and melted at 195° with decomposition. This product was not identified.

3. Triphenylstannyltriphenyllead (attempted)

A triphenyllead-lithium suspension was prepared by treating 0.06 mole of phenyllithium with 5.6 g. (0.02 mole) of lead chloride.[194] To this suspension was added 7.7 g. (0.02 mole) of triphenyltin chloride in one portion. No apparent change was observed after the addition. The reaction

mixture was stirred 5 hours at -5° and then was hydrolyzed with aqueous ammonium chloride solution and filtered. From the filtrate 0.2 g. of white crystals decomposing at 155° and melting at 224° was obtained. These appeared to be hexaphenyldilead. The insoluble tan solid (14.5 g.) turned gray upon heating, but it did not melt below 360°. Three g. of this product was extracted with ether for 3 days in a Soxhlet extractor. The extract was evaporated at room temperature with the aid of a water pump to leave 2.3 g. of colorless plates. Upon heating, part of the sample began to decompose at 93°, forming a light brown liquid; then it changed to gray at 120°. From that temperature until 225° there was no further change in the sample, a mixture of wet white solid containing some black precipitate. At 225° it melted to form a colorless liquid with some black precipitate. In the extractor, 0.3 g. of insoluble solid was recovered which did not melt upon heating. It seemed to be inorganic matter.

The colorless plates thus obtained changed on standing. Some black,lustrous spots gradually appeared on the center of some of these plates. A sample of these plates was heated on a melting point block. At about 70° it turned brown and then black without melting. Apparently, this product is unstable on standing.

IV. DISCUSSION

A. Organosilicon Compounds

In this investigation a number of organosilicon compounds have been prepared by the reaction of triphenylsilylpotassium with an organic halide. Triphenylsilylpotassium is a very reactive intermediate. It not only reacts with a large number of organic halides but also adds to the carbonyl group (such as the addition to Michler's ketone in Color Test I[184]) and to the carbon-carbon double bond of trans-stilbene. The last reaction is of interest because only very reactive organometallic compounds can add to the ethylenic linkage.[195] Similar reactions have not been observed for triphenyltin-lithium, which does not give a positive Color Test I or add to trans-stilbene.[190]

Among various compounds studied in this investigation it was found that hexaphenyldisilane is the best starting material for the preparation of triphenylsilylpotassium. The use of hexaphenyldisilane has some advantages which are not found in any other starting material such as triphenylchlorosilane, triphenylethoxysilane, or tetraphenylsilane.

---

[195] For a general discussion of the reactivity of various kinds of organometallic compounds, see H. Gilman, "Organic Chemistry", 2nd ed., John Wiley and Sons, New York, 1943, pp. 520-529.

First, hexaphenyldisilane can be made in excellent yields by coupling triphenylchlorosilane with sodium. The procedure is very simple and the product obtained directly from the reaction is good enough for the preparation of triphenylsilylpotassium without further purification. As a matter of fact, it has been observed that the cleavage reaction with the recrystallized hexaphenyldisilane is not as satisfactory as that using the "crude" hexaphenyldisilane which is actually of high purity. The reason for the slow reaction of the recrystallized hexaphenyldisilane is not due to the absence of catalytic substances which might be present in the unpurified hexaphenyldisilane but rather due to the degree of subdivision of the starting material because the hexaphenyldisilane is separated from the coupling reaction of triphenylchlorosilane as a finely divided granular crystalline substance while the recrystallized product tends to form rather large crystals. In a heterogeneous reaction like the cleavage of hexaphenyldisilane with sodium-potassium alloy, the rate of reaction depends a great deal on the surface area of the reactants, the larger the surface area the faster the reaction. Other starting materials are either not available or difficult to purify. For example, triphenylethoxysilane has to be made and purified. Triphenylchlorosilane, although commercially available, is difficult to keep due to its ease of hydrolysis. Hexaphenyldisilane can be dried conveniently

by putting it in an oven at 110° to insure the absence of moisture while this cannot be applied to low-melting compounds like triphenylchlorosilane. The stability of hexaphenyldisilane makes it possible to keep it indefinitely.

