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PREPARATION AND BASIC CLEAVAGE

OF SOME ARYLSILANES

by

Lewis Samuel Miller

A Dissertation Submitted to the

Graduate Faculty in Partial Fulfillment of

The Requirements for the Degree of

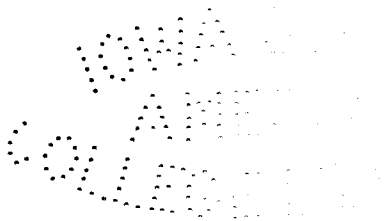DOCTOR OF PHILOSOPHY

Major Subject: Organic Chemistry

Approved:

In Charge of Major Work

Head of Major Department

Dean of Graduate College

Iowa State College

1950

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ACKNOWLEDGEMENT

The author wishes to express his appreciation to
Dr. Henry Gilman for the advice, criticism, and encouragement
given throughout the course of this investigation.

TABLE OF CONTENTS

Page

Organosilicon Compounds (continued):

Page

INTRODUCTION

Many investigations have been reported whose ultimate purposes have been to establish a general series by which the relative ease of cleavage of organic radicals from metals could be predicted[1]. Silicon, although not generally considered to be a metal, has been found to behave in a manner qualitatively analogous to the metals in these cleavage reactions. The major part of this work has employed acidic or electrophilic reagents such as hydrogen chloride, the halogens, or metallic halides. This type of cleavage reaction of organometallic compounds has been reviewed recently by F. J. Marshall[2]. The use of metals as cleavage agents has been reviewed by Bindschadler[3] and Haubein[4].

The basic or nucleophilic cleavage reagents have received relatively less attention by investigators, although enough work has been done to indicate that the order of ease of cleavage of the radicals from metals is often considerably different

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[1] For general references, see (a) Gilman, "Organic Chemistry, An Advanced Treatise", John Wiley and Sons, New York, 1943, pp. 489-579, and (b) Krause and von Grosse, Die Chemie der metallorganischen Verbindungen , Borntraeger, Berlin, 1937.

[2] Marshall, Doctoral Dissertation, Iowa State College (1948). See also Gilman and Marshall, J. Am. Chem. Soc., 71, 2066 (1949).

[3] Bindschadler, Doctoral Dissertation, Iowa State College (1941).

[4] Haubein, Doctoral Dissertation, Iowa State College (1942).

from that obtained with acidic reagents. The literature records few concerted studies of this type with the exception of some fairly extensive work which has been done on cleavages of one organometallic reagent by another, the metal-metal interconversions. The early work of this latter type, covering derivatives of a large range of metals, is summarized briefly by Jones[5]. Fairly extensive investigations have also been carried out in recent years on the basic cleavage of various halogen- or oxygen-substituted alkylsilanes.

The purpose of the present investigation was to extend these basic cleavage studies to the field of aryl- and mixed alkylaryl-silanes. In addition, an attempt was made to show a correlation between the acid strength of a hydrocarbon (as determined in studies by Conant and Wheland and others[6]), and the ease with which the corresponding carbanion could be cleaved from silicon by a nucleophilic reagent, the radicals corresponding to the carbanions of the stronger acids splitting off more readily.

Many of the arylsilanes which were made were previously unknown, and extensive applications of organolithium reagents were purposely used in their preparation in order to extend our knowledge of these versatile organometallic compounds.

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[5]Jones, Doctoral Dissertation, Iowa State College (1941).

[6]Conant and Wheland, J. Am. Chem. Soc., 54, 1212 (1932); McEwen, ibid., 58, 1124 (1936).

Another group of organosilanes was prepared which contains
groups present in active insecticides and these compounds were
submitted to Dr. C. H. Richardson[7] for evaluation in order to
compare their insecticidal activity with those of related
carbon analogues.

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[7]Department of Entomology, Iowa State College.

HISTORICAL

The following survey summarizes the work described in the literature in which a carbon-to-silicon or carbon-to-metal bond has been cleaved by a basic or nucleophilic reagent. A nucleophilic reagent is generally considered to be one in which the attacking species is a nucleus-seeking group containing an unshared pair of electrons[8]. The agents considered include OH^-, NH_2^-, CN^-, OR^-, R^- (the carbanion, or negative portion of an ion-pair, from an organometallic compound) and water, alcohols and amines. A few generalizations about cleavages of bonds between silicon and elements other than carbon have been included for orientation purposes.

Cleavages of Organosilicon Compounds by Basic or Nucleophilic Reagents

Until recently, no planned series of studies has been described in the literature in which the relative ease of cleavage of various radicals from silicon by a basic reagent was sought. However, various data are encountered in the early literature which indicate the relative stability or instability of certain groups.

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[8]Hammett, "Physical Organic Chemistry", McGraw-Hill Book Co., Inc., New York, N. Y., 1940.

The importance of even traces of alkali in the cleavage of bonds of various elements to silicon has been demonstrated. Stock and Somieski[9] found that silane, SiH_4, was not decomposed by water when kept in vessels of fused quartz, but that traces of alkali extracted by the water from an ordinary glass flask would catalyze the decomposition. Recently Swain[10] and his coworkers, while measuring the rate of hydrolysis of triphenyl-fluorosilane, found the rate of this reaction to be over a million times greater in the presence of an appreciable concentration hydroxyl ion than in pure water.

In general, silicon bonds to iodine, bromine, and chlorine are cleaved very readily[11] by nucleophilic reagents, bonds to fluorine, hydrogen and silicon less readily, and bonds to carbon least readily. Alkoxy groups are generally hydrolyzed only slowly by water[11] and their hydrolysis was shown by Krieble and Burkhard[12] to involve only the splitting of a silicon-oxygen bond. These investigators hydrolyzed optically active dimethyldi-D-2-butoxysilane and obtained D-2-butanol which had maintained its original activity unchanged.

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[9]Stock and Somieski, Ber., 51, 989 (1918).

[10]Swain, Esteve and Jones, J. Am. Chem. Soc., 71, 965 (1949).

[11]Kipping, Proc. Roy. Soc. (London), 159, 139 (1937); Robinson, Sci. J. Roy. Coll. Sci., 15, 24 (1945).

[12]Krieble and Burkhard, J. Am. Chem. Soc., 69, 2689 (1947).

$$(CH_3)_2Si-(O-\underset{\underset{\underline{D}}{H}}{\overset{\overset{CH_3}{|}}{C}}-C_2H_5)_2+H_2O \xrightarrow{\text{trace}}_{HCl} (CH_3)_2Si(OH)_2+2HO-\underset{\underset{\underline{D}}{H}}{\overset{\overset{CH_3}{|}}{C}}-C_2H_5$$
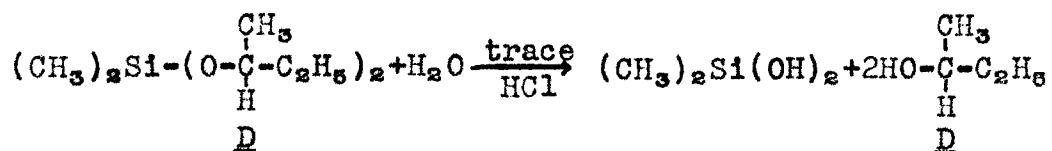
The silicon-sulfur bond in alkylmercapto silanes is somewhat more stable to water and alkalies than is the corresponding silicon-oxygen bond in alkoxy silanes[11]. The silicon-nitrogen bonds are resistant to hydrolysis by alkaline solutions but are very easily hydrolyzed by dilute acids[13]. Bonds between two or more silicon atoms are generally split readily by aqueous alkali to yield hydrogen and silanols or siloxanes; however, polysilanes substituted entirely by alkyl or aryl radicals are often more resistant to alkaline hydrolysis, although the higher polymers are still cleaved quite readily[14].

Early workers in the organosilicon field demonstrated the stability of the unsubstituted alkylsilanes in the presence of alkaline reagents. Friedel and Ladenburg[15] noted that ethyltriethoxysilane was not completely decomposed on heating with alcoholic potassium hydroxide although it was decomposed by concentrated sulfuric acid. Pape[16] found tetra-n-propyl-

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[13]Sauer and Hasek, _J. Am. Chem. Soc._, _68_, 241 (1946).

[14]Rochow, "An Introduction to the Chemistry of the Silicones", John Wiley and Sons, New York, 1946.

[15]Friedel and Ladenburg, _Ann._, _159_, 259 (1871).

[16]Pape, _ibid._, _222_, 354 (1884).

silane to be stable on heating with a strong potassium hydroxide
solution. More recently Krieble and Elliott[17] obtained methane
by heating hexamethyldisiloxane, or mono- or di-methyl silicone
polymers, with aqueous sodium hydroxide at 200°. Tatlock and
Rochow[18] also obtained methane by treating hexamethyldisiloxane
with excess 12 $\underline{N}$ potassium hydroxide, but showed that by using
fused potassium hydroxide with excess dry hexamethyldisiloxane,
the main product formed was the potassium salt of trimethyl-
silanol.

$$(CH_3)_3SiOSi(CH_3)_3 + KOH_{(aq.)} \longrightarrow (CH_3)_2Si(OK)OSi(CH_3)_3 + CH_4$$
$$(CH_3)_3SiOSi(CH_3)_3 + 2KOH_{(dry)} \longrightarrow 2(CH_3)_3SiOK$$
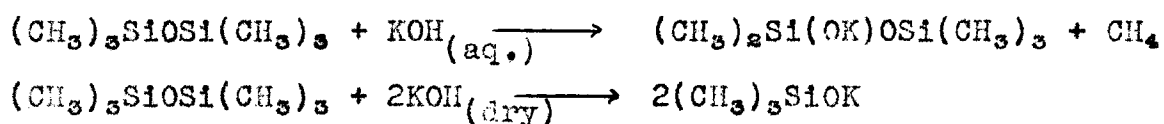
They concluded that cleavage of methyl groups was much easier
in hydroxylated solvents than in aprotic solvents.

A number of unsaturated alkyl derivatives of silicon
have been prepared and some of these are cleaved readily by
nucleophilic reagents. Vol'nov and Reutt[19] prepared hexa-
ethynyldisiloxane and (phenylethynyl)-triethoxysilane and
reported that the ethynyl and phenylethynyl groups, respect-
ively, are cleaved partially even by cold water.

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[17]Krieble and Elliott, J. Am. Chem. Soc., 68, 2291 (1946).

[18]Tatlock and Rochow, ibid., 72, 528 (1950).

[19]Vol'nov and Reutt, J. Gen. Chem. (U.S.S.R.), 10,
1600 (1940) /C.A., 35, 2853 (1941)_7.

Trimethylallylsilane gave propylene on treatment with potassium hydroxide in methanol[20]. The authors proposed the following mechanism, the electron shift being initiated by an attack of the OH^- on the back side of the silicon atom.

$$(CH_3)_3Si-CH_2-CH=CH_2+KOH \xrightarrow{CH_3OH} (CH_3)_3SiOCH_3+CH_2=CH-CH_3$$
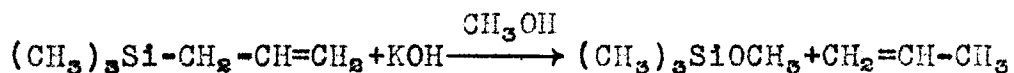
No cleavage of unsubstituted vinylsilanes, such as vinyltrichlorosilane, was obtained when they were treated with water in ether solution[21], and the deactivating effect of the vinyl double bond was mentioned with respect to the hydrolysis of chlorovinyl silanes[22]. (See p.16 of this thesis.)

A rather large amount of work has been reported on reactions of halogen-substituted alkylsilanes with basic reagents. Krieble and Elliott[23] prepared derivatives of dimethyldichlorosilane in which one, two, or three of the hydrogen atoms on one of the methyl groups were replaced by chlorine atoms. They found the order of ease of cleavage of these three halogenated radicals to be: trichloromethyl > dichloromethyl > chloromethyl, the first group being cleaved by water alone, while the latter group required an alkaline

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[20] Sommer, Tyler and Whitmore, J. Am. Chem. Soc., 70, 2872 (1948).

[21] Hurd, ibid., 67, 1813 (1945).

[22] Agre, ibid., 71, 300 (1949).

[23] Krieble and Elliott, ibid., 67, 1810 (1945).

reagent. Upon basic hydrolysis, the above three groups yielded chloroform, methylene chloride, and methyl chloride, respectively.

Somewhat later[24], (trichloromethyl)-trichlorosilane was prepared and found to cleave on contact with distilled water at room temperature to yield chloroform.

Whitmore and Sommer[25] reported the preparation of trimethyl-(chloromethyl)-silane and found that the chlorine in this compound was more reactive to nucleophilic reagents (which attack the back side of the carbon atom attached to the chlorine) than the chlorine in its carbon analog, neopentyl chloride. Sodium iodide reacted with the former chloride to give a 70% yield of trimethyl-(iodomethyl)-silane. No cleavage of the chloromethyl group was reported.

Trimethyl-(dichloromethyl)-silane was cleaved by sodium ethoxide in ethanol[26] to give a 71% yield of methylene chloride and a 73% yield of hexamethyldisiloxane. When the same compound was heated with sodium acetate in acetic acid, no reaction took place during nineteen hours at 150°, but at 200° formaldehyde (presumably resulting from cleavage of the dichloro-

[24]DiGiorgio, Sommer and Whitmore, J. Am. Chem. Soc., 70, 3512 (1948).

[25]Whitmore and Sommer, ibid., 68, 481 (1946).

[26]Speier and Daubert, ibid., 70, 1400 (1948).

methyl group) was evolved. The same authors treated dimethyl-bis-(chloromethyl)-silane with potassium acetate in acetic acid and obtained a 90% yield of dimethyl-bis-(acetoxymethyl)-silane, $(CH_3)_2Si(CH_2OCOCH_3)_2$. The results again demonstrate the greater ease of cleavage of the dichloromethyl group as compared with the chloromethyl group.

In a later paper[27], Speier treated trimethyl-(chloro-methyl)-silane with sodium methoxide in boiling methanol and obtained a 75% yield of trimethyl-(methoxymethyl)-silane with no cleavage. The same compound, when treated with sodium ethoxide in boiling ethanol gave 11% cleavage (to methyl chloride) and a 70% yield of trimethyl-(ethoxymethyl)-silane. With sodium n-butoxide in boiling n-butanol, 31% cleavage product (trimethyl-n-butoxysilane) and 19% trimethyl-(n-butoxymethyl)-silane were recovered. Whether the greater extent of cleavage with the sodium n-butoxide was due to the higher temperature at which the reaction was carried out, or to the nature of the cleavage agent, was not demonstrated.

Trimethyl-(chloromethyl)-silane was cleaved on boiling with 75% aqueous potassium hydroxide to give a polymeric con-densation product of the resulting silanol[28]. Pentamethyl-(chloromethyl)-disiloxane, $(CH_3)_3SiOSi(CH_3)_2(CH_2Cl)$, gave only

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[27] Speier, J. Am. Chem. Soc., 70, 4142 (1948).

[28] Speier, Daubert and McGregor, ibid., 70, 1117 (1948).

cleavage of the carbon-to-chlorine bond on treatment with potassium acetate in acetic acid, to yield hexamethyldisiloxane[29]. Krieble and Elliott[17], however, treated pentamethyl-(chloromethyl)-disiloxane and pentamethyl-(dichloromethyl)- disiloxane with 10% potassium hydroxide in n-butanol, obtaining 42% cleavage to methyl chloride in the former case and 78% cleavage to methylene chloride in the latter case. Both compounds were cleaved more readily than the corresponding trimethyl-(chloromethyl)- and trimethyl-(dichloromethyl)-silanes. The authors explain these results by relating these compounds to their carbon analogs. For example, in compounds of the type X_3C-AY_3, where A is a carbon or silicon atom which is attacked by the hydroxyl ion, cleavage of the C-A rather than the X-C bond usually occurs in the carbon analog only if all three X atoms are halogen (or a similar negative group) and at least two of the Y positions are occupied by oxygen. When A is silicon, only one X need be a halogen atom and only one Y an oxygen atom in order to get cleavage of the C-A bond. However, the more X and Y positions that are occupied by negative groups, the easier the cleavage of the C-A bond will be. These authors also predict that the group which will dissociate most readily from the positive center, A, will be that group which most readily forms a negative ion.

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[29]Speier, Daubert and McGregor, J. Am. Chem. Soc., 71, 1474 (1949).

The cleavage by alkaline solutions of chloromethyl groups from silicon atoms in polysiloxanes is reported to yield methyl chloride and the corresponding silanol[30]. This silanol can then undergo further condensation on heating.

The first preparation of a chloroethylsilane was made by Friedel and Crafts[31] who chlorinated tetraethylsilane to obtain a triethyl-(chloroethyl)-silane. This compound was converted to the corresponding acetate by heating at 180° with a sodium acetate and ethanol. The acetate was subsequently hydrolyzed to a triethylsilylethanol by treatment with dilute aqueous potassium hydroxide at 120-130°. This work was later repeated by Niedzielski[32] who obtained a 48% yield of the final alcohol. Neither work demonstrated whether the substituent groups were in the alpha or the beta position. Ushakov and Itenburg[33] isolated the alpha- and the beta-(chloroethyl)-triethylsilanes and reported that the beta-chlorine is easily lost on treatment with alcoholic sodium hydroxide, but that the alpha-chlorine derivative must be heated at 145° in a sealed tube before the chlorine is lost and triethylvinylsilane is formed.

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[30]British Thompson-Houston Co. Ltd., British Patent 611, 495, Oct. 29, 1948 /C.A. 43, 3238 (1949)_7.

[31]Friedel and Crafts, Ann., 138, 19 (1866).

[32]Niedzielski, J. Am. Chem. Soc., 62, 3519 (1940).

[33]Ushakov and Itenburg, J. Gen. Chem. (U. S. S. R.), 7, 2495 (1937) /C.A., 32, 2083 (1938)_7.

Recent studies by Whitmore and his coworkers have shown that cleavage of alkyl groups which are substituted in the beta position by halogens or oxygen takes place with great ease in the presence of base. Thus (2-chloroethyl)-trichlorosilane cleaves quantitatively on titration with dilute aqueous sodium hydroxide[34] as follows:

$$ClCH_2CH_2SiCl_3 + 4NaOH \longrightarrow C_2H_4 + Si(OH)_4 + 4NaCl$$
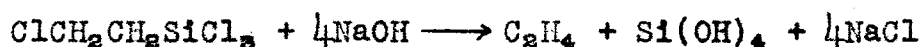
Diethyl-(2-chloroethyl)-chlorosilane and diethyl-(2-chloroethyl)-fluorosilane may be titrated similarly[35]. In contrast, (1-chloroethyl)-trichlorosilane reacted with only three equivalents of sodium hydroxide (cold) and the α-chloroethyl group was not cleaved. Similar behavior was noted in the reaction of methylmagnesium bromide with (2-chloroethyl)-trichlorosilane[36]. Three equivalents of Grignard reagent reacted normally to yield trimethyl-(2-chloroethyl)-silane, but an excess caused cleavage:

$$ClCH_2CH_2Si(CH_3)_3 + CH_3MgBr \longrightarrow (CH_3)_4Si + C_2H_4 + MgClBr$$

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[34] Whitmore and Sommer, J. Am. Chem. Soc., 68, 485 (1946).