Second, hexaphenyldisilane is the ideal starting material for the preparation of triphenylsilylpotassium when the lack of by-product is being considered. The reaction of hexaphenyldisilane with sodium-potassium alloy proceeds according to the equation:

$$(C_6H_5)_3SiSi(C_6H_5)_3 + 2K(Na) \longrightarrow 2(C_6H_5)_3SiK$$

In other words, one mole of hexaphenyldisilane gives two moles of triphenylsilylpotassium. The only foreign materials in this system are the excess alloy and the solvent, ether. However, when other compounds are used there are some by-products present in the system which, in some cases, might induce side reactions, rendering the yield and the purity of the products low. Thus, when triphenylethoxysilane was used as the starting material for the preparation of triphenylsilylpotassium a 48 per cent yield of tetraphenylsilane was obtained following treatment with bromobenzene while a 96 per cent yield of tetraphenylsilane can be obtained when hexaphenyldisilane is used as starting material under similar conditions. Benkeser and co-workers[196] cleaved triphenylmethoxysilane with sodium-potassium alloy followed

---

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

by treatment with triethylchlorosilane and obtained 41 per cent of 1,1,1-triphenyl-2,2,2-triethyldisilane while a 60 per cent yield of the same compound can be obtained from triphenylchlorosilane.[132] The impurities in the former case are potassium methoxide and sodium methoxide while those in the latter case are the alkali metal chlorides. None of these by-products are formed from hexaphenyldisilane. The use of this compound leads to the best possible purity of triphenylsilylpotassium, and this is particularly important for the investigation of new reactions.

Third, the cleavage reaction of hexaphenyldisilane starts immediately on stirring a suspension of the disilane with sodium-potassium alloy and then goes smoothly. Any uncleaved starting material may be recovered as such with ease due to the high stability and low solubility of hexaphenyldisilane. This is not the case when compounds like triphenylsilane are used. This merit of using hexaphenyldisilane is important because it enables one to trace the starting material and to study a reaction more accurately.

The cleavage of hexaphenyldisilane of sodium-potassium alloy in ether is carried out in a heterogeneous system containing two liquid phases and a solid phase. In this type of reaction the rate-determining process is physical rather than chemical. The rate is affected by the method of mixing, concentration, and the relative volume of the

reactants, the size and shape of the container, the solubility of the reactant, and the tendency of the reactant to cling to the metallic globules. Accordingly, a high concentration and starting materials free from impurities (especially moisture and acids) should be used to insure a successful cleavage reaction particularly at the very beginning of the cleavage reaction. The liquid state of the sodium-potassium alloy furnishes the advantage that, on stirring, a new surface of the alloy is produced continuously to provide active spots for the reaction. Needless to say, if the reactants and the solvent are not pure and dry, the alloy will be coated and no reaction will proceed.

The problem of separating the excess alloy from the triphenylsilylpotassium or vice versa is very important in the successful application of triphenylsilylpotassium to the synthesis of organosilicon compounds. If the excess alloy were allowed to remain in the system it would react with the organic halides or add to the unsaturated linkages so that a clean-cut reaction in these cases would not be possible. Furthermore, the presence of alloy in the system may be hazardous for the subsequent processes such as hydrolysis. For compounds which are not stable to bases the presence of unnecessary alkali metals is definitely undesirable.

It was thought that there might be two ways of separating the unused alloy from the triphenylsilylpotassium suspension. First, this could be done if a solvent could be

found which would dissolve triphenylsilylpotassium but not the alloy. Second, opposite to the first, a solvent might be used to dissolve the alloy but not the organosilicon-metallic compound. With the former object in mind, a number of solvents, including toluene, triethylamine, and di-n-butyl ether at moderately high temperatures, have been tried without success. Triphenylsilylpotassium is such a highly polar compound that it seems unlikely that a solvent exists which dissolves but does not react with it. Therefore, the second possibility, i.e., to find a substance which dissolves only the excess alloy, was explored. Mercury is the ideal substance for this particular purpose. After some preliminary studies, a procedure for the removal of excess alloy from triphenylsilylpotassium was worked out.

The advantages of amalgamation of the excess alloy may be mentioned briefly. Mercury dissolves sodium and potassium in all proportions but neither mercury nor the amalgam is reactive enough to displace potassium from triphenylsilylpotassium. The amalgam is much heavier than the triphenylsilylpotassium suspension so that it is very easy to separate them by decantation or by means of a siphon. By properly adjusting the amount of mercury a viscous, semi-liquid amalgam can be formed which makes possible the separation from the organosilicon-metallic suspension with great ease. Finally, the reactivity of the alkali metals is diminished considerably by amalgamation, so that the fire

hazard is substantially reduced. As a matter of fact, small amounts of the amalgamated alloy can be taken out in the open air and treated with water safely.

It is of interest to point out that in some reactions the excess of sodium-potassium alloy need not be removed for the reaction of triphenylsilylpotassium with some halogen compounds. Thus, triphenylsilylpotassium reacts with bromobenzene and with trimethylchlorosilane in the presence of excess alloy to give good yields of tetraphenylsilane and 1,1,1-triphenyl-2,2,2-trimethyldisilane, respectively. In other reactions, however, the presence of excess alloy is definitely undesirable. For example, in the reaction of triphenylsilylpotassium with triphenyltin chloride, a 76 per cent yield of pure triphenylsilyltriphenyltin is obtained following the removal of the excess alloy, while only 36 per cent of the product is obtained if the excess alloy is not removed. Some hexaphenyldítin is formed as a by-product due to the coupling of triphenyltin chloride with the excess sodium-potassium alloy. Excess alloy would certainly compete with triphenylsilylpotassium the addition reaction to the ethylenic linkage of trans-stilbene.

The reaction of triphenylsilylpotassium with halobenzenes shows that, as one should expect, bromobenzene is more reactive than chlorobenzene, which, in turn, is more reactive than fluorobenzene. Thus, even in the presence of excess alloy bromobenzene reacts with triphenylsilylpotassium

in a period of 15 minutes to give a 96 per cent yield of tetraphenylsilane. With chlorobenzene in a period of 1 hour a 53 per cent yield of tetraphenylsilane is obtained under the experimental conditions. Fluorobenzene, however, gives only a 12 per cent yield of tetraphenylsilane in a period of 70 hours. Although the experimental conditions of these reactions studied were not exactly the same (it is difficult to attain uniformity in a heterogeneous system), the general trend of the reactivities of these halides is evident.

The difficulties in obtaining a good yield of the partially phenylated hexachlorodisilanes, such as 1,1,1,2-tetraphenyl-2,2-dichlorodisilane and 1,1,1-triphenyl-2,2,2-trichlorodisilane, are partly due to the possible side reactions and partly due to the instability of these chloro compounds. For example, when silicon tetrachloride is treated with an equivalent amount of triphenylsilylpotassium, one, two, or more of the chlorine atoms in silicon tetrachloride may be substituted by the triphenylsilyl group, giving rise to a mixture of compounds. Also, one would expect the compound 1,1,1-triphenyl-2,2,2-trichlorodisilane to hydrolyze easily because there are three chlorine atoms on one silicon atom. Thus, although pure pentaphenylchlorodisilane can be kept even in air for a long time, the di- and the tri-chlorodisilanes change on standing for a short time.

Triphenylsilylpotassium has been used successfully for the preparation of phenylated polysilanes. Octaphenyltrisilane and decaphenyltetrasilane were made. They are the only examples known so far of octasubstituted trisilanes and decasubstituted tetrasilanes although a number of polysilanes of the formula $(R_2Si)_n$ have been reported.[176,177] The method of preparation of these polysilanes may well be extended to prepare the higher homologs.

A large number of organodisilanes, both symmetrical and unsymmetrical, can be made by the reactions of organosilicon-metallic types. The coupling reaction of an organosilicon-metallic compound with an organohalosilane may be repeated so that the resulting organosilane has a silicon chain twice as long as that of either of the reactants. The synthesis of decaphenyltetrasilane is an example. When triphenylsilylpotassium is treated with diphenyldichlorosilane, pentaphenylchlorodisilane is formed. When this disilane is treated with sodium, decaphenyltetrasilane is obtained. By this method, it seems quite possible to prepare higher polysilanes containing phenyl and other groups, although the maximum attainable length of the silicon chain is not comparable with that of carbon.

Phenylated disilanes containing one, two, or three chlorine atoms have been made. These chloro derivatives not only serve as the starting materials for the preparation of polysilanes but are also used as an alternative way of

preparing a number of unsymmetrical disilanes containing different groups on different silicon atoms.

There are ten different ways of putting two different groups on the two silicon atoms in the hexasubstituted disilane. All of the disilanes containing phenyl groups and p-tolyl groups have been prepared in this investigation for the purpose of studying the possibility of dissociation of these compounds. It is found, as a result of these studies, that, as one would expect, the melting point and the solubility vary in accordance with the degree of symmetry of the molecules. The more symmetrical the disilane is, the less soluble and the higher melting the silicon compound is. The melting points of the organodisilanes containing phenyl and p-tolyl groups are given in Table I.

From the melting point studies it is seen that the most symmetrical disilanes (hexaphenyl and hexa-p-tolyl) have the highest melting points, while the most unsymmetrical disilane (1,1,2-triphenyl-1,2,2-tri-p-tolyldisilane) has the lowest melting point in this series. The nature and the position of the substituted group also show some effects on the melting point of the molecule. Thus, while hexaphenyldisilane has a higher melting point than the hexa-p-tolyl compound, the reverse is observed in the pentasubstituted series; penta-p-tolylphenyldisilane has a higher melting point than pentaphenyl-p-tolyldisilane. The symmetrical tetraphenyldi-p-tolyldisilane has a higher melting point than the