[35] Sommer, Bailey, Strong and Whitmore, ibid., 68, 1881 (1946).

[36] Sommer, Goldberg, Dorfman and Whitmore, ibid., 68, 1083 (1946).

(1-Chloroethyl)-trichlorosilane reacted normally with methyl-
magnesium chloride to give trimethyl-(1-chloroethyl)-silane
with no attack on the alpha chlorine[34]. (2-Chloro-n-propyl)-
trichlorosilane in a like manner evolved propylene upon
treatment with aqueous alkali at room temperature. The authors
pointed out the similarity between this type of reaction (b)
and 1:2 eliminations of alkyl halides (a), the silicon acting
as the electron attractor for the nucleophilic reagent, rather
than hydrogen:

(a) $\bar{Y} \cdot \rightarrow$ H-CR$_2$-CR$_2$-Cl $\longrightarrow$ YH + CR$_2$=CR$_2$ + Cl$^-$

(b) $\bar{Y} \cdot \rightarrow$ -Si-CH$_2$-CH$_2$-Cl $\longrightarrow$ -Si-Y + CH$_2$=CH$_2$ + Cl$^-$
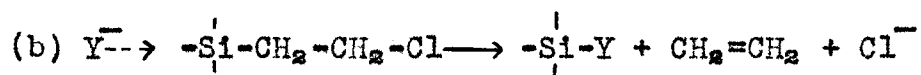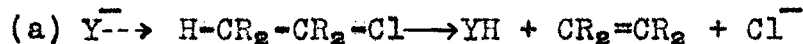
In a later paper[37], diethyl-(2-chloroethyl)-chlorosilane,
$(C_2H_5)_2(ClCH_2CH_2)SiCl$, diethyl-(2-chloroethyl)-fluorosilane,
$(C_2H_5)_2(ClCH_2CH_2)SiF$, and triethyl-(2-chloroethyl)-silane,
$(C_2H_5)_3SiCH_2CH_2Cl$, were all found to undergo this beta
elimination with alcoholic bases, aqueous bases, water,
potassium acetate in acetic acid, methylmagnesium bromide,
aluminum chloride, silver nitrate in ethanol, and, in the case
of the latter compound, by heat alone. In contrast to the
first two, the last compound reacts very slowly with bases.
This reduced activity was attributed to an inhibition

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[37]Sommer, Bailey and Whitmore, J. Am. Chem. Soc., 70,
2869 (1948).

of nucleophilic attack on silicon, caused by the replacement
of the halogen with an alkyl group.

Hurd[21] was able to prepare vinyltrichlorosilane in good
yield by heating a mixture of alpha- and beta- (chloroethyl)-
trichlorosilanes with quinoline. Sommer and his coworkers[37]
confirmed this experiment using (2-chloroethyl)-trichloro-
silane, isolating only a small amount of silicon tetrachloride
due to cleavage. They attribute this lack of cleavage to the
inability of tertiary amines like quinoline to form a nucleo-
philic anion for combination with silicon.

Tetraethylsilane was brominated by Larsson and Knopp[38]
to yield a triethyl-(bromoethyl)-silane and a triethyl-
(dibromoethyl)-silane. The monobromo derivative gave tri-
ethylvinylsilane on heating with 1 $\underline{N}$ alcoholic potassium
hydroxide, while the dibromo derivative cleaved to give tri-
ethylsilanol, ethylene and some vinyl bromide. (3-Chloro-$\underline{n}$-
propyl)-trichlorosilane, $ClCH_2CH_2CH_2SiCl_3$, containing a halogen
atom in the gamma position, was cleaved by refluxing sodium
hydroxide in aqueous ethanol to yield cyclopropane[39]. Trimethyl-
(3-bromo-$\underline{n}$-propyl)-silane was not cleaved under similar con-
ditions. The corresponding beta elimination took place more

[38]Larsson and Knopp, Acta. Chem. Scand., 1, 268 (1947)
/C.A., 42, 5416 (1948)7.

[39]Sommer, Dorfman, Goldberg and Whitmore, J. Am. Chem.
Soc., 68, 488 (1946); Sommer, Van Strien and Whitmore, ibid.,
71, 3056 (1949).

easily, since (2-chloro-n-propyl)-trichlorosilane could be cleaved quantitatively on titration with 0.5 N alkali.

Agre[40] described reactions of a compound which he called (1,2-dichlorovinyl)-trichlorosilane but which is probably (2,2-dichlorovinyl)-trichlorosilane, $Cl_2C=CHSiCl_3$, as was pointed out later by Wagner and Pines[41]. These latter authors prepared both of the above compounds and obtained 1,2-dichloroethylene from the former and 1,1-dichloroethylene from the latter on treating them with potassium hydroxide. Agre indicated that his compound was not cleaved by titration with dilute sodium hydroxide or by excess ethylmagnesium bromide and he attributed this stability (in contrast to the saturated silanes containing the β-chloroethyl group) to the deactivating effect of the double bond. Agre[40] also prepared 1,2-bis-(trichlorosilyl)-1,2-dichloroethane, $Cl_3SiCHClCHClSiCl_3$, (1,1,2,2-tetrachloroethyl)-trichlorosilane, $CHCl_2CCl_2SiCl_3$, and (1,2-dibromo-1,2-dichloroethyl)-trichlorosilane, $CHClBrCClBrSiCl_3$, and cleaved these compounds by titrating them with dilute sodium hydroxide to yield (2-chlorovinyl)-silanetriol (as its condensation products), trichloroethylene, and 1-bromo-1,2-dichloroethylene, respectively. The first compound gave some cleavage on heating with methanol, but

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[40]Agre, _J. Am. Chem. Soc._, _71_, 300 (1949).

[41]Wagner and Pines, _ibid._, _71_, 3567 (1949).

with pyridine and methanol, only 1,2-bis-(trimethoxysilyl)-1,2-dichloroethane, $(CH_3O)_3SiCHClCHClSi(OCH_3)_3$, was formed.

Certain compounds containing oxygen in a position beta to silicon have also been shown to undergo cleavage rather readily. Thus (trimethylsilyl)-methylmagnesium chloride yielded acetone when treated with acetyl chloride, and acetic acid on carbonation[42]. In each case fission of the expected product was postulated. As described in a later paper[43], the same Grignard reagent reacted with ethyl chloroformate to yield ethyl(trimethylsilyl)-acetate. This latter compound was stable in water, but was cleaved readily with dilute acids or alkalies as follows:

$$2(CH_3)_3Si-CH_2-\overset{\overset{\textstyle O}{\|}}{C}-OC_2H_5 + H_2O \overset{OH^-}{\longrightarrow} (CH_3)_3SiOSi(CH_3)_3 + 2CH_3COOC_2H_5$$
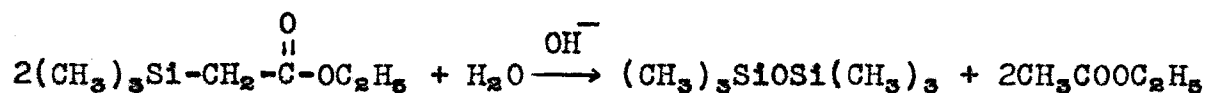
A similar cleavage took place on heating this ester with absolute ethanol to yield trimethylethoxysilane and ethyl acetate. Speier and Daubert[26], on reacting this same (trimethylsilyl)-methylmagnesium chloride with phenylisocyanate got an 80% yield of the cleavage product, acetanilide, instead of the expected (trimethylsilyl)-acetanilide.

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[42]Whitmore, Sommer, Gold and Van Strien, J. Am. Chem. Soc., 69, 1551 (1947).

[43]Gold, Sommer and Whitmore, ibid., 70, 2874 (1948).

In one of the first preferential basic cleavages of an
organosilane to be reported, Kipping[44], during his work on the
preparation of an optically active organosilicon compound,
found that 1,3-diethyl-1,3-di-$\underline{n}$-propyl-1,3-bis-($\underline{p}$-sulfobenzyl)-
disiloxane, $/C_2H_5(\underline{n}-C_3H_7)(\underline{p}-HO_3SC_6H_4CH_2)Si/_2O$, was decomposed
by strong basic solutions to yield sodium-$\underline{p}$-toluenesulfonate.
Boiling the disiloxane with sodium carbonate gave slight de-
composition, while concentrated sodium hydroxide at 100° gave
slow but complete cleavage. The product was identified as
the $\underline{l}$-menthylamine salt. Previously Kipping had reported[45]
that the benzyl group in ethyl-$\underline{n}$-propylbenzylsilanol (or the
corresponding disiloxane) could be sulfonated without any
cleavage taking place, whereas ethyl-$\underline{n}$-propylbenzylphenylsilane
was cleaved on attempted sulfonation to yield benzene (result-
ing from the cleavage of phenyl groups) but not toluene (which
would have resulted had benzyl groups been cleaved). The
benzyl-silicon bond was thus shown to be stable to strong
acids, but easily cleaved by strong bases whereas the phenyl-
silicon bond is easily cleaved by strong acids but (as will
be illustrated later) is relatively stable in the presence of
strong alkalies.

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[44]Kipping, J. Chem. Soc., 93, 457 (1908).
[45]Kipping, ibid., 91, 209 (1907).

Bygden[46] later found a similar cleavage to take place when trimethyl-(p-sulfobenzyl)-silane was refluxed with 30% aqueous potassium hydroxide. The cleavage product was identified, after treatment with phosphorus pentachloride, as p-toluenesulfonyl chloride.

In 1927, Kipping[47] treated tribenzylchlorosilane with quinoline and with dimethylamine in an attempt to split hydrogen chloride from the molecule. However, no apparent reaction took place, indicating that these bases were unable to cause cleavage of the benzyl-silicon bonds.

Steele and Kipping[48] reacted dibenzyldichlorosilane with sodium and potassium in the absence of oxygen and obtained, in addition to a little hexabenzyldisiloxane and 15% tetrabenzyl-silane, a resinous material for which the authors suggested the structure, $[(C_6H_5CH_2)_2Si]_4O$. On heating this material with alkali in aqueous acetone, they eventually obtained its complete solution. In addition, further experiments showed that toluene was formed when the fractionated product above was heated with piperidine and 5% aqueous sodium hydroxide. At this point they state (48, p. 1439):

[46] Bygden, J. prakt. Chem., 96, 86 (1917).

[47] Kipping, J. Chem. Soc., 104 (1927).

[48] Steele and Kipping, ibid., 1431 (1928).

This unsuspected instability of the Si-CH₂Ph binding towards alkali is also shown by the fact that when dibenzylsilicol is heated on a water bath with a 5-10% solution of sodium hydroxide in aqueous acetone during about thirty minutes, it is almost completely decomposed with formation of toluene . . . .

The stability of the phenyl-silicon bond to alkali was demonstrated by Kipping[49] when he heated a polymeric substance having the general formula $\llbracket (C_6H_5)_2Si \rrbracket_n$ with sodium hydroxide in methanol, and with sodium ethoxide at 220° for three hours, without obtaining decomposition of the material. Later[50], a diphenylsilicone polymer $\llbracket (C_6H_5)_2SiO \rrbracket_n$ was found to be stable when refluxed in a solution of potassium hydroxide in aqueous acetone for three hours. However, when this same material was heated at 150° with concentrated alkali, decomposition took place giving benzene and an alkali silicate. When diphenylsilanediol was heated under reduced pressure on a water bath with 20% aqueous potassium hydroxide for three hours, about 1% of the material had cleaved yielding benzene, which was isolated as m-dinitrobenzene.

A nitration product of triethylphenylsilane containing approximately 83% para- and 17% meta-nitrophenyl-triethyl-silanes was slowly attacked by boiling alkalies, giving nitrobenzene[51]. The related bis-(m-nitrophenyl)-diethylsilane

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[49] Kipping, J. Chem. Soc., 125, 2291 (1924).

[50] Kipping and Murray, ibid., 1427 (1928).

[51] Kipping and Cusa, ibid., 1088 (1935).

behaved similarly. Both of these compounds are also cleaved rapidly by acids. The latter compound was reduced catalytically to bis-(m-aminophenyl)-diethylsilane which, on heating for one hour with a 10% solution of potassium hydroxide, gave about 10.5% of its weight of aniline. In contrast, the hydrochloride of this amine was not decomposed by boiling hydrochloric acid.

Tetrakis-(m-nitrophenyl)-silane[52] was decomposed by boiling 10% aqueous sodium hydroxide to yield nitrobenzene but was relatively stable to aqueous acids. Its reduction product, tetrakis-(m-aminophenyl)-silane, on the other hand, was found to be very stable when boiled with saturated aqueous or alcoholic potassium hydroxide[53]. At the same time, a nitration product of tetraphenylsilane containing a complex mixture of meta- and para- nitrophenyl groups was found to be unstable to aqueous alkalies and the p-nitrophenyl groups (but not the m-nitrophenyl groups) were cleaved by hydrochloric acid. The catalytic reduction of this complex mixture in neutral solvent gave a solid which was apparently a mixture of isomeric tetraaminotetraphenylsilanes from which only the tetrakis-(m-aminophenyl)-silane could be isolated. The p-aminophenyl groups present in the reduction products were found to be cleaved by dilute hydrochloric acid, dilute

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[52]Kipping and Blackburn, J. Chem. Soc., 2200 (1932).

[53]Kipping and Blackburn, ibid., 1085 (1935).

ammonium hydroxide, or even on attempted recovery using neutral solvents, giving aniline. In the course of this same work, a compound which the authors conclude is probably tris-(m-aminophenyl)-silanol was found not to yield aniline on boiling with 10% aqueous potassium hydroxide.

A few instances of cleavages of organic groups from silicon by organometallic compounds have been reported. Ladenburg[54] reacted diethylzinc with phenyltrichlorosilane at 230° and isolated tetraethylsilane and diethyldiphenylsilane as well as the expected triethylphenylsilane. However, the tetraethylsilane and diethyldiphenylsilane probably resulted from a disproportionation of the triethylphenylsilane on heating in the presence of the zinc chloride, which was also formed (see Calingaert[55] for a description of other similar disproportionations).

The cleavage of trimethyl-(2-chloroethyl)-silane by methylmagnesium bromide[36] follows a course similar to the cleavage of this compound by base. (See p. 13 of this thesis.)

During studies in which it was shown that tetraphenyltin and tetraphenyllead were cleaved by diethylstrontium and diethylbarium, it was found that the corresponding tetraphenyl-

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[54]Ladenburg, Ber., 7, 387 (1874).

[55]Calingaert, Soroos and Hnizda, J. Am. Chem. Soc., 62, 1107 (1940); Calingaert, Beatty and Neal, ibid., 61, 2755 (1939).

silane (as well as tetraphenylgermanium) did not react with
the latter reagent on refluxing the mixture in benzene solution
for thirteen hours[56].

Recently, several silanols have been cleaved successfully
with $\underline{n}$-butyllithium[57]:

$$R_3SiOH + \underline{n}-C_4H_9Li \longrightarrow R_3SiOLi + \underline{n}-C_4H_{10}$$
$$R_3SiOLi + \underline{n}-C_4H_9Li \longrightarrow R_2-\underline{n}-C_4H_9SiOLi + RLi$$
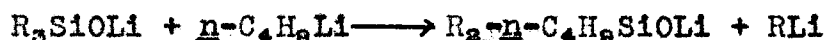
By this reaction, after carbonation of the RLi product,
triphenylsilanol gave a 70% yield of benzoic acid (in addition
to $\underline{n}$-butyldiphenylsilanol), tri-$\underline{p}$-tolylsilanol gave 61% $\underline{p}$-
toluic acid, diphenyl-$\underline{p}$-tolylsilanol gave 6% benzoic acid and
18% $\underline{p}$-toluic acid, and tri-α-naphthylsilanol gave no detect-
able acidic product. Under similar conditions, $\underline{n}$-butyl-
magnesium bromide gave no acidic product with triphenylsilanol
and phenyllithium did not cleave tri-$\underline{p}$-tolylsilanol. When hexa-
phenyldisiloxane was treated with $\underline{n}$-butyllithium, both the
silicon-to-carbon and the silicon-to-oxygen bonds were broken.
The reaction was formulated as follows:

$$(C_6H_5)_3SiOSi(C_6H_5)_3 + \underline{n}-C_4H_9Li \longrightarrow (C_6H_5)_3SiC_4H_9-\underline{n} + (C_6H_5)_3SiOLi$$
$$(C_6H_5)_3SiOLi + \underline{n}-C_4H_9Li \longrightarrow \underline{n}-C_4H_9(C_6H_5)_2SiOLi + C_6H_5Li$$

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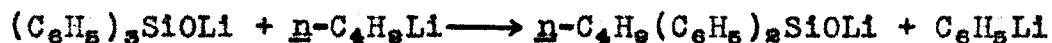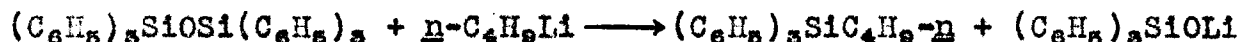
[56]Gilman, Haubein, O'Donnel and Woods, J. Am. Chem. Soc.,
67, 922 (1945).

[57]Gilman, Benkeser and Dunn, ibid., 72, 1689 (1950).

No diphenyldi-n-butylsilane was isolated, as might be expected
if the carbon-to-silicon bond were attacked prior to the
oxygen-to-silicon bond. In addition, studies by H. N. Benedict[58]
have shown that many disiloxanes are cleaved by phenyllithium
according to the following equation:

$$R_3SiOSiR_3 + C_6H_5Li \longrightarrow R_3SiC_6H_5 + R_3SiOLi$$
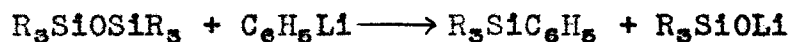
(No cleavage of a carbon-to-silicon bond was encountered in
any of this latter work.) The following silanes containing
four carbon-to-silicon bonds were not cleaved by n-butyllithium
under the conditions used in the above silanol reactions[57]:
tetraphenylsilane, triphenyl-n-butylsilane, trimethylphenyl-
silane, triethylphenylsilane, tetra-p-tolylsilane, trimethyl-
α-naphthylsilane, and triphenyl-2-thienylsilane. (This
last silane gave triphenyl-2-thienyl-5-carboxysilane after
carbonation of the reaction mixture.) No cleavage of trimethyl-
9-fluorenylsilane took place on reaction with n-butyllithium
followed by hydrolysis, but if the reaction mixture was
carbonated and then hydrolyzed, fluorene-9-carboxylic acid
was recovered. The authors proposed the following series
of reactions to explain this behavior:

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[58]Benedict, Master's Thesis, Iowa State College (1950).