Table I

Melting Points of Hexasubstituted Disilanes Containing Phenyl and p-Tolyl Groups

Disilane	Formula	M. p., °C
Hexaphenyl-	Y_3SiSiY_3[a]	360-362[b]
Pentaphenyl-p-tolyl-	$Y_3SiSiZY_2$	283-285
1,1,2,2-Tetraphenyl-1,2-di-p-tolyl-	$Y_2ZSiSiZY_2$	252-253
1,1,1,2-Tetraphenyl-2,2-di-p-tolyl-	Y_3SiSiZ_2Y	229-230
1,1,1-Triphenyl-2,2,2-tri-p-tolyl-	Y_3SiSiZ_3	262-264
1,1,2-Triphenyl-1,2,2-tri-p-tolyl-	$Y_2ZSiSiZ_2Y$	226-227
1,2-Diphenyl-1,1,2,2-tetra-p-tolyl-	YZ_2SiSiZ_2Y	240-241
1,1-Diphenyl-1,2,2,2-tetra-p-tolyl-	$Y_2ZSiSiZ_3$	240-241
Phenylpenta-p-tolyl-	YZ_2SiSiZ_3	288-290
Hexa-p-tolyl-	Z_3SiSiZ_3	354-356

[a] In this table Y represents the phenyl group and Z the p-tolyl group.

[b] Recently a batch of hexaphenyldisilane melting at 368-370° was obtained from the purified triphenylchlorosilane.

unsymmetrical compound but this is not observed in the diphenyltetra-p-tolyl series. In the latter case the symmetrical and unsymmetrical diphenyltetra-p-tolyldisilanes have the same melting point and a mixture of these two compounds also melts at the same temperature, 240-241°.

Mixed melting point studies of the hexasubstituted disilanes containing phenyl and p-tolyl groups show that, like other compounds, the more similar the compounds the less depression occurs in their mixed melting points. Thus, a mixture of approximately equal amounts of pentaphenyl-p-tolyldisilane and phenylpenta-p-tolyldisilane melts 35 degrees lower than the melting point of the lower melting component. The mixed melting points of a mixture of disilanes containing same number of phenyl and p-tolyl groups show very little depression.

The small depressions in the mixed melting points of a mixture of two closely similar compounds have been reported in the literature. Drew and Landquist[29] studied the mixed melting points of a mixture of tetraphenyl compounds of carbon, silicon, germanium, tin, and lead and observed that there was very little depression in the melting point of a mixture of two of these compounds. Even a mixture of five of all these compounds melts at 220-221°, a melting point range usually considered a criterion of a pure compound.

The solubilities of the hexasubstituted disilanes in

general vary with the symmetry of the molecules. Hexaphenyldisilane and hexa-p-tolyldisilane are only slightly soluble in hot benzene. The unsymmetrical compounds like 1,1-diphenyl-1,2,2,2-tetra-p-tolyldisilane and 1,1,2-triphenyl-1,2,2-tri-p-tolyldisilane are very soluble in benzene and other solvents. The solubilities, however, have not been determined quantitatively.

The symmetrical disilanes are made by the coupling reaction of a triarylchlorosilane with sodium. The unsymmetrical disilanes are formed either by coupling a triarylsilylpotassium with a trisubstituted halosilane or by treating the partially arylated hexachlorodisilane with an appropriate aryllithium compound. It has been found that the coupling reaction gives a better yield and purer disilanes than the reaction of the halodisilane with an aryllithium. For example, pentaphenyl-p-tolyldisilane is obtained in 28 per cent yield by treating pentaphenylchlorodisilane with p-tolyllithium and in 77 per cent yield by the reaction of triphenylsilylpotassium with diphenyl-p-tolylchlorosilane. Similarly, 1,1,1,2-tetraphenyl-2,2-di-p-tolyldisilane is obtained in 14 per cent yield from the organolithium reaction and 72 per cent from the coupling reaction; 1,1,1-triphenyl-2,2,2-tri-p-tolyldisilane is obtained in 11 per cent yield by the organolithium reaction and 26 per cent yield by the coupling reaction.

It has been shown that under ordinary conditions, hexaaryldisilanes do not dissociate into triarylsilyl radicals analogous to the triarylmethyls. A contrasting example is provided by the fact that hexa-p-biphenylylethane is highly dissociated even in the solid state[197] while the silicon analog shows no evidence of dissociation.[159] In this work two hexaaryldisilanes with improved solubilities over hexaphenyldisilane have been treated with oxygen and iodine but there is no indication of the formation of the triarylsilyl radicals. One of the hexaaryldisilanes prepared, the 1,1,2-triphenyl-1,2,2-tri-p-tolyldisilane, was sent to Northwestern University for magnetic susceptibility measurements. Following is a copy of a letter addressed to Dr. Henry Gilman from Dr. P. W. Selwood of the Northwestern University.