CHSi(CH₃)₃ $\xrightleftharpoons[H_2O]{n\text{-}C_4H_9Li}$ CSi(CH₃)₃ (Li) $\xrightarrow{CO_2}$

COOLi CSi(CH₃)₃ $\xrightarrow{H_2O}$ CHCOOLi + (CH₃)₃SiOH
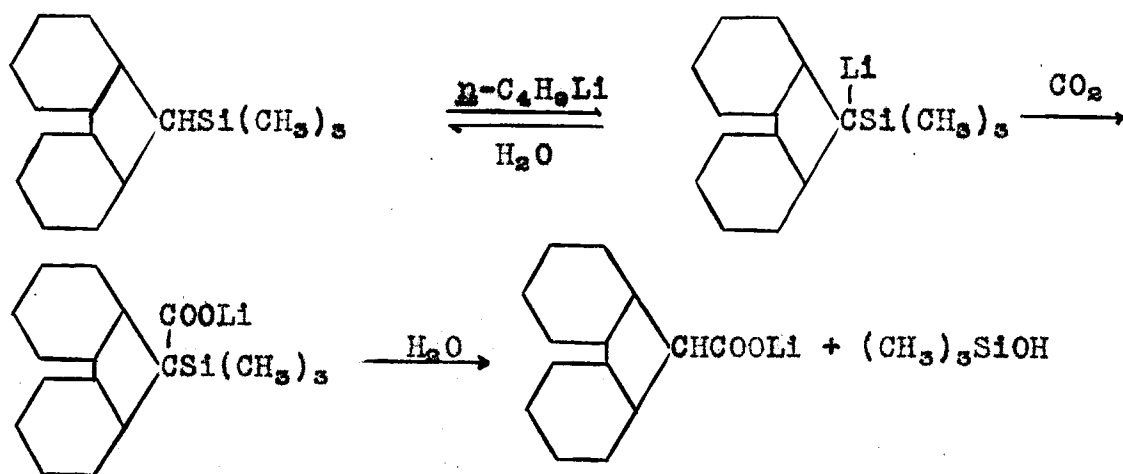
Very recent studies[59] have shown that triphenyl-(phenyl-
ethynyl)-silane can be cleaved with n-butyllithium under the
above conditions to yield n-butyltriphenylsilane and phenyl-
propiolic acid.

[59] Unpublished studies by H. A. Hartzfeld.

Cleavages of Organometallic Compounds

by Basic or Nucleophilic Reagents

Cleavages by Water, Alcohols, or Bases. A first approx-
imation of the reactivities of organometallic compounds can
be made by dividing them roughly into two categories: those
which react with water and those which do not. Since the re-
action of these compounds with water is merely one example of
a reaction with a substance containing an active hydrogen,
this latter type of reaction should be a rough measure of the
order of reactivity involved in reactions with hydroxylated
or basic reagents.

Some of the common elements have been arranged according
to the reactivities of their respective organo-derivatives
toward reagents containing active hydrogen[60]. The decreasing
order of reactivity found was as follows: K, Na, Li, Ca, Mg,
Zn, Al, Cd, B, Pb, Hg, Bi, Sn and Si. Cadmium roughly divides
this series into those elements whose organo-derivatives react
with water (cadmium and the elements preceding it) and those
elements whose organo-derivatives are stable in water (elements
following cadmium). Elements other than those listed whose
organo-derivatives are reported to be decomposed by water[1a]

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[60]Nelson, Doctoral Dissertation, Iowa State College (1937);
Gilman and Nelson, J. Am. Chem. Soc., 59, 935 (1937).

include: Cs, Rb, Ba, Sr, Sc, Y, Cu, Ga, Mn and Fe. For tho
present consideration of the order of ease with which radicals
are cleaved from organometallic compounds, those compounds
which are at least moderately stable in water are of chief
interest.

The organometallic compounds of the elements in the A-
family of the first group of the periodic table are all de-
composed rapidly by hydroxylated compounds. In group I-B,
the organometallic derivatives were found to be relatively un-
stable. Phenylcopper was reported[61] to react with water to
form biphenyl and some benzene. Since the formation of R-R
compounds like biphenyl is characteristic of the thermal de-
composition of these organometallic derivatives, the biphenyl
may have been formed in this latter manner[1a].

In group II, mercury is the only element whose organometallic
compounds are not decomposed by hydroxylated solvents[1a]. The
alkyl and aryl mercury compounds appear to be stable in at
least moderate concentrations of strong base. Thus ethyl-
mercuric chloride has been treated with 40% potassium hydr-
oxide in methanol to yield ethylmercuric hydroxide with no
reported cleavage of the ethyl radical[62]. Phenylmercuric
hydroxide was prepared by boiling a solution of phenylmercuric

[61]Gilman and Straley, Rec. trav. chim., 55, 821 (1936).

[62]Rumpf, Bull. soc. chim., 11, 550 (1944).

nitrate in an approximately 1 N aqueous sodium hydroxide solution[63]. This phenylmercuric hydroxide was found to be weakly basic, having a pH of 7-7.5.

Diallylmercury has been made by treating allylmercuric iodide with a concentrated solution of potassium cyanide in water or ethanol without any reported cleavage of allyl groups[64]. Dibenzylmercury is reported to be stable in boiling water[65]. Di-α-naphthylmercury is not decomposed on heating with sodium amalgam in alcohol[66], however di-β-naphthyl-mercury yields β,β-binaphthyl on distillation over soda lime.

Koton and his coworkers have studied the reactions of alcohols with R_2Hg or RHgX types at temperatures of 150-200°. They showed that straight pyrolysis of diphenyl-mercury[67] required a temperature of about 275°, whereas heating this compound with ethanol at 150-200° gave benzene, mercury and acetaldehyde. The proposed course of this latter reaction was:

$$(C_6H_5)_2Hg \longrightarrow Hg + 2C_6H_5-$$
$$2C_6H_5- + CH_3CH_2OH \longrightarrow 2C_6H_6 + CH_3CHO$$
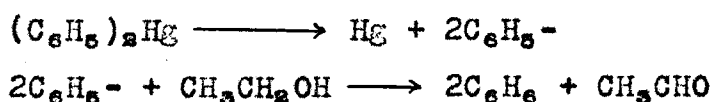
[63]Schramm, J. Am. Chem. Soc., 69, 1831 (1947).

[64]Vijayaraghavan, J. Indian Chem. Soc., 20, 318 (1943) $\sqrt{}$ C.A., 38, 2006 (1944)$\sqrt{}$.

[65]Wolff, Ber., 46, 64 (1913).

[66]Otto and Mories, Ann., 147, 164 (1868); Chattaway, J. Chem. Soc., 65, 877 (1894).

[67]Razuvaev and Koton, J. Gen. Chem. (U.S.S.R.), 1, 864 (1931) $\sqrt{}$ C.A., 26, 2719 (1932)$\sqrt{}$.

The reaction rate was accelerated by the addition of acet-
aldehyde, decelerated by the addition of benzene, and was
independent of the volume of ethanol used. Later they found
the following percentages of decomposition of diphenylmercury
in six hours by the respective alcohols[68]: methyl, 91; ethyl,
19.8; n-propyl, 26.6; n-butyl and isobutyl, 7.7; isoamyl, 79.7;
benzyl, 59.7; ethylene glycol, 97.7; glycerol, 67.0; and
mannitol, 92.6. They noted that the aliphatic alcohols with
an odd number of carbon atoms gave more rapid decomposition
than those with an even number of carbon atoms and also that
the polyhydric alcohols were more effective than the mono-
hydric alcohols of the same number of carbon atoms.

The decomposition of a series of RHgBr compounds by
ethanol at 175° for twelve hours gave the following series
for the R groups, arranged according to decreasing rate[69]:
phenyl, n-butyl, ethyl, n-propyl, and α-naphthyl. Similar
decomposition of a series of halogen-substituted C_6H_5HgX-
type compounds gave the following order for the halogens,
arranged according to decreased rate[70]: fluorine, iodine,
bromine, and chlorine. For the phenylmercuric bromide and

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[68]Koton, J. Gen. Chem. (U.S.S.R.), 8, 1791 (1938)
/¯C.A., 33, 4969 (1939) ¯/.

[69]Koton and Florinskii, ibid., 9, 2196 (1939) /¯C.A., 34,
4053 (1940) ¯/.

[70]Koton, ibid., 11, 179 (1941) /¯C.A., 35, 7382 (1941)¯/.

chloride, the products formed were the corresponding mer-
curous halide, benzene and acetaldehyde, while the iodide
and fluoride gave mercuric halides and free mercury in place
of the mercurous halide.

$$2C_6H_6HgBr + C_2H_5OH \longrightarrow Hg_2Br_2 + C_6H_6 + CH_3CHO$$
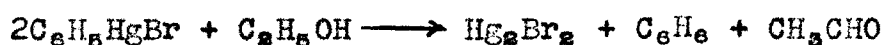
These reactions of alcohols on organomercury compounds at
high temperature are not to be expected to give a cleavage
series of radicals comparable with a series obtained by a
purely nucleophilic-type reaction, since the thermal stabil-
ities and reducing action of the mercury compounds are prob-
ably relatively important here.

Nesmeyanov and his coworkers[71] treated mercuric chloride
with acetylene and obtained a quasicomplex , from which
they isolated both the _cis_ and _trans_ isomer of bis-(2-chloro-
vinyl)-mercury. On treating the _cis_ isomer with potassium
cyanide (among other reagents) it decomposed to yield acety-
lene and mercuric chloride. The _trans_ isomer, however, may
be treated with sodium ethoxide or other basic reagents in
dry ethanol or ether to give some mercury acetylide with only
partial loss of hydrogen chloride, the average composition of
the product being $C_8H_8Hg_3Cl$.

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[71]Nesmeyanov, Borisov and Gus'kova, _Bull. acad. sci._
_U.R.S.S._, _Classe sci. chim._, 639 (1945) _/ C.A._, _40_, 4659
(1946)_/; Nesmeyanov, Kochetkov and Freidlina, _ibid._, 657
(1947) _/ C.A._, _42_, 5847 (1948)_/.

The organic compounds of boron of the R_3B type have been classed between R_3Al and R_2Zn compounds with respect to reactivity in addition reactions to the carbonyl group[1a], yet they appear to be uncommonly stable to the action of water and alcohols. The $RB(OH)_2$ types are extremely stable to alkali; for example, n-butylboric acid dissolves in 10-20% aqueous sodium hydroxide without decomposition to give a complex of the type[72]: $Na\underline{/}\underline{n}-C_4H_9BO_2H\cdot1/2H_2O\underline{/}$. In ammoniacal silver oxide, the following reaction was reported to take place[72]:

$$2\underline{n}-C_4H_9B(OH)_2 + 2Ag(NH_3)_2^+ + 2H_2O \longrightarrow \underline{n}-C_8H_{18} + 2Ag + 2H_3BO_3 +$$
$$2NH_3 + 2NH_4^+$$
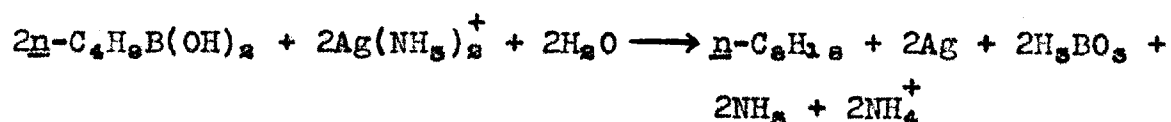
The other members of group III-A are decomposed promptly by water, as are the group III-B elements. Hilpert and Gruttner[73] obtained biphenyl as well as benzene on treating triphenylaluminum with water. Triethylgallium, which was found to react vigorously with water, is stabilized by the formation of coordination compounds such as $\underline{/}(C_2H_5)_3Ga\cdot NH_3\underline{/}$. This latter ammine reacted only slowly with water[74].

In group IV-B, the relatively few organogermanium derivatives that are described appear to be stable to strong bases.

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[72]Snyder, Kuck and Johnson, J. Am. Chem. Soc., 60, 105 (1938).

[73]Hilpert and Gruttner, Ber., 45, 2828 (1912).

[74]Dennis and Patnode, J. Am. Chem. Soc., 54, 132 (1932).

Tetraphenylgermanium was reported to be stable to boiling aqueous caustic alkali[75] and triphenylgermanium oxide, $[(C_6H_5)_3Ge]_2O$, was not attacked by 50% aqueous sodium hydroxide[76].

Methyl stannonic acid, CH_3SnOOH, was decomposed by boiling, concentrated potassium hydroxide to yield methane, trimethyltin hydroxide, and dimethyltin oxide[77]. Generally, however, the alkyl and aryl tin derivatives are stable to alkalies. Compounds of the type R_3SnOH and R_2SnO have been made by the action of dilute alkalies on the corresponding halides. Tetraphenyltin was refluxed with 40 g. of sodium hydroxide in 200 ml. of 95% ethanol for three hours without decomposition[78]. Triphenyl-(o-hydroxyphenyl)-tin, when treated similarly, underwent cleavage to give an amorphous precipitate of meta-stannic acid or its derivatives[78]. The same result had been obtained previously on treating triethyl-(o-hydroxyphenyl)-tin with 15% potassium hydroxide, the product being reported as a solid amorphous mass[79].

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[75]Kraus and Foster, J. Am. Chem. Soc., 49, 457 (1927).

[76]Morgan and Drew, J. Chem. Soc., 127, 1760 (1925).

[77]Pfeiffer and Lehnardt, Ber., 36, 1054 (1903).

[78]Arntzen, Doctoral Dissertation, Iowa State College (1942); Gilman and Arntzen, J. Org. Chem., 15, 000 (1950).

[79]Kocheshkov, Nesmeyanov and Pusyrewa, Ber., 69, 1639 (1936).

Organolead compounds likewise are generally base-stable. Triethyllead chloride when heated with alkali gives only the triethyllead hydroxide, which itself is strongly alkaline[80].

Steam distillation of triethyllead halides or hydroxides has led to a type of redistribution reaction[81];

$$2(C_2H_5)_3PbX \longrightarrow (C_2H_5)_2PbX_2 + (C_2H_5)_4Pb$$

$$(C_2H_5)_2PbX_2 \longrightarrow C_2H_5PbX_3 + (C_2H_5)_3PbX$$

$$\text{or } (C_2H_5)_2PbX_2 \longrightarrow PbX_2 + \underline{n}\text{-}C_4H_{10}$$

In these equations, X may be a halogen or hydroxyl group. Under the conditions of steam distillation, the triethyllead halides decomposed less readily than the diethyllead dihalides, whereas the reverse was true of the corresponding hydroxides.

Bis-(2-chlorovinyl)-lead dibenzoate was prepared and found to be stable in water but was decomposed by 20% aqueous potassium hydroxide to give a 99.75% yield of acetylene[82].

The phenyl derivatives of lead such as diphenyllead oxide, are stable in boiling alkali[83].

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[80]Cahours, Ann., 122, 48 (1862).

[81]Calingaert, Shapiro, Dykstra and Hess, J. Am. Chem. Soc., 70, 3902 (1948).

[82]Nesmeyanov, Freidlina and Kochetkov, Izvest. Akad. Nauk S. S. S. R., Otdel Khim. Nauk, 127 (1948) /C.A. 43, 1716 (1949)_7.

[83]Polis, Ber., 20, 716 (1887).

Organobismuth and antimony compounds are also base stable, i.e. triphenylantimony dichloride may be refluxed with alcoholic potassium hydroxide without cleavage during the preparation of triphenylantimony dihydroxide[84].

An addition compound of antimony pentachloride and acetylene, bis-(2-chlorovinyl)-antimony trichloride, however, was reported to be immediately hydrolyzed by water[85], presumably giving evolution of acetylene.

Metal-metal Interconversion Reactions. Metal-metal inter-conversion reactions are usually considered to involve the attack of the carbanion or the negative portion of the ion-pair of the more reactive organometallic compound on the metal of the less reactive organometallic compound. The reactions have been shown to be reversible[86], however, unless the reactivities of the metals and/or the radicals involved are very similar, the equilibrium is largely displaced in one direction. In these reactions, the more electron-attracting, or the more labile organic radical is considered to be that group which shows a predominant tendency to become or remain combined with the more

[84]Michaelis and Reese, Ann., 233, 49 (1886).

[85]Nesmeyanov and Borisov, Bull. acad. sci. U. R. S. S., Classe sci. chim., 251 (1945) /C.A. 40, 2123 (1946)_/.

[86]Gilman and Jones, J. Am. Chem. Soc., 63, 1439 (1941).

reactive metal. Because of the similarity between these reactions and inorganic double decomposition reactions, it is not surprising that the polarity of the solvent and the solubility of the reactants and products has been found to influence the position of equilibrium.

Ziegler and Dersch[87] established the interconversions between phenyllithium and isopropylmagnesium bromide, and between phenyllithium and benzylmagnesium bromide, to yield isopropyllithium and benzyllithium, respectively, and diphenylmagnesium.

$$2C_6H_5Li + i\text{-}C_3H_7MgBr \longrightarrow i\text{-}C_3H_7Li + (C_6H_5)_2Mg + LiBr$$

The isopropyllithium was characterized by its rapid addition to 1,1-diphenylethylene in contrast to phenyllithium, which adds slowly, and RMgX compounds, which do not add at all. The reversibility of the similar reaction between n-butyllithium and diphenylmagnesium was later demonstrated[86].

The reaction between ethyllithium and dimethylmercury was used by early workers to prepare methyllithium, since the latter is insoluble in the petroleum ether[88] and benzene[89] used as

[87]Ziegler and Dersch, Ber., 64, 448 (1931).

[88]Schlenk and Holtz, ibid., 50, 262 (1917).

[89]Hein, Petzchner, Wagler and Segitz, Z. anorg. allgem. Chem., 141, 161 (1925).

solvents. Phenyllithium was obtained in the same manner from diphenylmercury and ethyllithium[88,89].

$$2C_2H_5Li + (C_6H_5)_2Hg \longrightarrow 2C_6H_5Li + (C_2H_5)_2Hg$$

A suspension of n-butylsodium in petroleum ether treated with diphenylmercury gave phenylsodium and di-n-butylmercury[90]. Benzyllithium was obtained in a similar way from dibenzylmercury and ethyllithium[89], n-butyllithium[91], or other organolithium compounds (used as part of a method for their determination)[92].

Gilman and Jones[86] found the p-tolyl group to be more labile than the phenyl group in reactions between di-p-tolylmercury and phenyllithium or between diphenylmercury and p-tolyllithium in ether solution.

$$2C_6H_5Li + (p-CH_3C_6H_4)_2Hg \longrightarrow (C_6H_5)_2Hg + 2p-CH_3C_6H_4Li$$

The high lability of the phenyl and p-tolyl groups relative to ethyl and n-butyl was demonstrated when practically complete interconversions were obtained between diphenylmercury and n-butyllithium, di-p-tolylmercury and n-butyllithium, diphenyl-

[90]Gilman and Bebb, J. Am. Chem. Soc., 61, 109 (1939).

[91]Ziegler and Schafer, Ann., 479, 150 (1930).

[92]Ziegler, Crossmann, Kleiner and Schafer, ibid., 473, 1 (1929).

mercury and ethylmagnesium bromide, and di-p-tolylmercury and ethylmagnesium bromide. Reactions between diphenylmercury and p-tolylmagnesium bromide and between di-p-tolylmercury and phenylmagnesium bromide gave some interconversion, but the rates of reaction were slow, so that a state of equilibrium had probably not been attained in the reaction times allowed.