Department of Chemistry
Northwestern University
Evanston, Illinois
January 11, 1952

Prof. Henry Gilman
Department of Chemistry
Iowa State College
Ames, Iowa

Dear Professor Gilman:

The sample of disilane which you sent us appears to be diamagnetic with the susceptibility of approximately -0.6×10^{-6}. This value is obtained both for the solid and when the substance is in benzene solution. The precision of the results is not very

---

[197] E. Müller, I. Müller-Rodloff, and W. Bunge, Ann., 520, 235 (1935).

high because of the relatively large volume of solution we are forced to use in our present apparatus and, also, because the solid, like many similar substances, is remarkable for the electrostatic charge which it tends to pick up.

However, I feel completely confident that no appreciable free radical is formed and, perhaps, on the basis of these measurements we could say that an upper limit for dissociation would be not over 5% in the benzene solution. Taken together with your own observations on these substances, I am sure we can say that the disilanes are entirely different from the hexaarylethanes so far as their dissociation is concerned.

With best wishes,

Very sincerely yours,

P. W. Selwood

The lack of dissociation of hexaaryldisilanes is probably due to the small resonance stabilization of the triaryl groups which necessitates a structure containing a silicon-to-carbon double bond the contribution of which is considered to be small. However, dipole moment measurements of trimethylarylsilanes favor the postulation of structures involving a double bond between a carbon and a silicon atom.[198] Perhaps we can say that structures containing carbon-silicon double bonds may form under certain favorable conditions, but the contribution of these structures in some hexaaryldisilanes may be too small to stabilize the triarylsilyl radicals. Nevertheless, if the six aryl groups of

---

[198] H. Soffer and T. DeVries, J. Am. Chem. Soc., 73, 5817 (1951).

the hexaaryldisilane (preferably an unsymmetrical one because of higher solubility) have very bulky ortho-substituted groups to increase the steric hindrance of the molecule, the chances of dissociation of the silicon-silicon bond might be appreciably increased. The bond energy of the silicon-silicon bond is considerably smaller than that of the carbon-carbon bond (Si-Si, 45 kcal/mole; C-C, 80 kcal./mole[199]) and it has been shown, in this investigation, that the silicon-silicon bond of some hexaaryldisilanes can be cleaved by a number of reagents such as sodium-potassium alloy[143] and bromine.

The infrared spectra of the hexasubstituted disilanes containing phenyl and p-tolyl groups have been studied by Dr. V. A. Fassel and Mr. M. Margoshes. Samples of these disilanes are dissolved in carbon disulfide and the infrared absorption spectra are taken. The phenyl group attached to silicon gives absorption bands at 13.5μ($\pm$ 0.1μ) and 14.3μ($\pm$ 0.1μ) and the p-tolyl groups at 12.5μ($\pm$ 0.1μ). The $\ln(\frac{I_o}{I})$* values of each compound are determined. The values

$$\frac{\ln\left(\frac{I_o}{I}\right)_{13.5\mu} + \ln\left(\frac{I_o}{I}\right)_{14.3\mu}}{\ln\left(\frac{I_o}{I}\right)_{12.5\mu}}$$

---

[199] I. S. Pitzer, ibid., 70, 2140 (1948).

*I_o = percentage of transmittance if there were no absorption band.

I = actual percentage of transmittance.

are plotted as the ordinate versus the values

$$\frac{\text{Number of phenyl groups}}{\text{Number of p-tolyl groups}}$$

as the abscissa. A straight line passing through the origin is obtained. A similar procedure is carried out on the monosilanes containing phenyl and p-tolyl groups. The points plotted for this series also lie on the same line. This shows that the intensity of the absorption bands of the phenyl and the p-tolyl groups depend on the number but not on the position of these groups. Thus, both 1,1,2-triphenyl-1,2,2-tri-p-tolyldisilane and 1,1,1-triphenyl-2,2,2-tri-p-tolyldisilane give the same point on the straight line.

It is of interest to point out that for trisubstituted chlorosilanes containing phenyl and p-tolyl groups, a straight line passing through the origin can also be obtained but this line has a different slope from the other one in which no chlorine atom is present in the molecules.

In the studies of the cleavage of the silicon-silicon bond of hexaaryldisilanes, it is found that, among the chemicals tested, only reactive alkali metals and halogens can cleave the silicon-silicon bond. Sodium-potassium alloy is the most useful reagent in that it is easy to prepare and it cleaves hexasubstituted disilanes smoothly to give high yields of triarylsilylpotassium. Sodium cannot cleave

hexaphenyldisilane in boiling xylene, hot dioxane, or ether, but it may do so in liquid ammonia although the reaction is not as clean as the cleavage reaction with sodium-potassium alloy in ether. Possibly lithium may cleave hexaphenyldisilane in liquid ammonia or ethylamine.

Among the halogens, iodine is too unreactive to initiate any cleavage reaction of hexaaryldisilanes although it reacts rapidly with hexaarylethanes to form the iodides. Bromine, however, is active enough to cause the cleavage reaction of the organodisilane but the reaction is rather slow. Thus, in 42 hours 33 per cent of triphenylbromosilane is obtained by the cleavage of hexaphenyldisilane by bromine while a 55 per cent yield is obtained in a period of 6 days. Probably the more active halogens, chlorine and fluorine, would be found to cleave hexaphenyldisilane in a more rapid rate.

A number of oxidizing agents have been tried as cleavage agents for hexaphenyldisilane, including oxygen gas. The last chemical is known to react readily with some hexaarylethanes to give peroxides. However, this has not been observed for hexasubstituted disilanes containing phenyl and p-tolyl groups. Hydrogen peroxide does not cleave the silicon-silicon bond under the experimental conditions employed. Chromic acid oxidizes some of the hexaphenyldisilane but no pure product can be obtained probably because chromic acid attacks the carbon-hydrogen bond or even the carbon-

carbon bond in addition to the silicon-silicon bond. It is believed that some oxidizing agents might be found which cleave only the silicon-silicon bond of hexaaryldisilane.

One of the typical reducing agents, lithium aluminum hydride, has been tried as a cleavage agent for hexaphenyldisilane. Results show that the disilane is completely inert to this reducing agent. Phenyllithium, too, does not react with hexaphenyldisilane.

In 1933 Kraus and Eatough[140] treated triphenylbromosilane with lithium in ethylamine and claimed that the solvated free radical "triphenylsilicyl ethylammine" was isolated which could be distilled at 150° in a high vacuum without decomposition. According to these workers this compound melts at 45° and has the formula, $(C_6H_5)_3Si \cdot C_2H_5NH_2$. When it was treated with another equivalent of lithium, "lithium triphenylsilicide" was obtained which reacted with bromobenzene and with ammonium bromide to give tetraphenylsilane and triphenylsilane, respectively. This solvated free radical, according to the same report, gave almost quantitative yield of hexaphenyldisilane on solution in ether followed by the evaporation of the ethereal solution to dryness.

In this investigation several experiments have been carried out in order to check the above results. It was found that triphenylchlorosilane reacts with ethylamine in the presence or absence of lithium to give a product melting

at 50° and, contrary to the findings of Kraus and Eatough, this compound does not react with lithium to give triphenylsilyllithium. (No tetraphenylsilane is formed by the treatment of the so-called "lithium triphenylsilicide" with bromobenzene.) Also, when the so-called "triphenylsilicyl ethylammine" is evaporated with ether, no hexaphenyldisilane is formed. It is believed that the reaction of triphenylchlorosilane with lithium in ethylamine produces triphenylethylaminosilane, $(C_6H_5)_3SiNHC_2H_5$. It seems unlikely that a triphenylsilyl free radical can be isolated as such. More improbable is the statement[140] that the free radical can be distilled at a high temperature without decomposition. The work of Kraus and Eatough[140] could not be reproduced in another laboratory.[200] Under the experimental conditions, Benkeser[200] found that an almost quantitative yield of the N-ethyl compound was obtained but no solvated free radical was formed. It appears that triphenylhalosilanes are not suitable for the preparation of triphenylsilyllithium in ethylamine because they react easily with the solvent. Hexaphenyldisilane probably can be cleaved by lithium in liquid ammonia or liquid ethylamine as it can with sodium, if the reactivity of lithium is high enough. Under such circumstances the competitive amination reaction

---

[200] Private communication to Dr. Henry Gilman from Dr. R. A. Benkeser of Purdue University, 1951.

of triphenylhalosilane is ruled out because there is no organohalosilane in this system.

Triphenylsilylpotassium adds to the carbon-carbon double bond of trans-stilbene to give β-triphenylsilyl-α,β-diphenylethylpotassium according to the following equation:

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

The potassium compound is derivatized by hydrolysis and by carbonation. The addition reaction furnishes a convenient way of synthesizing some organosilicon compounds. The addition of an organometallic compound such as phenylisopropylpotassium to an olefinic group is well known, but no report has been found on similar reactions of the silicon compounds. The addition of an organogermylsodium compound to the ethylenic linkage has not been studied, but triphenyltinlithium does not add to the carbon-carbon double bond of trans-stilbene.[190] The addition of organosilicon-metallic compounds to multiple linkages is interesting for the purpose of correlating the chemical properties of the organosiliconmetallic types with the carbon analogs.