Both diphenylmercury and dibenzylmercury reacted much more rapidly with n-butyllithium than with t-butyllithium in benzene-petroleum ether solution[93]. The yields of benzoic acid obtained, after carbonation of the reaction products of these two mercury compounds with n-butyllithium, were 62% and 53%, respectively, in two minutes, indicating that the two compounds have a comparable order of reactivity under these conditions. The same authors showed that methyllithium undergoes rapid interconversion with dibenzylmercury in ether solution.

The reaction of bis-(p-bromophenyl)-mercury with n-butyllithium and with methyllithium in ether for three minutes gave predominantly p-bromobenzoic acid rather than terephthalic acid, showing that the metal-metal interconversion reaction took place much more rapidly than the halogen-metal interconversion. The yields of the former acid were 66% and 79%, respectively, for the n-butyllithium and the methyllithium reactions.

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[93]Gilman, Moore and Jones, J. Am. Chem. Soc., 63, 2482 (1941).

Challenger and Ridgeway[94], in 1922, carried out inter-conversions between some organic mercury and bismuth compounds. Diphenylmercury and tri-α-naphthylbismuth did not react when they were refluxed for two hours in benzene-chloroform solution, but on heating their mixture for ninety minutes at 200° without solvent, di-α-naphthylmercury, triphenylbismuth, and diphenyl-α-naphthylbismuth were isolated from the reaction mixture, along with some starting materials. In the same way, the fusion of tri-p-tolylbismuth and diphenylmercury at 180° for one hour gave 75% conversion to di-p-tolylmercury. Although not strictly comparable with metal-metal interconversion reactions in solution, these reactions do show a greater tendency for the α-naphthyl and p-tolyl groups, as compared with the phenyl group, to become attached to the slightly more reactive mercury.

In the reaction of phenylmercuric bromide with α-naphthyl-magnesium bromide in ether-benzene solution at 25°, some di-α-naphthylmercury was formed[94]. Similarly, Kharasch and Swartz[95] obtained diphenylmercury in good yield from phenyl-magnesium bromide and allylmercuric iodide.

$$CH_2=CHCH_2HgI + 2C_6H_5MgBr \longrightarrow$$
$$(C_6H_5)_2Hg + CH_2=CHCH_2MgBr + MgBrI$$
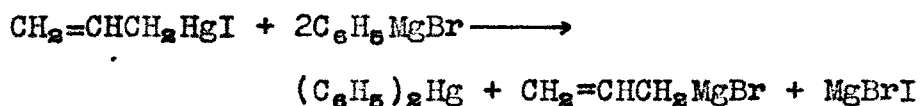
[94] Challenger and Ridgeway, J. Chem. Soc., 121, 104 (1922).

[95] Kharasch and Swartz, J. Org. Chem., 3, 405 (1938).

The presence of the halide ion in this type of interconversion may lead to some radical redistribution so that results comparable with disubstituted derivatives are not to be expected. Thus, in one of their studies of the redistribution reaction, Calingaert and his coworkers[96] heated diethylmercury and tetramethyllead with aluminum chloride at 80° for five hours and obtained a random equilibrium mixture in which mercury showed a greater relative affinity than did lead for the methyl radicals as compared with the ethyl radicals.

Recently[97], comparable experiments were reported in which diarylmercury compounds were treated with n-butyllithium in ether solution. Dimesitylmercury gave 72.5% β-isodurylic acid (after carbonation), bis(-p-chlorophenyl)-mercury gave 51.1% and 67.8% p-chlorobenzoic acid, di-p-tolylmercury gave 28.2% and 41.5% p-toluic acid, and diphenylmercury gave 29.4% and 22.8% benzoic acid. The order of decreasing lability of groups thus indicated is mesityl, p-chlorophenyl, p-tolyl, phenyl. The position of the phenyl radical compared to the p-chlorophenyl radical was verified by cleavages of phenyl-(p-chlorophenyl)-mercury with n-butyllithium to yield 57.5% and 50.9% p-chlorobenzoic acid and 4.0% and 4.9% benzoic acid.

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[96]Calingaert, Soroos and Thompson, J. Am. Chem. Soc., 62 1542 (1940).

[97]Gilman and Yale, ibid., 72, 8 (1950).

Nesmeyanov and his coworkers have reported several metal-metal interconversions or cleavages during the course of their extended studies of organometallic compounds. Methylmercuric hydroxide was treated with phenylboric acid to yield methyl-phenylmercury and boric acid[98].

$$CH_3HgOH + C_6H_5B(OH)_2 \longrightarrow CH_3HgC_6H_5 + B(OH)_3$$

Phenylmercuric chloride reacted with phenyltrichlorotin or with phenylbismuth oxide, in the presence of sodium hydroxide, to yield diphenylmercury[98]. (o-Hydroxyphenyl)-mercuric chloride was treated with ethylmagnesium bromide to yield 20% salicylic acid after carbonation[99].

$$o\text{-}HOC_6H_4HgCl + C_2H_5MgBr \xrightarrow{CO_2} o\text{-}HOC_6H_4COOH + C_2H_5HgCl$$
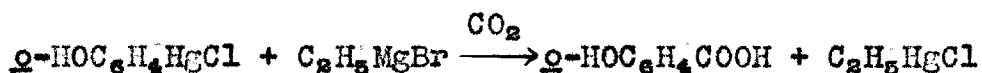
cis-(2-Chlorovinyl)-mercuric chloride was treated with phenyl-trichlorotin to give an 8.2% yield of diphenylmercury[100].

The order of ease of cleavage of radicals from organo-mercury compounds can be summarized approximately by the following series, arranged according to the decreasing ease of cleavage of the radical: allyl, mesityl, (p-chlorophenyl,

[98]Kocheshkov and Nesmeyanov, J. Gen. Chem. (U.S.S.R.), 4, 1102 (1934) /C.A., 29, 3993 (1935)_/.

[99]Nesmeyanov and Pecherskaya, Bull. acad. sci. U.R.S.S., Classe sci. chim., 317 (1943) /C.A., 38, 5492 (1944)_/.

[100]Nesmeyanov, Freidlina and Broisov, ibid., 146 (1945) /C.A., 40, 3451 (1946)_/.

p-bromophenyl), α-naphthyl, p-tolyl, phenyl, (methyl, butyl, ethyl). The 2-chlorovinyl, benzyl and o-hydroxyphenyl radicals are cleaved easily, but their exact position in the series is problematical.

The treatment of triphenyllead chloride with more than one equivalent of p-tolyllithium was found by Austin[101] to yield some tetra-p-tolyllead. Tetraethyllead on similar treatment gave no cleavage and triphenyllead chloride, on treatment with p-dimethylaminophenyllithium gave only the expected triphenyl-(p-dimethylaminophenyl)-lead.

A somewhat similar reaction was encountered later when triphenyllead chloride was treated with diethylbarium in ether solution to yield tetraphenyllead in addition to ethyltriphenyl-lead[56]. The following series of reactions was postulated:

$$2(C_6H_5)_3PbCl + (C_2H_4)_2Ba \longrightarrow 2(C_6H_5)_3PbC_2H_5 + BaCl_2$$
$$2(C_6H_4)_3PbC_2H_5 + (C_2H_5)_2Ba \longrightarrow 2(C_6H_5)_2Pb(C_2H_5)_2 + (C_6H_5)_2Ba$$
$$2(C_6H_5)_3PbCl + (C_6H_5)_2Ba \longrightarrow 2(C_6H_5)_4Pb + BaCl_2$$
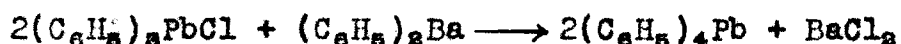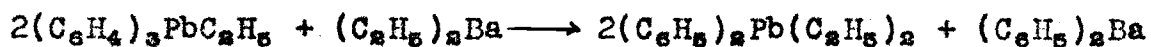
Triphenyltin chloride under the same conditions gave an 85.8% yield of ethyltriphenyltin, with no reported formation of tetraphenyltin.

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[101] Austin, J. Am. Chem. Soc., 54, 3726 (1932).

This same paper reports the treatment of ethyltriphenyl-
lead, tetraphenyllead and tetraphenyltin, with diethylbarium
for twenty-four hours in ether at 25° to yield (after carbon-
ation), 9.1%, 0.0%, and 32% benzoic acid, respectively. Under
the duplicated conditions, 10.7% benzoic acid was obtained
from tetraphenyltin and diethylstrontium. Tetraphenylsilane
and tetraphenylgermanium in benzene solution were not cleaved
in thirteen hours by diethylbarium.

Gilman and Moore[102] reported the treatment of tetra-
phenyllead, hexaphenyldilead, tetra-p-tolyllead, and hexa-p-
tolyldilead with n-butyllithium in ether to yield (after
carbonation), 0% benzoic acid, 14% benzoic acid, 28% p-toluic
acid, and 62% p-toluic acid, respectively. Tetraphenyllead
was cleaved by n-butyllithium in ether-benzene solution at
60° to yield 40% tetra-n-butyllead after thirty minutes and
75% tetra-n-butyllead after sixty minutes or longer. However,
tetraphenyllead did not react with either n-butylmagnesium
bromide in ether or with benzylsodium in benzene solution.
Diphenyldi-p-tolyllead was cleaved by n-butyllithium in ten
minutes to yield 31% and 79% p-toluic acid and < 1% and 21%
benzoic acid, respectively, in two experiments. The greater
lability of the p-tolyl radical compared to the phenyl radical
is thus confirmed.

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[102] Gilman and Moore, J. Am. Chem. Soc., 62, 3206 (1940).

Gilman, Moore and Jones[93] found the decreasing order
of effectiveness of various organolithium reagents for the
cleavage of tetraphenyllead, tetrakis-(p-chlorophenyl)-lead
and dibenzylmercury to be: ethyllithium, n-propyllithium,
n-butyllithium, methyllithium, phenyllithium, and phenyl-
ethynyllithium. In the series of isomeric butyllithiums, the
decreasing order of effectiveness for the cleavage of tetrakis-
(p-chlorophenyl)-tin was: normal > iso > tertiary.

The greater electron attracting ability of the p-chloro-
phenyl group as compared with the phenyl group was indicated
when the above authors obtained 2% benzoic acid and 98%
p-chlorobenzoic acid on treating diphenyl-bis-(p-chlorophenyl)-
lead with n-butyllithium followed by carbonation. Triphenyl-
(p-chlorophenyl)-lead similarly gave 24% benzoic acid and 76%
p-chlorobenzoic acid.

The authors state that with n-butyllithium there is only
a 30% cleavage of tetraphenyllead under conditions where tetra-
phenyltin is cleaved to the extent of 45%. However, the
corresponding data were not given and the difference between
these percentages does not seem sufficient to warrant the
conclusion that there is any great difference in the ease of
cleavage of the radicals in these two compounds. The fact
that only a 3% cleavage of tetra-o-tolyllead was obtained under
the same conditions was attributed to steric factors. The
complete lack of cleavage of tetrakis-(p-chlorophenyl)-tin by

t-butyllithium was also evidence that steric factors are
of importance in this type of reaction, since the p-chloro-
phenyl radical is usually cleaved with great ease by organo-
lithium compounds.

This paper[93] contains data on a large number of cleavages
of symmetrical lead, tin, and mercury compounds under various
conditions. n-Butylsodium in petroleum ether was less effect-
ive in the cleavage of tetraphenyllead than was n-butyllithium
in ether. Benzylsodium did not cleave tetraphenyltin in
twenty-four hours in refluxing heptane. Likewise phenyllithium
did not cleave tetraethyllead in twelve hours in ether solution
although it gave 53% cleavage of tetrakis-(p-chlorophenyl)-tin
in fifteen minutes. Treatment of triphenyl-(p-bromophenyl)-
lead with n-butyllithium gave no lead-containing acid after
carbonation, indicating that metal-metal interconversion had
taken place to the exclusion of any halogen-metal inter-
conversion.

In a manner somewhat analogous to the beta elimination
reactions of β-chloroethyl-substituted silanes, bis-(2-chloro-
vinyl)-lead dichloride has been treated with phenylmagnesium
bromide in ether at 25° to give a 34% yield of acetylene
and an 84% yield of tetraphenyllead[103].

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[103]Nesmeyanov, Freidlina and Kochetkov, Izvest. Akad.
Nauk S.S.S.R., Otdel Khim. Nauk, 127 (1948)/ C.A., 43, 1716
(1949)/

Recently S. D. Rosenberg[104] has obtained an almost
quantitative yield of tetraphenyltin in one hour by treating
triphenylbenzyltin with phenyllithium in ether at -35°.
Triphenylbenzyltin and ethylmagnesium bromide under the
same conditions, but at +35°, did not react.

The decreasing order of ease of cleavage of radicals
from tin and lead appears to be approximately: p-chloro-
phenyl, p-tolyl, phenyl, p-dimethylaminophenyl, (methyl,
n-butyl, n-propyl, ethyl), with benzyl and 2-chlorovinyl rating
positions toward the beginning of this series.

Woods[105] treated various symmetrical and unsymmetrical
organoantimony compounds with n-butyllithium in ether for
ten minutes. The following percentages are the yields of
acid after carbonation (a measure of the degree of cleavage
of the corresponding antimony compound): triphenyl, 6.5,
8.3; tri-p-tolyl, 5.9, 6.5; tri-(p-chlorophenyl), 38. For
the unsymmetrical derivatives, similarly: diphenyl-α-
naphthyl, 15.6% α-naphthoic acid; diphenylmesityl, 10.2%
benzoic acid; diphenyl-p-chlorophenyl, 3.9% benzoic acid,
20.2% p-chlorobenzoic acid.

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[104]Unpublished studies by S. D. Rosenberg.

[105]Woods, Doctoral Dissertation, Iowa State College (1943).

The following yields of acids were reported after the carbonation of the reaction products from the following symmetrical bismuth compounds with n-butyllithium in ether solution at 35°[106]: tri-p-tolyl (24 hours), 70% p-toluic acid; tri-α-naphthyl (18 hours), 48% α-naphthoic acid; tri-α-naphthyl (18 hours in benzene), no acid recovered; tris-(p-chlorophenyl) (20 hours), 90% p-chlorobenzoic acid; tri-p-phenetyl (11 hours), 27.4% p-ethoxybenzoic acid; and tri-o-phenetyl (11 hours), 29.9% o-ethoxybenzoic acid[107].

The following additional cleavages[97] of symmetrical bismuth compounds by n-butyllithium in ten minutes are reported to have been carried out under equivalent conditions to give the specified yields of acids after carbonation (duplicate experiments): Tris-(p-chlorophenyl), 44.7% and 48.8%; tris-(p-bromophenyl), 41.8%, 40.8%; tris-(p-fluorophenyl), 40%, 42.8%; triphenyl, 3.3%, 5.8%; tri-p-tolyl, 2.2%, trace; tri-p-phenetyl, 1.9%, 1.5%; tri-α-naphthyl, 1.3%; trimesityl, 0%; tri-o-tolyl, 0%; and tri-(o-chlorophenyl), 0%.

Under the same conditions the following unsymmetrical bismuth compounds were cleaved to give: diphenyl- -naphthyl, 21.6% α-naphthoic acid, 1.7% benzoic acid; diphenyl-(p-chloro-

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[106]Gilman, Yablunky and Svigoon, J. Am. Chem. Soc., 61, 1170 (1939).

[107]Svigoon, Master's Thesis, Iowa State College (1939).

phenyl), 30.7% and 28.1% p-chlorobenzoic acid, 3.4% and 10%
benzoic acid; di-p-tolyl-(p-chlorophenyl), 30.7% and 25.6%
p-chlorobenzoic acid, 7.3% and 8.0% p-toluic acid; bis-(p-
chlorophenyl)-α-naphthyl, 23.5% and 20.2% p-chlorobenzoic
acid, 22.9% and 22.4% α-naphthoic acid; bis-(p-chlorophenyl)-
o-tolyl, 42.2% and 34.5% p-chlorobenzoic acid, 0% o-toluic acid.

The approximate order of decreasing ease of cleavage of
the radicals in the case of the antimony compounds is: p-chloro-
phenyl, α-naphthyl, (phenyl, p-tolyl), and mesityl. In the
case of the bismuth compounds, the corresponding order is:
(p-chlorophenyl, p-bromophenyl, p-fluorophenyl), α-naphthyl
(except for tri-α-naphthylbismuth where its slight solubility
may have been a factor[97]), (p-tolyl, phenyl, p-phenetyl,
o-phenetyl), (mesityl, o-tolyl, o-chlorophenyl).

The metal-metal interconversion has been shown in several
cases to be more rapid than metalation[1a]. However, in an
analogous reaction of n-butyllithium with triphenylphosphorus,
metalation took place in the meta-position to the extent of
5.9%[108]. Other triphenyl derivatives of non-metals such as
nitrogen[109] and arsenic[110] have also given meta-metalation.

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[108]Gilman and Brown, J. Am. Chem. Soc., 67, 824 (1945).

[109]Gilman and Brown, ibid., 62, 3208 (1940).

[110]Gilman and Stuckwisch, ibid., 63, 3532 (1941).

EXPERIMENTAL

Organosilicon Compounds

Tris-(p-chlorophenyl)-ethoxysilane. A solution of p-chlorophenyllithium in 300 ml. of ether was prepared from 0.151 mole of n-butyllithium[111,112] and 0.166 mole of p-chloro-bromobenzene (Gilman, Langham and Moore[113] reported a 90% yield of p-chlorobenzoic acid after carbonation). This solution was stirred for thirty minutes and then added to 10.4 g. (0.05 mole) of ethyl orthosilicate. After stirring one hour, Color Test I[114] was negative. The product was hydrolyzed with dilute acid and the ether layer was separated and dried over sodium sulfate. After removing the ether and other materials volatile below 150° at 20 mm., the residue solidified on standing. Two crystallizations from 95% ethanol gave 6.0 g. (29.5%) of white crystals melting at 128°. This material was shown to contain no active hydrogen by treatment with a solution of methylmagnesium iodide.

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[111]Gilman, Beel, Brannen, Bullock, Dunn and Miller, J. Am. Chem. Soc., 71, 1499 (1949).

[112]Gilman and Haubein, ibid., 66, 1515 (1944). This paper describes a procedure for the analysis of RLi compounds.

[113]Gilman, Langham and Moore, ibid., 62, 2327 (1940).

[114]Gilman and Schulze, ibid., 47, 2002 (1925).

Anal. Calcd. for $C_{20}H_{17}O\ Cl_3Si$: Si, 6.88. Found[115]: Si, 6.84.

Hexakis-(p-chlorophenyl)-disiloxane. A sample of tris-(p-chlorophenyl)-ethoxysilane was refluxed for twenty minutes with 90% formic acid[116]. After filtering, the solid was crystallized from methanol to give a product melting at 210°. This compound was also obtained as described under trichloromethyltris-(p-chlorophenyl)-silane.

Anal. Calcd. for $C_{36}H_{24}OCl_6Si_2$: Si 7.58. Found: Si, 7.68.

Tris-(p-chlorophenyl)-silanol. Three grams of tris-(p-chlorophenyl)-ethoxysilane was dissolved in 20 ml. of a 1:1 dioxane-ethanol solution containing 0.73 mole of potassium hydroxide and 1.90 moles of water per liter. After warming for fifteen minutes, the mixture was acidified with dilute acid and extracted with ether. Evaporation of the ether layer and recrystallization of the residue from petroleum ether (b.p. 60-70°) gave 2.6 g. (93%) of crystals melting at 121°.

Anal. Calcd. for $C_{18}H_{13}OCl_3Si$: Si, 7.41. Found: Si, 7.54.

The silicon analysis of this compound was carried out according to the following micro procedure:

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[115]Gilman, Hofferth, Melvin and Dunn, J. Am. Chem. Soc., 72, 0000 (1950). The macro method used for the determination of silicon is described in this paper.

[116]Unpublished studies by H. W. Melvin.

Procedure for the Microdetermination of Silicon[117]. A five to fifteen milligram sample is weighed into a platinum boat, which, along with a platinum cylinder, has been previously tared. One drop of conc. sulfuric acid is carefully added to the sample and the boat is placed in the cylinder. The boat and cylinder are then inserted in the end of a Vicor tube heated electrically[117b] by a three foot length of No. 30 michrome wire wound around the tube for a distance of six centimeters. The other end of the tube is bent down slightly and heated with a burner to provide a current of air over the boat. The temperature of the cylinder and contents is raised slowly over a ten minute period (or until all the acid has evaporated) by slowly increasing the voltage across the heating coil by means of a variable transformer. The voltage is then increased abruptly until the cylinder becomes a dull red and the ignition is continued for five minutes. The cylinder, boat and contents are then cooled and weighed together.

Tetrakis-(p-chlorophenyl)-silane. An ethereal solution of p-chlorophenyllithium prepared from 0.27 mole of n-butyl-lithium and 51.7 g. (0.27 mole) of p-chlorobromobenzene was added to 10.4 g. (0.05 mole) of ethyl orthosilicate in 50 ml.

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[117](a) Niederl and Niederl, "Micromethods of Quantitative Organic Analysis", John Wiley and Sons, New York, N. Y., 2nd Ed., 1942, p. 62. (b) Rodden, Mikrochemie, 18, 97 (1935).

of ether. After stirring thirty minutes, the reaction mixture
was poured into a dilute hydrochloric acid-ice mixture and the
ether layer was dried over sodium sulfate. After removing
the ether, the residue was distilled to remove material volatile
below 210° at 26 mm. The residue was crystallized three times
from ethanol-petroleum ether (b.p. 77-120°) to yield 15.5 g.
(65%) of a white crystalline solid, m.p. 181°.

Anal. Calcd. for $C_{24}H_{16}Cl_4Si$: Cl, 29.8; Si, 5.93. Found:
Cl, 29.6; Si, 6.03.

Phenyltriethoxysilane[118]. This compound was prepared by
adding a solution of 0.4 mole of phenyllithium in 269 ml. of
ether to 83.4 g. (0.4 mole) of ethyl orthosilicate in 200 ml.
of ether. Distillation of the product gave 31.0 g. (32.4%)
of liquid boiling at 150° at 33 mm.

Anal. Calcd. for $C_{12}H_{20}O_3Si$: Si, 11.66. Found: Si, 11.48,
11.62.

Phenyl-tris-(p-chlorophenyl)-silane. To 15.0 g. (0.0625
mole) of phenyltriethoxysilane was added a solution of p-chloro-
phenyllithium prepared by adding 0.36 mole of n-butyllithium
in 360 ml. of ether to 68.5 g. (0.357 mole) of p-chlorobromo-
benzene in 100 ml. of ether. After stirring ten minutes,
the product was recovered as described for tris-(p-chlorophenyl)-

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[118] Corning Glass Works, U. S. Patent 2,386,452 (1945);
/C.A., 40, 603 (1946)_7.

ethoxysilane. The solid material remaining was crystallized
three times from ethanol to give 13 g. (47.5%) of white
crystals melting at 134°.

Anal. Calcd. for $C_{24}H_{17}Cl_3Si$: Cl, 24.2; Si, 6.39. Found:
Cl, 24.0; Si, 6.42.

Diphenyl-bis-(p-chlorophenyl)-silane. Diphenyldiethoxy-
silane[119] was prepared by adding 0.543 mole of phenyllithium
in 480 ml. of ether to 56.5 g. (0.271 mole) of ethyl ortho-
silicate in 100 ml. of ether over a one hour period. After
filtration of the ethereal solution, the ether was removed
and the residue was fractionated yielding 29.5 g. of product
boiling at 117-120° at 0.12 mm. To 25 g. (0.092 mole) of
this product was added a solution of p-chlorobromobenzene and
0.30 mole of n-butyllithium. After stirring one hour, the
product was recovered as for tris-(p-chlorophenyl)-ethoxysilane.
Crystallization of the residue from 95% ethanol gave 23 g.
(61.5%) of white solid melting at 131°.

Anal. Calcd. for $C_{24}H_{18}Cl_2Si$: Cl, 17.58; Si, 6.94.
Found: Cl, 17.5; Si, 6.98.

Triphenyl-(p-chlorophenyl)-silane. Triphenylethoxysilane[120]
was prepared by adding 0.3 mole of phenyllithium in 200 ml.

[119]Kipping, J. Chem. Soc., 125, 2728 (1927).

[120]Polis, Ber., 19, 1012 (1886).

of ether to 20.8 g. (0.1 mole) of ethyl orthosilicate. This solution was added to an excess of p-chlorophenyllithium and the product was recovered as for tris-(p-chlorophenyl)-ethoxy-silane. Crystallization of the residue from ethanol gave 20 g. (54%) of white solid melting at 157°.

Anal. Calcd. for $C_{24}H_{18}ClSi$: Cl, 9.57; Si, 7.57. Found: Cl, 9.57; Si, 7.59.

In another preparation, the p-chlorophenyllithium prepared from 0.3 mole of n-butyllithium and 57.3 g. (0.3 mole) of p-chlorobromobenzene in 800 ml. of ether was added rapidly to 55.0 g. (0.2 mole) of triphenylchlorosilane (from the Dow Chemical Co., m.p. 92°). Color Test I[114] was still positive after stirring the mixture for one hour. The product was recovered as above to yield 65.0 g. (87.6%), m.p. 151-153°. Recrystallization from ethyl acetate gave 55 g. (74.1%) of material, m.p. 157-158° which was identical with that obtained above (mixed melting point).

Methyl-tris-(p-chlorophenyl)-silane. To the p-chloro-phenyllithium prepared from 0.30 mole of n-butyllithium and 59 g. (0.31 mole) p-chlorobromobenzene in 330 ml. of ether was added 15.0 g. (0.1 mole) of methyltrichlorosilane[121] in 50 ml. of ether. After stirring for three hours at room temperature the reaction mixture was poured into acidified water

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[121]Anderson Laboratories, Inc., Adrian, Michigan.

and the ether layer was separated and dried over sodium sulfate. The ether was removed and the residue distilled at 200-220° at 0.15 mm. After two crystallizations from methanol, 20 g. (53%) of white crystalline product was recovered, m.p. 86°.

Anal. Calcd. for $C_{19}H_{16}Cl_3Si$: Cl, 28.2; Si, 7.42. Found: Cl, 28.0; Si, 7.43.

(Trichloromethyl)-tris-(p-chlorophenyl)-silane. Ten grams (0.0265 mole) of methyl-tris-(p-chlorophenyl)-silane was placed in a tube equipped with an alundum gas-dispersion inlet tube and a reflux condenser. The exit line led to a trap cooled with a dry ice-acetone mixture. The tube was heated to 170° and irradiated with light from an ultraviolet lamp while chlorine was passed through at a slow rate for three hours. At this time 2.6 g. (0.0732 g. atom) of chlorine had been absorbed. After flushing the system with nitrogen for one minute, the reaction mixture was cooled to room temperature and extracted four times with hot methanol. An insoluble residue was crystallized from petroleum ether (b.p. 79-119°) to yield 2.8 g. (22%) of white crystals, m.p. 161°. A sample of this product was boiled for fifteen minutes in water and in 30% aqueous hydrochloric acid, respectively, without change. However, a small sample was converted to hexakis-(p-chlorophenyl)-disiloxane, m.p. 210° (mixed melting point), by warming for ten minutes with 50% aqueous sodium hydroxide.

Anal. Calcd. for $C_{18}H_{12}Cl_8Si$: Cl, 44.3; Si, 5.84. Found:
Cl, 44.2; Si, 5.68.

Dimethyl-bis-(p-chlorophenyl)-silane. [A]. From
Dimethyldichlorosilane. To a solution of p-chlorophenyllithium
prepared from 0.33 mole of n-butyllithium and 63 g. (0.22 mole)
of p-chlorobromobenzene in 520 ml. of ether was added 19.3 g.
(0.15 mole) of dimethyldichlorosilane[121] in 50 ml. of ether.
After stirring two hours at room temperature, the product
was poured into acidified ice water and the ether layer was
separated and dried over sodium sulfate. Subsequent to remov-
ing the ether, the residue distilled at 135-175° at 0.2 mm.
The distillate solidified on cooling and the solid melted at
47° after two crystallizations from methanol. The yield was
29.9 g. (71%). In another run, 0.27 mole of dimethyldichloro-
silane gave 60 g. (0.216 mole) (80%) of product, b.p. 168° at
0.5 mm., m.p. 47°.

Anal. Calcd. for $C_{14}H_{14}Cl_2Si$: Cl, 25.2; Si, 10.0. Found:
Cl, 25.0; Si, 10.0.

[B]. From Dimethyldiethoxysilane. The dimethyldiethoxy-
silane[122] was prepared by the reaction of 0.165 mole of methyl-
magnesium bromide with 31.2 g. (0.15 mole) of ethyl ortho-
silicate in 352 ml. of ether. Filtration and fractionation of
the product gave a 5.2 g. fraction, b.p. 113-117°. This 5.2 g.

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[122]Corning Glass Works, U. S. Patent 2,380,057 (1945);
[C.A., 40, 88 (1946)].

(0.035 mole) of dimethyldiethoxysilane in 50 ml. of ether was
added to the p-chlorophenyllithium prepared from 0.087 mole
n-butyllithium and 15.3 g. (0.08 mole) of p-chlorobromobenzene
in 310 ml. of ether. The product was recovered as above to
yield 9.9 g. (71%) of product, m.p. 47°. A mixed melting
point with the product from /A_7 showed no depression.

Direct Chlorination of Dimethyl-bis-(p-chlorophenyl)-
silane. Seven grams (0.0249 mole) of dimethyl-bis-(p-chloro-
phenyl)-silane was treated with chlorine under the same con-
ditions as those used for methyl-tris-(p-chlorophenyl)-silane.
During the chlorination, some crystals which sublimed onto
the condenser were identified as p-dichlorobenzene by mixed
melting point. After the reaction mixture plus the trap
contents had gained 2.65 g. in weight (equivalent to 0.0736 g.
atom of chlorine) the mixture was flushed with nitrogen. No
crystals formed on cooling or on extraction with methanol. On
distillation at 50 mm. a white solid sublimed onto the condenser.
This solid melted at 53-54° and was identified as p-dichloro-
benzene by a mixed melting point with an authentic specimen.
The residue became dark on continued heating and no other
product was isolated.

Another five grams (0.0178 mole) of dimethyl-bis-(p-chloro-
phenyl)-silane was dissolved in 20 ml. of carbon tetrachloride
and treated with a rapid stream of chlorine for two hours at
gentle reflux temperature with ultraviolet irradiation. The

carbon tetrachloride was removed on a steam cone leaving a viscous liquid which would not crystallize from methanol solution. An attempt to distill the liquid at 1 mm. resulted in some decomposition taking place above 200°. Two grams of clear distillate was obtained under high vacuum, b.p. 165-170° at 0.00001 mm.; N_D^{20} 1.6062, d_4^{20} 1.349. MR_D calcd.[123] for methyl-(dichloromethyl)-bis-(p-chlorophenyl)-silane: 89.14. Obs., 89.54.

Anal. Calcd. for $C_{14}H_{12}Cl_4Si$: Cl, 40.4. Found: Cl, 39.7. (The calculated chlorine analysis for methyl-(trichloromethyl)-bis-(p-chlorophenyl)-silane is 46.1%.)

Another 10 g. (0.0356 mole) of dimethyl-bis-(p-chlorophenyl)-silane was treated with 0.148 g. atom of chlorine (measured by means of a flowmeter) over a three hour period at 50°, with ultraviolet irradiation. Some crystals of p-dichlorobenzene distilled onto the condenser of the reactor during the chlorination. The product was fractionated through a wire spiral column to yield 1.5 g. of material, b.p. 100° at 0.5 mm., N_D^{20} 1.5663; 6.8 g., b.p. 160-180°, N_D^{20} 1.6010; and 1.4 g., b.p. 180°, N_D^{20} 1.6081. These distillates were slightly yellow and darkened rapidly on standing.

Chlorination of Dimethyl-bis-(p-chlorophenyl)-silane with Sulfuryl Chloride. To 10 g. (0.0356 mole) of dimethyl-bis-(p-chlorophenyl)-silane dissolved in 20 ml. of carbon tetrachloride was added 6.75 g. (0.05 mole) of sulfuryl chloride

[123]Warrick, J. Am. Chem. Soc., 68, 2455 (1946).

and 0.1 g. of benzoyl peroxide. The solution was refluxed
for five hours in a dry atmosphere. The product was fraction-
ated through a wire spiral column to yield 8 g. of light straw-
colored liquid, b.p. 160-170° at 0.2 mm.; N_D^{20} 1.5978.

Anal. Calcd. for $C_{14}H_{18}Cl_3Si$: Cl, 33.5; Calcd. for
$C_{14}H_{12}Cl_4Si$: Cl, 40.4. Found: Cl, 35.6.

The analysis indicates that this product is a mixture
of methyl-(mono- and di-chloromethyl)-bis-(p-chlorophenyl)-
silane.

Another 10 g. (0.0356 mole) of dimethyl-bis-(p-chloro-
phenyl)-silane in 20 ml. of carbon tetrachloride was refluxed
with 20.25 g. (0.15 mole) of sulfuryl chloride and 0.2 g. of
benzoyl peroxide for 16 hours. Fractionation of the product
gave 7.0 g. of liquid, p.p. 170° at 0.1 mm.; N_D^{20} 1.6068.
This refractive index corresponds closely to that of the
methyl-(dichloromethyl)-bis-(p-chlorophenyl)-silane previously
identified.

Methyl-(trichloromethyl)-dichlorosilane[23]. A slow stream
of chlorine gas was bubbled into 26.5 g. (0.205 mole) of
dimethyldichlorosilane contained in the apparatus used for
the chlorination of methyl-tris-(p-chlorophenyl)-silane. The
addition was continued for twenty-two hours at 20°, at which
time the reaction mixture had solidified. Distillation of
the reaction mixture gave 27.5 g. (58%) of white solid which
boiled at 108-109° at 150 mm. Some higher boiling liquid

residue was not investigated further.

An attempt was made to prepare methyl-(trichloromethyl)-bis-(p-chlorophenyl)-silane by treating the above methyl-(trichloromethyl)-dichlorosilane with p-chlorophenyllithium at room temperature. None of the desired product was obtained and p-dichlorobenzene was formed on attempted distillation of the product.

Methyltriphenylsilane[124]. An ethereal solution containing 0.613 mole of phenyllithium was added rapidly to 29.9 g. (0.2 mole) of methyltrichlorosilane, with cooling by an ice bath to keep the temperature at 10°. The mixture was refluxed overnight and hydrolyzed. The ether layer was separated, dried over sodium sulfate, and distilled to yield 52.0 g. (95%) of product boiling at 155° at 0.3 mm., b.p. 67°.

(Trichloromethyl)-triphenylsilane. Forty grams (0.1457 mole) of methyltriphenylsilane was treated with chlorine at 150°, with ultraviolet irradiation, in the apparatus used for the chlorination of methyl-tris-(p-chlorophenyl)-silane. The chlorination was continued until the weight increase was 15.5 g., equivalent to 0.437 g. atom chlorine. On cooling, the mixture solidified. This solid was extracted three times with hot methanol and then crystallized from a benzene-petroleum ether (b.p. 77-115°) mixture to yield 21.2 g. (38.6%) of a white

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[124] Marsden and Kipping, J. Chem. Soc., 93, 198 (1901); Kraus and Eatough, J. Am. Chem. Soc., 55, 5008 (1933).

solid, melting at 192-194°. Two further crystallizations from petroleum ether (b.p. 77-122°) gave white needles melting at 194°.

Anal. Calcd. for $C_{19}H_{16}Cl_6Si$: Cl, 28.2; Si, 7.45. Found: Cl, 28.2; Si, 7.66.

Two later chlorinations of methyltriphenylsilane were carried out in attempts to prepare a larger quantity of (trichloromethyl)-triphenylsilane. In the first reaction, 105 g. of methyltriphenylsilane dissolved in 120 ml. of carbon tetrachloride was treated with chlorine, with ultraviolet irradiation, at reflux temperature for ten hours. The product solidified partially on cooling and the 69 g. of solid melted at 135-165° after extraction with methanol and crystallization from petroleum ether (b.p. 77-115°). No appreciable nuclear chlorination of this material had taken place, since a 1 g. sample, when refluxed with 40% aqueous potassium hydroxide and acetone for ten minutes gave very pure hexaphenyldisiloxane, m.p. 221-222° after washing with water and filtration. A mixed melting point of this product with an authentic sample of hexaphenyldisiloxane showed no depression. In the second reaction, 161 g. of methyltriphenylsilane was treated with chlorine at 150-170° for thirty hours in the absence of any solvent and with ultraviolet irradiation. The golden brown product only partially solidified on cooling and when the reaction mixture was crystallized from petroleum ether (b.p. 77-115°) only 18 g.

of solid material, melting from 175 to 185°, was obtained.
The remaining viscous liquid from this reaction was not
identified further.

The combined solid products from these two larger scale
preparations (87 g.) were fractionally crystallized from
500 ml. of chloroform by distilling off 60 ml. portions of
solvent between each crystallization. The following fractions
were obtained:

Fraction	Weight, g.	Melting Range, °C.
1	11.2	187-193
2	11.1	182-188
3	1.8	173-188
4	8.3	172-182
5	9.7	162-166
6	9.0	140-150
7	6.4	135-150
8	11.9	120-130

Fractions 1 and 2 above were combined and recrystallized
from chloroform to give a product melting at 192-194°, which
analyzed 28.2% chlorine indicating that it is quite pure (tri-
chloromethyl)-triphenylsilane. Fraction 8 analyzed 18.4%
chlorine which is slightly lower than the calculated value
(20.6%) for (dichloromethyl)-triphenylsilane.