B. Organotin Compounds

Reactions of tetraphenyltin with stannic chloride furnish a simple, convenient, and efficient method for the preparation of phenyltin chlorides. It has been found that an

excess of stannic chloride is desirable because of the relative volatility of stannic chloride. Yields around 70 per cent of triphenyltin chloride are obtained by varying the ratio of tetraphenyltin to stannic chloride. The difficulty of obtaining a higher yield may be attributed to the fact that under these conditions, some diphenyltin dichloride and perhaps some phenyltin trichloride are also formed. These last two compounds can be removed easily from triphenyltin chloride by recrystallization. If some unconverted tetraphenyltin is left over in the preparation, its separation from triphenyltin chloride is a little more difficult. Therefore, an excess of stannic chloride is preferable unless the reaction is carried out in a sealed tube.

In this Laboratory triphenyl-p-bromophenylsilane has been made by the reaction of triphenylchlorosilane with p-bromophenyllithium.[192] However, under similar conditions triphenyl-p-bromophenyltin is not formed by the reaction of triphenyltin chloride with p-bromophenyllithium. Nevertheless, when the lithium compound is converted to the Grignard reagent good yields of triphenyl-p-bromophenyltin can be obtained. The failure to obtain the desirable product is probably due to the cleavage of the carbon-tin bond of the organotin compounds by the organollithium compound. Since the Grignard reagent is less reactive than the organolithium compound, no cleavage of the carbon-tin bond occurs and the

expected product can be obtained. The carbon-silicon bond is much stronger than the carbon-tin bond. Consequently, no cleavage occurs when triphenylchlorosilane is treated with p-bromophenyllithium and the triphenyl-p-bromophenylsilane can be obtained. The difficulty in synthesizing triphenyl-p-carboxyphenyltin by the reaction of triphenyltin chloride with lithium p-lithiobenzoate is probably due to the same reason, i.e., cleavage of the carbon-tin bond by the organolithium compound. The insolubility of the lithium salt in this case also makes it more difficult for the reaction to proceed.

Evidence for the cleavage of the carbon-tin bond and the carbon-lead bond has been observed previously in this Laboratory. Tetraphenyltin[201] and tetraphenyllead[202] can be cleaved by n-butyllithium to give tetra-n-butyltin and tetra-n-butyllead, respectively. The corresponding metal-metal interconversion reaction with tetraphenyllead and n-butylmagnesium bromide does not occur in the same length of time.[202]

The reaction of triphenyl-p-tolyltin with N-bromosuccinimide did not give the bromomethylphenyl compounds. Under similar conditions, triphenyl-p-tolylsilane reacts with one equivalent of N-bromosuccinimide to give 73 per

---

[201] H. Gilman, F. W. Moore, and R. G. Jones, J. Am. Chem. Soc., 63, 2482 (1941).

[202] H. Gilman and F. W. Moore, ibid., 62, 3206 (1940).

cent of triphenyl-p-bromomethylphenylsilane; with two equivalents of N-bromosuccinimide 63 per cent of triphenyl-p-dibromomethylphenylsilane can be obtained.[41] The difficulty of brominating the p-tolyl group of the tin compound may also be due to the relatively unstable carbon-tin bond which might be cleaved by N-bromosuccinimide under the experimental conditions.

From the studies of the water-solubility of organotin compounds containing quaternary ammonium groups and the corresponding lead analogs,[133] it is seen that in general the organotin compound is more soluble than the organolead compound. Organotin and organolead compounds containing three phenyl groups and an alkylaminoalkyl group are more soluble than those containing three phenyl groups and a p-dimethylaminophenyl group. For compounds having the same number of quaternary ammonium groups the methosulfates are more soluble than the methiodides. Finally, the solubility of the organotin and the organolead compounds increases with increasing number of quaternary ammonium groups in the molecules.

To illustrate these generalizations, for example, the methosulfate and the methiodide of triphenyl-p-dimethylaminophenyltin and those of triphenyl-p-dimethylaminophenyllead[133] are practically insoluble in water, while the tetramethiodides of tetrakis-(p-dimethylaminophenyl)-lead[133] and

tetrakis-(p-dimethylaminophenyl)-tin are quite soluble in water. The last compound can be recrystallized from hot water. Triphenyl-γ-diethylaminopropyllead methiodide is essentially insoluble in water while the corresponding methosulfate is extremely soluble in water.[133] The tin analog, triphenyl-γ-diethylaminopropyltin methiodide, is soluble in hot water, while the corresponding methosulfate is soluble even in cold water, but it is very difficult to purify.

C. Organic Compounds Containing Bonds Between Two Different Group IV-B Elements

Only a few compounds of this type are known. These have been mentioned in the Historical Part of this dissertation. Organic compounds containing a silicon-germanium, silicon-tin, and germanium-tin bond have been made, but no compounds containing a silicon-lead, tin-lead, or germanium-lead bond have been obtained.

These types of compounds are all made by the coupling of an R_3EM compound with an $R'_3E'X$ compound, the X and the M atoms may be interchanged depending on the availability of the material. For example, triphenylsilyltriphenyltin can be made by the reaction of triphenyltin-lithium with triphenylchlorosilane in 71 per cent yield[152] or by the reaction of triphenylsilylpotassium with triphenyltin chloride

in 76 per cent yield. However, when this method is applied to the synthesis of organolead compounds containing a silicon-lead or a tin-lead bond, no expected pure product can be obtained. In the organolead reactions there is a tendency toward the formation of inorganic lead halide, hexaphenyldilead, and probably diphenyllead. The purification of these products is further complicated by the fact that the unreacted starting material may hydrolyze to give the hydroxy compound or its derivatives. For example, in the attempted synthesis of triphenylsilyltriphenyllead the starting material triphenylchlorosilane hydrolyzes to yield triphenylsilanol. The products obtained by the reaction of triphenyllead-lithium with triphenyltin chloride may also be contaminated by a mixture containing the hydrolysis products of the starting materials. It is of interest to observe that one of the unidentified products decomposes on standing to give some black spots on the surface of the crystals. This seems to show that organolead compounds containing a direct linkage between lead and a Group IV-B element except carbon are too unstable to be made.

The difficulty of preparation of these organolead compounds may be due to the weakness of the lead bonds connected to other Group IV-B elements. It has been mentioned repeatedly in the Historical Part that for the same type of compounds the stability decreases with increasing atomic

weight of the central Group IV-B element. For example, all types of organic hydrides of silicon, germanium, and tin are known but none of the organolead hydrides has been synthesized. However, it would not seem advisable to draw broad conclusions because of the unusually small amount of work which has been done along these lines.

V. SUMMARY

A comparison has been made of the properties of various types of organic compounds containing Group IV-B elements.

A procedure for the preparation of triphenylsilylpotassium has been worked out. It was found that hexaphenyldisilane is the best starting material for the preparation of triphenylsilylpotassium. Sodium-potassium alloy is preferable as the cleaving agent for hexaphenyldisilane. The amalgamation method was applied successfully for the removal of the excess alloy in the preparation of triphenylsilylpotassium.

The reaction of triphenylsilylpotassium with phenyl halides showed that bromobenzene is more reactive than chlorobenzene, which, in turn, is more reactive than fluorobenzene.

Octaphenyltrisilane and decaphenyltetrasilane have been prepared by the reactions with triphenylsilylpotassium. These compounds are the first ones known of the type R_8Si_3 and $R_{10}Si_4$.

A complete series of hexaaryldisilanes containing phenyl and p-tolyl groups has been made. The solubilities and the melting points of these compounds vary with the degree of symmetry of the molecules. These compounds can be cleaved

by sodium-potassium alloy to give the triarylsilylpotassium compounds but they do not react with oxygen or iodine. There has been no indication of dissociation of these molecules.

The silicon-silicon bond of hexaphenyldisilane can be cleaved by sodium in liquid ammonia, potassium in di-n-butyl ether, sodium-potassium alloy in ether, or by bromine. The bond was not cleaved by sodium dispersion, sodium amalgam, lithium aluminum hydride, phenyllithium, or hydrogen peroxide. Treatment of hexaphenyldisilane with chromic acid apparently led to the oxidation of the whole molecule.

Treatment of triphenylchlorosilane with lithium in ethylamine resulted in the formation of triphenylethylaminosilane and no triphenylsilyl free radical was formed. This is contrary to the findings reported in the literature.

Triphenylsilylpotassium adds to the carbon-carbon double bond of trans-stilbene to give β-triphenylsilyl-α, β-diphenylethylpotassium.

Triphenyl-p-bromophenyltin was made by the reaction of p-bromophenylmagnesium iodide with triphenyltin chloride, but it cannot be obtained from the corresponding lithium compound. An explanation for this difference has been given.

There is a definite increase in the water-solubility of organotin compounds on the introduction of one or more quaternary ammonium groups. The methosulfates are more soluble than the methiodides. Comparisons with the

corresponding lead compounds have been made.

Triphenylsilyltriphenyltin has been made by the reaction of triphenylsilylpotassium with triphenyltin chloride. Attempts were made to prepare organolead compounds containing a lead-silicon and a lead-tin bond.

VI. ACKNOWLEDGMENTS

The author wishes to express his appreciation and gratitude to Dr. Henry Gilman for the suggestions, criticisms, and encouragement given throughout the course of this investigation. Thanks are also due to Eastman Kodak Company for a fellowship which made part of this work possible.