62

<u>n-Dodecyl-tris-(p-chlorophenyl)-silane</u>. n-Dodecyltri-

chlorosilane was prepared essentially by the procedure of

Whitmore, et al.[125] by adding dropwise 0.17 mole of laurylmag-

nesium bromide in 185 ml. of ether to 26.5 g. (0.187 mole) of

silicon tetrachloride in 150 ml. of ether. The product was

filtered under nitrogen, the ether was removed, and the residue

was fractionated to yield 27.0 g. (52%) of clear liquid boil-

ing at 145-146° at 7 mm. To 15.2 g. (0.05 mole) of n-dodecyl-

trichlorosilane in 50 ml. of ether was added an excess of

p-chlorophenyllithium prepared from 0.3 mole of n-butyllithium

and 57.3 g. (0.3 mole) of p-chlorobromobenzene. The product

was refluxed four hours, then the ether was removed, chloro-

form was added, and the mixture was poured into a dilute hydro-

chloric acid solution. The chloroform layer was separated,

dried over calcium chloride, and the solvent was removed at

reduced pressure on the steam bath. The residue was distilled

at 0.1 mm. to give a small fore-fraction boiling at 48°. The

remaining residue did not distill up to 240° at 0.1 mm., but

when the dark brown residue was heated in a Hickmann molecular

still for eight hours, 17 g. (64.1%) of a viscous straw-colored

distillate was obtained; d_4^{22} 1.106, N_D^{22} 1.5679. MR_D. obs.:

157.0; calcd.[123]: 155.3.

[125]Whitmore, et al., J. Am. Chem. Soc., 68, 475 (1946).

Anal. Calcd. for $C_{30}H_{37}Cl_3Si$: Si, 5.28. Found: Si, 5.11.

1,3-Dimethyl-1,1,3,3-tetrakis-(p-chlorophenyl)-disiloxane.

This compound was obtained during an attempted preparation of methyl-bis-(p-chlorophenyl)-silanol. (p-Chlorophenyl)-magnesium bromide was prepared in 70% yield by the method of Gruttner and Krause[126] by treating 6.25 g. (0.257 g. atom) of magnesium in 100 ml. of ether with 47.5 g. (0.25 mole) of p-chlorobromobenzene over a ninety minute period followed by refluxing for twenty hours. The solution of 0.175 mole of (p-chlorophenyl)-magnesium bromide in 136 ml. of ether was added slowly to 12.4 g. (0.083 mole) of methyltrichlorosilane in 100 ml. of ether. The resulting solution was refluxed for three days, then the ether was distilled off and the mixture was heated for twenty hours at 60° before a negative Color Test I[114] was obtained. The reaction products were hydrolyzed by stirring for thirty minutes with 50 ml. of acetone and 100 ml. of 1:20 hydrochloric acid. The resulting mixture was evaporated almost to dryness at 100° and 20 mm. The residue was extracted for forty-eight hours in a Soxhlet apparatus with petroleum ether (b.p. 60-70°) and the resulting extract was distilled, after removal of the solvent, to yield 14.2 g. (31%) of straw-colored liquid, b.p. 174-185° at 0.1 mm. This liquid could not be

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[126] Gruttner and Krause, _Ber._, 50, 1559 (1917).

crystallized from methanol or petroleum ether (b.p. 60-70°),
however on standing several months, large crystals formed
which melted at 68-69°. This product gave a negative test
for active hydrogen when treated with methylmagnesium iodide.

Anal. Calcd. for $C_{36}H_{32}OCl_2Si_2$: Cl, 25.8; Si, 10.2.
Found: Cl, 25.6; Si, 9.96.

Triphenyl-(p-aminophenyl)-silane (Attempted). The lithium
salt of p-aminophenyllithium[127] was prepared by slowly adding
an ethereal solution containing 0.00845 mole of n-butyllithium
per milliliter to a solution of 5.16 g. (0.03 mole) of p-bromo-
aniline in 30 ml. of ether. After the addition of 36 ml.
(0.0304 mole) of n-butyllithium, the purple color which had
formed on the addition of the first drop of solution changed
to a light tan. An additional 41 ml. (0.0338 mole) of
n-butyllithium solution was added and the mixture was refluxed
for ninety minutes during which time a gummy precipitate formed
on the sides of the flask. A solution of 3.3 g. (0.0112 mole)
of triphenylchlorosilane in 50 ml. of ether was then added to
the reaction mixture. There was a vigorous reaction, and after
stirring thirty minutes, the product was hydrolyzed in ammonium
chloride solution. No product was isolated from the brown,
tarry mixture which remained after evaporation of the dried
ether layer.

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[127] Gilman and Stuckwisch, J. Am. Chem. Soc., 65, 1461
(1943); Gilman and Gainer, ibid., 69, 877 (1947).

Another preparation was made by adding 0.39 mole of n-butyllithium in 400 ml. of ether to 22.2 g. (0.13 mole) of p-bromoaniline in 100 ml. of ether at -60°. Nine minutes after the completion of the addition of n-butyllithium, a solution of triphenylchlorosilane (prepared by adding 0.40 mole of phenyllithium in 250 ml. of ether to 18.42 g. (0.13 mole) of silicon tetrachloride in 100 ml. of ether) was added dropwise over a ten minute period. The temperature of the reaction mixture was allowed to rise to 25° while stirring over a one hour period. The product was hydrolyzed in a cracked ice sludge containing 75 g. of ammonium chloride and a little ammonium hydroxide and the ether layer was separated and dried over sodium sulfate. Removal of the ether left a brown liquid and a light-colored solid. The latter was shown to be starting p-bromoaniline by mixed melting point. Again no product was isolated from brown oil. A small amount (2 g.) of material which separated from the ether layer contained no nitrogen and was shown to be tetraphenylsilane by mixed melting point with an authentic specimen. This latter product was probably formed during the preparation of the triphenylchlorosilane.

n-Propyltriphenylsilane. n-Propyllithium[111] was prepared by adding 12.3 g. (0.1 mole) of Eastman grade n-propyl bromide (fractionated through a column of 16 theoretical plates, b.p. 69-71° at 742 mm.) in 30 ml. of ether to 2.0 g. (0.286 g. atom)

of lithium in 70 ml. of ether at -10°. The yield was 78% as determined by the double titration method[112]. A solution of 0.06 mole of n-propyllithium in 81 ml. of ether was added rapidly to 14.8 g. (0.05 mole) of triphenylchlorosilane in 150 ml. of ether and the mixture was stirred for twenty hours at room temperature, at which time Color Test I[114] was positive. After hydrolyzing the reaction mixture in dilute hydrochloric acid, the ether layer was separated, dried over sodium sulfate, and distilled leaving 13.4 g. (89%) of product melting from 75° to 85° after one crystallization from methanol. After two additional crystallizations from methanol, the melting point was raised to 84°.

Anal. Calcd. for $C_{21}H_{22}Si$: Si, 9.29. Found: Si, 9.48.

n-Amyltriphenylsilane. n-Amyllithium[111] was prepared by adding a solution of 15.1 g. (0.1 mole) of Eastman grade n-amylbromide in 30 ml. of ether to 2.0 g. (0.286 g. atom) of lithium in 70 ml. of ether at -10° over a thirty minute period. After the addition was complete, the mixture was stirred for an additional two hours at 0° to 10° and filtered through glass wool. The yield was 0.0723 mole or 72.3% as determined by the double-titration method[112]. This 0.0723 mole of n-amyllithium in 118 ml. of ether was added rapidly to 14.8 g. (0.05 mole) of triphenylchlorosilane[121]. After an immediate reaction which caused the ether to reflux, the mixture was stirred for one hour and then hydrolyzed by pouring it onto crushed ice to which

5 ml. of concentrated hydrochloric acid had been added. The ether layer was separated and dried over calcium chloride, and the ether was then removed and the residue heated to 100° at 20 mm. This residue was crystallized twice from ethanol to yield 6.5 g. (39.4%) of white flaky crystals, m.p. 47°.

Anal. Calcd. for $C_{23}H_{26}Si$: Si, 8.49. Found: Si, 8.52.

A preparation identical with the above one was made starting with Eastman grade n-amyl bromide which had been fractionated through a column of sixteen theoretical plates giving a product boiling at 128.0-129.1°, N_D^{20} 1.4444. The yield of n-amyllithium obtained was 81% and the yield of pure n-amyltriphenylsilane, m.p. 47°, was 6.8 g. (41.2%). The melting point of a mixture of this product with that obtained above was 46-47°.

n-Amyltriphenylsilane was also prepared by adding 0.037 mole of n-amyllithium in 60 ml. of ether to 5.9 g. (0.0227 mole) of triphenylsilane[128] (this material, obtained from H. Melvin, melted at 46° after crystallization from ethanol). The solution was stirred for twenty-four hours at room temperature at which time Color Test I[114] was positive. The product was recovered as above yielding 3.2 g. (42.5%) of crystals melting at 44-45°. The mixed melting point of this product and those above was 44-45°.

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[128] Reynolds, Bigelow and Kraus, J. Am. Chem. Soc., 51, 3067 (1929).

n-Hexyltriphenylsilane. n-Hexyllithium[111] was prepared
by adding 16.5 g. (0.1 mole) of redistilled Eastman grade n-
hexyl bromide, b.p. 75-78° at 65 mm., in 30 ml. of ether to
2.0 g. (0.286 g. atom) of lithium in 70 ml. of ether at -10°.
The yield was 77% as determined by the double titration method[112].
A solution of 0.07 mole of n-hexyllithium in 100 ml. of ether
was added rapidly to 14.8 g. (0.05 mole) of triphenylchloro-
silane in 150 ml. of ether. After stirring for twenty-four
hours at room temperature, the product was recovered as
described for n-amyltriphenylsilane. The yield after one
crystallization from ethanol was 17 g. (99%), m.p. 75-76°.
A second crystallization from ethanol-methanol (1:5) raised
the melting point to 78°.

Anal. Calcd. for $C_{24}H_{28}Si$: Si, 8.15. Found: Si, 8.00.

Triphenylbenzylsilane[129]. To the benzylmagnesium chloride
prepared from 50.6 g. (0.4 mole) of benzyl chloride, 9.72 g.
(0.4 g. atom) magnesium and 240 ml. of ether was added 59.0 g.
(0.2 mole) of triphenylchlorosilane in 200 ml. of benzene.
There was no evidence of immediate reaction, so the ether and
most of the benzene were removed by distillation leaving a
viscous paste which was stirred at 180° for four hours. The
cooled residue was extracted with ether and hydrolyzed in
acidified ice water. The ether layer was separated, dried,

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[129]This compound was prepared previously by H. W. Melvin
in these laboratories.

and distilled giving 56.9 g. of distillate, b.p. 197-213° at 0.3 mm. Crystallization from ethyl acetate-methanol (5:1) gave 56.2 g. (80%) of solid, m.p. 97-98°. The mixed melting point of this product and a sample of triphenylbenzylsilane obtained from H. Melvin (m.p. 96-97°) was 96-97°.

Triphenylbenzohydrylsilane. The general procedure of Bebb[130] for metalations with n-butyllithium was used for the preparation of the benzohydryllithium. A solution of 0.158 mole of n-propyllithium in 130 ml. of ether was added to 26.9 g. (0.16 mole) of diphenylmethane and the mixture was stirred at reflux for eight hours. At this time the solution had become red and considerable light-colored precipitate had formed. To this solution of benzohydryllithium was added 29.5 g. (0.1 mole) of triphenylchlorosilane in 150 ml. of dry benzene. After refluxing for one hour, the solution was still red, so an additional 10 g. (0.034 mole) of triphenylchlorosilane was added. Within five minutes the red color had faded to a yellow-orange. The resulting mixture was stirred overnight and then hydrolyzed with an acidified ice-water sludge. Filtration of the ether layer gave 37.5 g. (66% based on total triphenyl-chlorosilane used) of white solid melting at 157-158°. Crystallization from ethyl acetate gave clear crystals melting at 159°.

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[130] Bebb, Doctoral Dissertation, Iowa State College (1938).

Anal. Calcd. for $C_{31}H_{26}Si$: Si, 6.59. Found: Si, 6.60.

Trimethyl-9-fluorenylsilane. This compound was prepared according to the method of Benkeser[57,131] with some variations. To 33.2 g. (0.2 mole) of fluorene in 140 ml. of ether was added 0.21 mole of n-propyllithium[111] in 300 ml. of ether and the mixture was refluxed for two hours, at which time Color Test IIa[132] was negative indicating that no n-propyllithium remained. A solution of 21.6 g. (0.2 mole) of trimethylchlorosilane was then added rapidly. Color Test I[114] was negative in fifteen minutes. The mixture was hydrolyzed and the ether layer was separated, dried over sodium sulfate, and distilled leaving an orange solid melting from 86° to 91°. Two crystallizations from 95% ethanol gave 33.5 g. (70%) of white crystals, m.p. 96-96.5°. A mixed melting point with a sample of trimethyl-9-fluorenylsilane obtained from Benkeser showed no depression.

Triphenyl-9-fluorenylsilane. A solution of 0.127 mole of n-propyllithium[111] in 175 ml. of ether was added rapidly to 16.6 g. (0.1 mole) of fluorene. After the mixture had refluxed for two hours, Color Test IIa[132] was negative and 19.5 g. (0.0662 mole) of triphenylchlorosilane in 100 ml. of benzene was added. After refluxing for sixteen hours, Color Test I[114]

[131] Benkeser, Doctoral Dissertation, Iowa State College (1947).

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

was still faintly positive. The product was hydrolyzed with dilute hydrochloric acid and 13.3 g. of solid, m.p. 181-183°, was filtered from the ether layer. An additional 6.2 g. of material, m.p. 182-184°, was recovered after removing the ether and washing the residue with ethanol. The yield was 19.5 g. (70% based on the triphenylchlorosilane). Crystallization from ethyl acetate gave clear crystals melting at 183-184°.

Anal. Calcd. for $C_{31}H_{24}Si$: Si, 6.61. Found: Si, 6.49.

β-Phenylethyllithium. (The preparation of this organometallic compound is apparently not described in the literature.) A mixture of 2.8 g. (0.4 g. atom) of lithium wire (cut in small pieces) and 30 ml. of ether was stirred at high speed with a Hershberg-type stirrer while a solution of 14.1 g. (0.0762 mole) of Eastman grade β-bromoethylbenzene in 60 ml. of ether was added slowly over a thirty minute period. A crystal of iodine was added to start the reaction and the internal temperature was then kept at 10° to 15° by immersing the flask in an ice-salt bath. The yield, as determined by the double titration method[112], was 86%. A portion of this solution containing 0.0426 mole of β-phenylethyllithium was carbonated by pouring it into a dry ice-ether slurry. The resulting mixture was extracted with ether and water. The water layer was separated, acidified, and extracted with ether. From this latter ether extract there was recovered 3.9 g. (0.026 mole)

(52%) of β-phenylpropionic acid, m.p. 47-48°; amide, m.p.
102-103°. Reported[133]: m.p. 48.5°; amide, m.p. 104°.

Triphenyl-(β-phenylethyl)-silane. A solution of 0.066
mole of β-phenylethyllithium in 72 ml. of ether was added
rapidly to 11.7 g. (0.04 mole) of triphenylchlorosilane in
50 ml. of ether. There was a vigorous reaction and after
refluxing two hours, the mixture was hydrolyzed in an ammonium
chloride solution. Ten grams of solid was filtered from the
ether layer and an additional 3.7 g. was recovered on evaporat-
ing the ether layer and extracting the residue with cold
ethanol. The yield was 13.7 g. (95%) of white solid melting
at 145-146°. Crystallization from ethanol-ethyl acetate (1:1)
gave 13.0 g. clear crystals, m.p. 147°.

Anal. Calcd. for $C_{26}H_{24}Si$: Si, 7.70. Found: Si, 7.69.

Triphenyl-(phenylethynyl)-silane. This compound was
prepared essentially according to the method of Plunkett[134]
from 10 g. (0.1 mole) of phenylacetylene and 0.1 mole of n-
butyllithium. After stirring the mixture for three hours at
room temperature, a solution of 29.5 g. (0.1 mole) of tri-
phenylchlorosilane in 200 ml. of ether was added. The product

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[133]Willgerodt and Merk, J. prakt. Chem., [2] 80, 196
(1909).

[134]Plunkett, Doctoral Dissertation, Iowa State College
(1947).

was stirred overnight and then hydrolyzed in a large excess of ammonium chloride solution. A total of 26 g. (72%) of large clear crystals, m.p. 100-101°, was obtained on successive concentrations of the dried ether layer. The mixed melting point of this material with a sample of triphenyl-(phonyl-ethynyl)-silane obtained from Plunkett was 99-100°.

Triphenyl-1-indenylsilane. A solution of 0.216 mole of n-propyllithium in 225 ml. of ether was added over a ten minute period to 22.8 g. (0.196 mole) of freshly distilled indene in 50 ml. of ether. After refluxing the mixture for fifteen minutes, Color Test IIa[132] was negative. Thirty minutes after the addition was complete, 29.5 g. (0.1 mole) of triphenylchlorosilane was added directly to the cooled solution of 1-indenyllithium[135]. After stirring and refluxing this solution for fifteen minutes, Color Test I[114] was positive. An additional 28.3 g. (0.096 mole) of triphenylchlorosilane was added and the mixture was stirred rapidly for fourteen hours at which time Color Test I was negative. The reaction mixture was hydrolyzed in an acidified ice-water sludge and 12.0 g. of white solid, m.p. 196-199° was filtered from the ether layer. The separated ether layer was dried over calcium chloride and distilled to remove materials volatile below 100° at 2 mm. The residue was extracted with cold methanol leaving

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[135]Schlenk and Bergmann, Ann., 463, 227 (1928).

a light-colored, viscous liquid from which 9.6 g. of white
solid, melting from 115-135° was recovered on crystallization
from ethyl acetate. Recrystallization from ethyl acetate-
methanol (5:1) gave clear crystals, m.p. 136°.

Anal. Calcd. for $C_{27}H_{22}Si$: Si, 7.50. Found: Si, 7.55.

1,1-Bis-(triphenylsilyl)-indene. The 12.0 g. of white
solid, m.p. 196-199°, which was filtered from the ether layer
during the preparation of triphenyl-1-indenylsilane was re-
crystallized twice from ethyl acetate to yield 9.8 g. of white
powdery material, m.p. 206°.

Anal. Calcd. for $C_{45}H_{36}Si_2$: Si, 8.88. Found: Si, 8.97.
As expected for an indene derivative substituted in the
1-position, this compound was cleaved very readily by base
(see Table I) to yield 85% of the expected silanol. The
free indene was not isolated due to its ready polymerization
in the presence of base. For steric reasons, the 1,3-bis-
(triphenylsilyl)-indene is a probable alternative structure
and this compound could undergo ready allylic rearrangement
(involving only a shift of the double bond and a proton) after
the cleavage of the first triphenylsilyl group, so that the
second group would then be in the easily cleavable 1-position.

Triphenyl-(m-trifluoromethylphenyl)-silane. m-Bromo-
benzotrifluoride (115.8 g.) was prepared according to the method
of Simons and Ramler[136] in 56% yield. m-Trifluoromethylphenyl-

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[136]Simons and Ramler, J. Am. Chem. Soc., 65, 389 (1943).

lithium[137] was prepared by adding 0.157 mole of n-butyllithium in 125 ml. of ether to 33.8 g. (0.15 mole) of m-bromobenzotrifluoride over a thirty minute period while the internal temperature of the solution was kept at 0° by means of a dry ice-acetone bath. After stirring thirty minutes more while the solution warmed to 20°, Color Test IIa[132] was negative. At this time 29.5 g. (0.1 mole) of triphenylchlorosilane in 300 ml. of ether was added rapidly. After stirring five hours at 25°, Color Test I[114] was positive. An additional 5 g. (0.034 mole) of triphenylchlorosilane was added and the mixture was stirred an additional twelve hours at 25° at which time Color Test I was negative. The product was hydrolyzed with dilute hydrochloric acid, and the ether layer was separated, dried over calcium chloride, and distilled to remove all material volatile below 100° at 0.04 mm. The viscous residue gave 60.5 g. of light solid melting from 94° to 96° after extraction with hot methanol. Two recrystallizations from methanol gave 39.0 g. (72% based on triphenylchlorosilane) of white crystals melting at 101°. Several attempts to analyze this compound for silicon by the sulfuric acid digestion method[115] gave erratic, low results, probably due to loss of silicon as silicon tetrafluoride.

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[137]Gilman and Woods, J. Am. Chem. Soc., 66, 1981 (1944).

<u>Anal</u>. Calcd. for $C_{28}H_{19}F_3Si$: C, 74.3; H, 4.74. Found: C, 75.8; H, 4.62. On later cleavage by base (see Table I), this compound gave triphenylsilanol and benzotrifluoride, b.p. 100-101°, $N_D^{18.6}$ 1.4155.

<u>Tetra-α-naphthylsilane</u> (Attempted). α-Naphthyllithium[138] was prepared by adding 82.8 g. (0.4 mole) of α-bromonaphthalene in 120 ml. of ether to 5.6 g. (0.8 g. atom) of lithium in 200 ml. of ether over a one hour period. After refluxing the mixture for two hours, the yield was 0.271 mole or 68% as determined by direct acid titration. The solution of α-naphthyllithium in 200 ml. of ether was added dropwise to 6.38 g. (0.045 mole) of silicon tetrachloride in 39.3 ml. of ether. The purple organometallic solution was immediately decolorized by the silicon tetrachloride. Color Test I[114] was negative after the addition of 110 ml. (0.149 mole) of the α-naphthyllithium solution, but positive after 130 ml. (0.176 mole) had been added. After stirring one hour, the reaction mixture was hydrolyzed with water and filtered. The filtrate was evaporated on a water bath to leave a viscous liquid. The residue from the filtration was extracted with benzene and this extract was added to the above viscous liquid and the benzene was removed by distillation. The resulting residue was extracted first with warm ethanol to remove any naphthalene or α-bromonaphthalene

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[138] Gilman, Zoellner and Selby, <u>J</u>. <u>Am</u>. <u>Chem</u>. <u>Soc</u>., <u>55</u>, 1252 (1933).

and the remaining dark red resinous solid was extracted with
hot benzene leaving 1.1 g. of red powder, melting from 250° to
260°. Three recrystallizations of this material from benzene
gave 0.7 g. of yellow crystals, m.p. 277° (uncorr.) which
were later shown to be perylene[139].

The benzene-soluble portion of the product was evaporated
to dryness and extracted with ether to yield 14.8 g. of light
yellow solid which is ether soluble, and 16.2 g. of dark red,
ether-insoluble material. The dark red material, after two
precipitations from benzene-petroleum ether (b.p. 77-115°)
melted with decomposition above 280° and analyzed 5.42%
silicon as determined by the perchloric acid method[140]. (The
calculated percent silicon for tetra-α-naphthylsilane is
5.26.) This work was not continued further, but later work
by C. G. Brannan indicates that the above colored products
contain considerable hydrocarbon material. The silicon-contain-
ing portion, which is extremely difficult to separate, might
contain some of the desired tetra-α-naphthylsilane, but may
also contain α-naphthylsilanols or their condensation products.
Mr. Brannan has not, as yet, been successful in isolating any
tetra-α-naphthylsilane from similar dark residues.

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[139] Gilman and Brannan, J. Am. Chem. Soc., 71, 657 (1949).

[140] Gilman, Clark, Wiley and Diehl, ibid., 68, 2728 (1946).

Reaction of (Trichloromethyl)-triphenylsilane with Three
Equivalents of n-Butyllithium. To a suspension of 10 g.
(0.0264 mole) of (trichloromethyl)-triphenylsilane in 100 ml.
of ether at 25° was added 0.08 mole of n-butyllithium in 90 ml.
of ether. During the addition of the first equivalent of
n-butyllithium, a yellow color, which immediately disappeared,
was formed as each drop was added. During the addition of
the second equivalent, the solution became progressively more
reddish-brown. The vigorous reaction had subsided five minutes
after the addition was complete and the mixture was then re-
fluxed under nitrogen overnight, at which time Color Test I[114]
was still positive. The reaction mixture was hydrolyzed with
dilute sulfuric acid and the ether layer was separated, dried
over sodium sulfate, and the ether was removed. The residue
was a viscous oil which was distilled giving 13.5 g. of straw-
colored distillate, b.p. 195-200° at 0.25 mm., and 1.3 g. amber
liquid, b.p. 235-240° at 0.2 mm. The former fraction partially
solidified on standing to give crystals melting from 68-76°.
Recrystallization of this material from petroleum ether (b.p.
60-70°) gave 1.3 g. of solid melting at 86°. The mixed melt-
ing point of this solid with a sample of n-butyltriphenylsilane
obtained from H. Melvin[141] showed no depression.

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

Reaction of (Trichloromethyl)-triphenylsilane with Three Equivalents of Phenyllithium. A solution of 0.05 mole of phenyllithium in 80 ml. of ether was added slowly, with stirring at 0°, to a suspension of 6.2 g. (0.0164 mole) of (trichloromethyl)-triphenylsilane in 100 ml. of ether. After standing overnight under nitrogen, the resulting solution gave a negative Color Test I[114]. The solution was then hydrolyzed with water and the ether layer was separated (along with a little insoluble material) and distilled on a water bath. The residue was heated at 100° and 20 mm. pressure and was then extracted with petroleum ether (b.p. 79-122°). The 0.3 g. of residue from this extraction melted at 232-234° and its mixed melting point with tetraphenylsilane showed no depression. The petroleum ether extract was a brown viscous material from which no definite product was isolated.

Trimethyl-(triphenylmethyl)-silane. [A] From Triphenylmethylsodium[142]. A mixture of 31.6 g. (0.114 mole) of triphenylchlorosilane *methane*, 300 ml. of ether, and sodium amalgam made from 187 g. of mercury and 5.8 g. of sodium was shaken for eighteen hours. The yield of triphenylmethylsodium, as determined by titration of a portion of the clear red solution obtained by decantation, was 0.0723 mole (63%). To 7.6 g. (0.070 mole) of trimethylchlorosilane in 100 ml. of ether at room temperature was added 0.0695 mole of triphenylmethylsodium in 350 ml. of

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[142] Blatt, *Org. Syn.*, *Coll. Vol. II*, 609 (1943).

ether. The blood-red color of the triphenylmethylsodium solution changed to yellow ten minutes after addition was complete. After thirty minutes additional stirring, the reaction mixture was hydrolyzed with an aqueous ammonium chloride solution and the ether layer was separated and dried over calcium chloride. Removal of the ether left 25.2 g. of yellow solid which was extracted with 70 ml. of ethanol leaving 5.5 g. of white solid, m.p. 161-164°. Two crystallizations from ethanol-ethyl acetate (1:2) gave 3.0 g. (13.6%) of pure white solid, m.p. 172-173°.

Anal. Calcd. for $C_{22}H_{24}Si$: Si, 8.87. Found: Si, 8.75.

[B]. **From Triphenylmethyllithium.** Triphenylmethyl-lithium[143] was prepared by the metalation of triphenylmethane. Ten grams (0.041 mole) of triphenylmethane in 100 ml. of ether, stirred for three hours at room temperature with 0.038 mole of phenyllithium, gave only 0.5 g. (0.0017 mole) (4.2%) of triphenylacetic acid after carbonation. Another 10 g. of triphenylmethane, refluxed for five hours with 0.038 mole of n-propyllithium in 95 ml. of ether, gave 1.2 g. (22%) of triphenylacetic acid after carbonation. A higher yield of triphenylmethyllithium was obtained by refluxing 29 g. (0.118 mole) of triphenylmethane with 0.14 mole of n-propyllithium in 250 ml. of ether for forty-eight hours. A red precipitate

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[143] Gilman and Young, *J. Org. Chem.*, **1**, 315 (1936).

was partially dissolved by adding 100 ml. of benzene. Carbon-
ation of a 10 ml. aliquot gave 0.8 g. of triphenylacetic acid
for a calculated yield of 70%. No trace of butyric acid was
evident by odor in the carbonation product, indicating that
no n-propyllithium remained. The yield, as determined by
the double titration method[112] was 70%. A later preparation
of triphenylmethyllithium under the same conditions, but
using a 1.5 to 1 mole ratio of n-propyllithium to triphenyl-
methane, gave a 93% yield (based on the triphenylmethane),
as determined by the double titration method. No yield of
triphenylmethyllithium is reported by Gilman and Young[143] or
by Grosse[144], who prepared the compound by the action of lithium
amalgam on triphenylmethyl chloride.

A solution of 0.037 mole of triphenylmethyllithium in
140 ml. of ether-benzene was added to 4.7 g. (0.043 mole) of
trimethylchlorosilane in 10 ml. of ether. After stirring the
mixture at reflux temperature for two hours, the color of the
solution had changed to a light orange. This color did not
change during eighteen hours additional stirring. The result-
ing mixture was filtered under nitrogen through a sintered
glass filter stick and the filtrate was evaporated to dryness.
Extraction of the residue with 150 ml. of ethanol left 6.7 g.
of white solid melting from 90° to 155°. Successive crystal-

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[144] Grosse, Ber., 59, 2646 (1946).

lizations from methanol, petroleum ether (b.p. 60-70°), and ethyl acetate raised the melting point to 172°. A mixture of this material and that obtained from triphenylmethyl-sodium melted at 172-173°.

_[c]_. From **Triphenylmethylmagnesium Chloride**. Triphenyl-methylmagnesium chloride was prepared in 97% yield by the method of Gilman and Zoellner[145]. A solution of 0.0485 mole of this triphenylmethylmagnesium chloride in 200 ml. of ether and 200 ml. of benzene was added to 5.0 g. (0.046 mole) of trimethylchlorosilane and the mixture was refluxed for twenty-four hours. The resulting reaction mixture was hydrolyzed with dilute hydrochloric acid, the ether-benzene layer was separated and dried over sodium sulfate, and the solvent was removed. Crystallization of the residue from acetic acid gave 2.0 g. (13.8%) of product melting at 172-173° which was shown by mixed melting point to be identical with the product obtained in Part _[A]_.

In order to determine whether an acidic triphenylmethane hydrogen remained in the above product (m.p. 173°), a 0.5 g. sample was treated with excess n-propyllithium in dry ether for two days. No red or yellow color of a substituted tri-phenylmethyl carbanion formed. No such reaction is expected of trimethyl-(triphenylmethyl)-silane, but it would be expected if the trimethylsilyl group were substituted on one of the phenyl groups of triphenylmethane.

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[145]Gilman and Zoellner, J. Am. Chem. Soc., 51, 3493 (1929).

<u>Cleavage</u> <u>of</u> <u>Trimethyl-(triphenylmethyl)-silane</u> <u>with</u>
<u>Hydrochloric</u> <u>Acid</u> (Attempted). According to the procedure of
Marshall[2], 1.0 g. of trimethyl-(triphenylmethyl)-silane was
refluxed with 20 ml. of glacial acetic acid for twenty hours
while dry hydrogen chloride was passed in at a slow rate. As
the reaction mixture cooled to room temperature, 0.9 g. of
white crystalline solid precipitated, which melted at 173°.
This product was identical (mixed melting point) with the
starting material.

<u>Cleavage</u> <u>of</u> <u>Trimethyl-(triphenylmethyl)-silane</u> <u>with</u>
<u>Aqueous</u> <u>Potassium</u> <u>Hydroxide</u> <u>in</u> <u>Acetone</u>. A 0.5 g. sample of
trimethyl-(triphenylmethyl)-silane was refluxed for twenty
hours with 10 ml. of acetone and 10 ml. of 40% aqueous potassium
hydroxide. The reaction mixture was poured into water, acid-
ified, and filtered to yield 0.36 g. (95%) of triphenylmethane
(m.p. 92-93°), confirmed by a mixed melting point with an
authentic specimen.

<u>Triphenyl-(triphenylmethyl)-silane</u> (Attempted). To 13 g.
(0.044 mole) of triphenylchlorosilane freshly crystallized
from petroleum ether (b.p. 60-70°) in a 500 ml. three-necked
flask equipped with a vapor-sealed Hershberg stirrer, a reflux
condenser connected to a source of dry, oxygen-free nitrogen,
and a dropping funnel, was added 0.037 mole of triphenylmethyl-
lithium dissolved in 100 ml. of benzene and 100 ml. of ether.
After stirring and refluxing the mixture for eighteen hours,

the deep red color of the triphenylmethyllithium solution had
not changed. At this time the ether and most of the benzene
were allowed to distill off leaving a thick red paste which
was stirred for an additional twenty-two hours at 125°. At
the end of this period, the paste was a light cream color.
Most of the remaining benzene was distilled off and the residue
was treated with 200 ml. of ether followed by an excess of
aqueous ammonium chloride. Filtration of this mixture gave
13.0 g. of white solid which melted from 270° to 340°.
Extraction of this solid with benzene-ethanol (5:1) left 5.4 g.
of solid, melting from 315° to 320°, which was purified further
by one crystallization from benzene and two crystallizations
from pyridine to give a white solid which melted to a red
liquid at 335°. This compound was analyzed for silicon and
its molecular weight was determined cryoscopically in p-di-
chlorobenzene.

Anal. Found: Si, 7.39; Mol. Wt., 790,720.

These analytical results correspond within experimental
error to bis-(triphenylsilyl)-triphenylmethane: mol. wt., 760;
Si, 7.38. However, the bis-(p-triphenylsilylphenyl)-phenyl-
methane prepared by another method, as described later, melts
at 315°, does not give a red liquid on melting, and its mixed
melting point with the above compound is 305°.

The portion of the above ether-insoluble residue which
had dissolved in the benzene-ethanol mixture was extracted

with ethyl acetate, leaving 1.4 g. of material melting
between 270° and 315°. The extract was concentrated and
crystallized to give 1.8 g. of solid melting from 200° to
210°. Recrystallization from ethyl acetate and acetone gave
a product melting from 210° to 215°.

Anal. Calcd. for $C_{37}H_{30}Si$ (triphenyl-triphenylmethyl)-
silane: Si, 5.60. Found: Si, 5.54. (The structure of this
compound, however, has not been established.)

A 0.251 g. (0.0005 mole) sample of this compound (m.p.
210-215°) was treated with 5 ml. of reagent D (see Table I),
for twelve hours at 94°. After pouring the reaction mixture
into dilute hydrochloric acid and filtering, 0.225 g. (90%)
of starting material (mixed melting point) was recovered.
Although the triphenylmethyl group would ordinarily be ex-
pected to be cleaved fairly readily from silicon by base,
it is possible that steric hinderance in tripheny-(triphenyl-
methyl)-silane would inhibit a back-side attack of the
hydroxyl ion on the silicon.

Some additional tan solid melting from 205° to 215°
was recovered on concentrating the original ether solution.
Recrystallization of this material from acetone did not
improve the melting point. Attempted crystallization of this
material from nitrobenzene gave small portions of solid melting
above 300°. The tan solid above was analyzed and found to
contain 6.31% silicon.

A second reaction was carried out by adding a solution of 0.06 mole of triphenylmethyllithium in 200 ml. of benzene and 55 ml. of ether to 20.0 g. (0.068 mole) of triphenyl-chlorosilane. After 200 ml. of the organolithium solution had been added, the mixture was refluxed until the red color had changed to a light cream (six hours), then the last 55 ml. of solution was added and the mixture was refluxed under nitrogen for four days. The product was recovered without hydrolysis by distilling off the benzene and extracting the residue with 300 ml. of dry ether to leave 22.1 g. of residue. This residue was extracted with 800 ml. of hot benzene and filtered, leaving 9.0 g. of insoluble residue containing inorganic material. The benzene was distilled from the filtrate and the still residue was extracted with acetone in a Soxhlet apparatus for six hours leaving 5.0 g. of white solid melting at 330-333° to a red liquid. The acetone extract, on cooling, deposited 5.3 g. of white solid melting from 310° to 320°, and further concentration of the solution yielded an additional 0.8 g. of yellow solid melting from 180° to 230°. Concentration of the original ether extract gave 5.0 g. of tan solid melting from 199° to 213°. Extraction of this solid with acetone yielded material melting from 209° to 214°, identical (mixed melting point) with the product obtained from the ether extract of the first preparation.

A third preparation was carried out as above except
that the reaction was stopped after refluxing twenty-four
hours in benzene. The benzene was removed at reduced pressure
and the residue was hydrolyzed, extracted with ether, and
filtered. The ether-soluble portion was a tan solid melting
from 205° to 215°.

Tri-p-tolylcarbinol[146,147]. The method of preparation
used was essentially that of Copenhaver, Roy and Marvel
except that an organolithium rather than a Grignard reagent
was employed. A solution of 85.5 g. (0.5 mole) of p-bromo-
toluene in 250 ml. of ether was added rapidly with cooling
to 7.1 g. (1.2 g. atom) lithium in 125 ml. of ether over
a one hour period. After decanting the reaction mixture
through glass wool, the yield of p-tolyllithium, as deter-
mined by acid titration, was 94.5%. To this solution was
added slowly 17.7 g. (0.150 mole) of ethyl orthocarbonate in
100 ml. of ether. Color Test I[114] was positive until the
last 5 ml. of solution had been added. The product was poured
into acidified ice-water and the ether layer was separated and
dried over sodium sulfate. Removal of the ether and crystal-
lization of the residue from petroleum ether (b.p. 60-70°)
yielded 35 g. (78%) of white solid melting at 94.5-95°.

146Kovache, Ann. chim., [9] 10, 199 (1918).

147Copenhaver, Roy and Marvel, J. Am. Chem. Soc., 57,
1311 (1935).

<u>Tri-p-tolylmethane</u>. Twenty-six grams of tri-p-tolyl-carbinol was refluxed overnight with 450 ml. of 98% formic acid. During this period, the initial deep yellow color of the solution had disappeared leaving a colorless upper layer. The reaction mixture was extracted with ether and the ether solution was extracted with water and dilute base. After drying the ether layer over sodium sulfate, the ether was removed and the residue was distilled, yielding 20 g. (78%) of clear viscous liquid, b.p. 189-190° at 0.05 mm. On standing four days, a portion of this liquid solidified, giving white crystals melting at 67° (the reported melting point is 63°[146]).

<u>Tri-p-tolylmethyllithium</u> $\sqrt{}$(p-CH$_3$C$_6$H$_4$)$_3$CLi$\underline{7}$. A solution of 0.06 mole of n-propyllithium in 100 ml. of ether was added rapidly to a solution of 11.4 g. (0.04 mole) of tri-p-tolyl-methane in 100 ml. of ether. The mixture was refluxed for two days during which time the solution became deep red and a red precipitate formed. The red precipitate was partially dissolved by the addition of 200 ml. of dry benzene and the resulting suspension was titrated by the double titration method. The yield of tri-p-tolylmethyllithium determined in this way was 0.028 mole (70%).

<u>Triphenyl-(tri-p-tolylmethyl)-silane</u> (Attempted). To the above solution of 0.028 mole of tri-p-tolylmethyllithium was added 8.9 g. (0.03 mole) of triphenylchlorosilane in 100 ml.

of benzene. The ether was removed by distillation and the remaining mixture was heated at 120° to 140°, with stirring, for twenty-four hours. After hydrolyzing with aqueous ammonium chloride and ice, the mixture was extracted with ether to give a clear solution. Removal of the ether and other components volatile below 100° at 20 mm. left a light brown residue which was crystallized from petroleum ether (b.p. 60-70°) to give 4.3 g. of triphenylsilanol, m.p. 150°. The remaining liquid was distilled giving 10 g. (0.035 mole) (87%) of tri-p-tolylmethane, b.p. 187° at 0.04 mm., m.p. 65°. Only a gummy, resinous residue remained in the distillation flask.

A second similar reaction was carried out in which the reactants were stirred for three days as a slurry in dry toluene. Again no ether-insoluble material was obtained and only triphenylsilanol and tri-p-tolylmethane were isolated.

Bis-(p-bromophenyl)-phenylcarbinol[148]. The p-bromophenyl-lithium prepared from 118 g. (0.5 mole) of p-dibromobenzene and 0.5 mole of n-butyllithium in 1400 ml. of ether was stirred at 0° until Color Test IIa[132] was negative, then 67.5 g. (0.45 mole) of ethyl benzoate in 100 ml. of ether was added dropwise. There was an immediate reaction, causing the ether to reflux, and Color Test I[114] became negative after the addition was

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[148] Gomberg and Cone, Ber., 39, 3274 (1906); Stagner, J. Am. Chem. Soc., 38, 2069 (1916).

just complete. The product was hydrolyzed in acidified ice-water and the ether layer was separated and distilled to remove all materials volatile below 100° at 1 mm. The residue was an oil which did not crystallize on standing. This oil was dissolved in petroleum ether (b.p. 60-70°) and the solution was allowed to stand at room temperature for several days. An oil separated on cooling, but crystals formed in the upper layer, and these were removed from time to time to give a total of 72.5 g. (39%) of white solid, m.p. 123-124° after recrystallization from benzene-petroleum ether (b.p. 60-70°).

Gomberg and Cone, and Stagner report 110° and 113.5°, respectively, for the melting point of this compound when prepared from p,p'-dibromobenzophenone and phenylmagnesium bromide (no yield was reported). The analyses obtained on the above compound, as given below, tend to substantiate its composition, as does the fact that it was reduced to the known bis-(p-bromophenyl)-phenylmethane, m.p. 100°, as described below, and this latter melting point agrees with that reported by Goldthwaite[149] for this compound.

Anal. Calcd. for $C_{19}H_{14}OBr_2$: Br, 38.2; Zerewitinoff H, 1.00. Found: Br, 38.7; Zerewitinoff H, 1.01.

Bis-(p-bromophenyl)-phenylmethane. A sample of 32.0 g. (0.0765 mole) of the above bis-(p-bromophenyl)-phenylcarbinol

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[149]Goldthwaite, Am. Chem. J., 30, 463 (1903).

was refluxed overnight with 550 ml. of 98% formic acid.

The initial red-yellow color of the solution had changed
to a very pale yellow and an oil had collected on the bottom
of the flask at the end of this time. The reaction mixture
was extracted first with water and then with ether and the
ether layer was washed three times with water, dried, and
distilled. The remaining residue was distilled to give 27.7 g.
(90%) of pale yellow liquid, b.p. 205° to 207° at 0.6 mm.,
which solidified on cooling to give white crystals melting
sharply at 100°. This melting point is identical with that
reported for this compound by Goldthwaite[149] who prepared it
by treating p,p' -dibromobenzohydrol with benzene and concen-
trated sulfuric acid.

Bis-/p-(triphenylsilyl)-phenyl_7-phenylcarbinol. A
solution of 0.086 mole of n-butyllithium in 95 ml. of ether
was added rapidly at 0° to 12.0 g. (0.0287 mole) of bis-
(p-bromophenyl)-phenylcarbinol in 150 ml. of ether. After
the mixture had been refluxed for three hours, a heavy white
precipitate had formed and Color Test IIa[132] was only barely
positive. At this point, a solution of 16.9 g. (0.0574 mole)
of triphenylchlorosilane in 100 ml. of dry benzene was added
rapidly and the mixture was refluxed overnight. Color Test I[114]
was negative at the end of this time. The mixture was hydro-
lyzed in dilute hydrochloric acid and filtered, leaving 14.6 g.
(66%) of white, ether-insoluble residue which melted from
270° to 280°. Two crystallizations from pyridine raised the
melting point to 290°.

<u>Anal</u>. Calcd. for $C_{55}H_{44}OSi_2$: Si, 7.22; Zerewitinoff
H, 1.00. Found: Si, 6.90; Zerewitinoff H, 0.94.

<u>Bis-/p-(triphenylsilyl)-phenyl/-phenylmethane</u>. Dry
hydrogen chloride gas was passed through a solution of 4.7 g.
(0.0061 mole) of bis-/p-(triphenylsilyl)-phenyl/-phenyl-
carbinol in 80 ml. of dry benzene for four hours. The result-
ing suspension was then treated slowly with an excess of 2 N
lithium aluminum hydride in ether. After refluxing this
mixture for a few minutes, it was hydrolyzed with dilute
hydrochloric acid and the resulting material was diluted with
100 ml. of ether and filtered to leave 3.3 g. (71%) of
product which melted at 315° after one crystallization from
pyridine.

<u>Anal</u>. Calcd. for $C_{55}H_{44}Si_2$: Si, 7.38; Mol. Wt., 761.0.
Found: Si, 7.62; Mol. Wt., 767, 700. (These molecular weights
were determined cryoscopically in p-dichlorobenzene, in which
solvent this compound was only sparingly soluble.

Basic Cleavage Reactions

The cleavage reactions of the silanes were carried out
with potassium hydroxide in the five solvents described in
Table I. The typical procedure used in each case is described
below and the data obtained are given in Table I.

Reagent (A). Cleavage of Trimethylphenylsilane
(Attempted). In a 100 ml. flask fitted with a reflux condenser
and a vapor trap cooled by a dry ice-acetone mixture was placed
5.0 g. (0.0333 mole) of trimethylphenylsilane[131], 10 ml. of
acetone, and 10 ml. of 50% aqueous potassium hydroxide. After
refluxing for 20 hours, the mixture was cooled, poured onto
cracked ice containing 3 ml. of concentrated hydrochloric
acid, and extracted with ether. The ether layer was dried over
sodium sulfate and carefully fractionated through a column of
fifteen theoretical plates. No benzene was isolated and 4.5 g.
(90%) of the starting material, b.p. 166-169°, was recovered.

Reagent (B). Cleavage of Triphenylbenzylsilane. To
10.0 g. (0.0286 mole) of triphenylbenzylsilane was added
25 ml. of acetone and 10 ml. of 20% aqueous potassium hydroxide.
The mixture was refluxed for sixteen and one-half hours with
the exit line connected to a trap immersed in a dry ice-
acetone mixture. No liquid collected in the trap, but
considerable acetone-insoluble white solid precipitated both
during the reaction and upon cooling the reaction mixture.
The product was filtered through a sintered glass funnel and
the residue was washed successively with methanol, water, and
methanol, leaving 3.7 g. of solid, m.p. 222°, which was shown
to be hexaphenyldisiloxane by mixed melting point. The filtrate
was treated with 200 ml. of dilute hydrochloric acid (1:20)
and filtered to leave a solid melting from 80-87°. In order

Table I

Cleavages of Silanes by Potassium Hydroxide

Silane			Cleavage Conditions				Recovered Material mole %	
Compound	g.	mole	Time, hrs.	Temp., °C.	Agent[a]			
					Type	Vol. ml.	Starting Silane	Products
Trimethylphenyl-silane	5.0	0.0333	20	(reflux)	A (1:1)	20	90	0
Triphenylbenzyl-silane	10.0	0.286	16.5	(reflux)	B (2.5-1)	35	25	b
Triphenylbenzyl-silane	3.50	0.01	44	70	C	20	71	-
Triphenylbenzyl-silane	1.40	0.004	16	70	C	20	69.6	-
Triphenylbenzyl-silane	1.40	0.004	1	60	D	20	76	-
Trimethyl-9-fluorenylsilane	10.0	0.42	14	(reflux)	B (2.5:1)	35	0	100 fluorene
Triphenyl-9-fluorenylsilane	1.0	0.00236	1	(reflux)	B (3-1)	4	10%	64 $[(C_6H_5)_3Si]_2O$
Trimethyl-9-fluorenylsilane	1.05	0.005	0.167	25	D		25	trace	88 fluorene

Table I - continued:

Silane			Cleavage Conditions				Recovered Material mole %	
Compound	g.	mole	Time, hrs.	Temp., °C.	Agent[a] Type	Vol. ml.	Starting Silane	Products
Triphenyl-9-fluorenylsilane	5.0	0.0118	16	(reflux)	B (1.2:1)	22	0	100 fluorene, 80 $\diagdown\!\!\!\![(C_6H_5)_3Si]_2O$
Triphenyl-9-fluorenylsilane	0.424	0.001	0.167	25	D	5	21.2	-
1,4-Bis-(trimethylsilyl)-benzene	1.0	0.0045	16	(reflux)	B (1:1)	10	100	0
n-Hexyltriphenyl-silane	2.0	0.0055	16	(reflux)	B (1:1)	20	100	0
Triphenyl-(2-phenylethyl)-silane	4.0	0.011	16	(reflux)	B (2:1)	15	100	0
Triphenyl-(2-phenylethyl)-silane	0.364	0.001	4	60	D	5	86	0
Triphenyl-(2-phenylethyl)-silane	0.364	0.001	2	85	D	5	85	0
Triphenyl-(2-phenylethyl)-silane	0.364	0.001	23	85	D	5	91	0
p-(Trimethylsilyl)-benzoic acid[c]	0.5	0.0026	16	(reflux)	B (1:1)	10	90	0
Phenyltrichloro-silane	13.55	0.0643	24	(reflux)	B	40	-	No C_6H_6

Table I - continued:

Silane			Cleavage Conditions				Recovered Material mole %	
Compound	g.	mole	Time, hrs.	Temp., °C.	Agent[a]			
					Type	Vol. ml.	Starting Silane	Products
Triphenyl-benzohydryl-silane	1.71	0.004	16	70	C	20	20.5	42 $[(C_6H_5)_3Si]_2O$
Triphenyl-benzohydryl-silane	1.71	0.004	1	70	D	20	0	-
Triphenyl-benzohydryl-silane	0.428	0.001	0.5	40	D	5	78.5	-
Triphenyl-benzohydryl-silane	0.428	0.001	0.5	60	D	5	9.3	-
Triphenyl-(phenylethynyl)-silane	1.44	0.004	0.5	70	C	20	0	d
Triphenyl-(phenylethynyl)-silane	0.360	0.001	0.167	25	D	5	0	-
Triphenyl-(m-trifluoromethyl-phenyl)-silane	0.405	0.001	21	60	D	5	65	-

Table I - continued:

Silane			Cleavage Conditions				Recovered Material mole %	
Compound	g.	mole	Time, hrs.	Temp., °C.	Agent[a]			
					Type	Vol. ml.	Starting Silane	Products
Triphenyl-(m-tri-fluoromethyl-phenyl)-silane	1.62	0.004	24	85	D	20	0	e
Triphenyl-(m-tri-fluoromethyl-phenyl)-silane	4.05	0.01	5	60	D	50	85	10.2 $(C_6H_5)_3SiOH$
Triphenyl-(p-anisyl)-silane	0.366	0.001	24	60	D	5	97	0
Triphenyl-(p-chlorophenyl)-silane	3.71	0.01	24	85	D	50	26.4	f
Triphenyl-1-naphthyl-silane	0.386	0.001	5	60	D	5	97	0
Triphenyl-1-naphthyl-silane	0.386	0.001	24	85	D	5	85	g
Triphenyl-1-indenyl-silane	0.374	0.001	0.167	25	D	5	0	83 $(C_6H_5)_3SiOH$

Table I - continued:

Silane			Cleavage Conditions				Recovered Material mole %	
Compound	g.	mole	Time, hrs.	Temp., °C.	Agent[a]			
					Type	Vol. ml.	Starting Silane	Products
1,1-Bis-(triphenyl-silyl)-indene	0.316	0.0005	0.167	25	D	5	0	85 $(C_6H_5)_3SiOH$
Triphenyl-(trichloromethyl)-silane	0.378	0.001	0.167	25	D	5	0	87 $(C_6H_5)_3SiOH$
Hexaphenyldi-siloxane	0.534	0.001	0.167	25	D	5	93	-
Hexaphenyldi-siloxane	0.534	0.001	1	60	D	5	47	-
Hexaphenyldi-siloxane	0.534	0.001	5	60	D	5	trace	95 $(C_6H_5)_3SiOH$
Triphenylsilane	0.039	0.00015	10 (sec.)	25	D	0.75	0	h

a. The agents employed had the following compositions: (A) - Acetone-50% aqueous KOH (the ratio is given in parentheses). (B) - Acetone-20% aqueous KOH (the ratio is given in parentheses). (C) - Dioxane-ethanol (4:1) which was 0.101 molar in KOH and 1.12 molar in H_2O. (D) - Dioxane-ethanol (1:1) which was 0.73 molar in KOH and 1.90 molar H_2O.

b. A few drops of toluene were isolated and identified by conversion to 2,4-dinitro-toluene, m.p. 70°.

c. Prepared by M. W. Bullock.

d. About 0.1 ml. of liquid, b.p. 140-142°, was isolated by distillation which had the odor of phenylacetylene.

e. Fractionation of the ether extract after hydrolysis of the reaction mixture gave 0.4 g. liquid, b.p. 100-102°, $N_D^{18.6}$ 1.4155; the reported[150] values for benzo-trifluoride are: b.p. 103°, $N_D^{18.6}$ 1.4154. The yields of products were 48% triphenylsilanol and 51% benzotrifluoride.

f. A few drops of chlorobenzene were recovered from this reaction mixture. This material was identified by odor and refractive index.

g. An ethanol extract of this product was purified by sublimation and shown to be naphthalene by a mixed melting point with an authentic specimen.

h. This reaction was run in an active hydrogen apparatus. The theoretical volume of hydrogen was evolved in ten seconds.

[150] Cotton and Mouton, Ann. chim. et phys., /8_7 28, (1913).

to separate the starting material and triphenylsilanol, this solid was refluxed for thirty minutes with formic acid[116] and the resulting mixture was diluted with excess water and filtered. The residue was extracted with three small portions of acetone leaving 1.5 g. of additional hexaphenyldisiloxane, m.p. 220-223°. The acetone extract was evaporated to dryness leaving a solid melting from 90-95° which gave 2.5 g. of starting material, m.p. 96-97° (mixed melting point) after crystallization from ethyl acetate.

The residue obtained after hydrolysis of the original reaction mixture was warmed in a micro-still to yield about 1 ml. of toluene which was identified by conversion to 2,4-dinitrotoluene, m.p. 70°.

Reagent (C). The procedure using this reagent was identical with that described for reagent (D) below. The reagent was prepared by adding 3.6 ml. of water and 1.12 g. of potassium hydroxide to 50 ml. of anhydrous ethanol and 200 ml. of dioxane which had been purified by refluxing over sodium for fifteen hours followed by fractionation. Aliquots of this solution were titrated for base with standard acid and for water plus base with the Fischer reagent[151]. The concentration of the water was then obtained by difference.

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151 Fischer, Angew. Chem., 48, 394 (1935); Mitchell and Smith, "Aquametry", Interscience Publishers, Inc., New York, N. Y., 1948.

Reagent (D). Cleavage of Triphenylbenzylsilane. This
reagent was prepared from 200 ml. of purified dioxane and
200 ml. of anhydrous ethanol (purified by refluxing over
potassium hydroxide and distilling) to which 10 ml. of water
and 20 g. of potassium hydroxide was added. This reagent was
titrated with acid and the Fischer reagent as was reagent (C).

To 1.40 g. (0.004 mole) of triphenylbenzylsilane contained
in a 50 ml. glass-stoppered volumetric flask was added 20 ml.
of reagent (D). The flask was placed, with occasional shaking,
in a constant temperature bath at $60\pm0.5°$ for one hour. The
reaction mixture was then poured immediately into an excess
of cold dilute hydrochloric acid (1:50) and the resulting
mixture was filtered. The residue was washed with 35 ml. of
90% aqueous methanol to leave 1.065 g. (76%) of starting
silane, m.p. 96-97°. No hexaphenyldisiloxane is formed in
the cleavages with this reagent, and it was found that tri-
phenylsilanol was soluble to the extent of 2.5 g. per 100 ml.
of 90% aqueous methanol while this solvent dissolved only
traces of the starting silanes. The above procedure was there-
fore used to determine the amount of starting material remain-
ing and therefore the extent of cleavage in reactions using
reagent (D).

Silanol Titrations with the Fischer Reagent

Preparation of the Fischer Reagent[151]. Two liters of
this reagent was made up from 538 ml. of Eastman pyridine
(which had been dried over potassium hydroxide and redistilled),
1334 ml. of methanol (dried over anhydrous calcium sulfate),
169.4 g. of redistilled iodine, and 128 g. of sulfur dioxide
which was bubbled into the ice-cold solution of the other
ingredients. A standard solution of water in methanol was
prepared which contained 0.001063 mole of water per ml. The
Fischer reagent was allowed to stand two days in the storage
bottle of a 10 ml. automatic burette and was then standardized
against the water-in-methanol solution delivered from a 5 ml.
microburette. This standardization was repeated each day the
solution was used.

Silanol Titrations. Five milliliters of pyridine or
methanol was pipetted into a dry 50 ml. glass-stoppered
volumetric flask and this solvent was titrated to the iodine
endpoint with Fischer reagent from a 10 ml. automatic burette.
The weighed sample of silanol was then added quickly. (Liquid
samples were weighed in a platinum boat). After washing down
the neck with a little Fischer reagent, the flask was stoppered
and shaken a few seconds to complete solution. This solution
was then titrated to the same iodine endpoint as that obtained
with the solvent. The apparent millimoles of water found
was calculated from the amount of Fischer reagent consumed
by the silanol.

Table II

Titration of Silanols with the Karl Fischer Reagent

Silanol[a]	Millimoles taken	Millimoles of apparent water found	Millimoles of apparent water found per millimole silanol
1. $(C_6H_5)_3SiOH$	4.52	4.47	0.99
2. $(C_6H_5)_2Si(OH)_2$	0.927	1.84	1.98
3. $(\underline{p}\text{-}C_6H_5C_6H_4)_3SiOH$	0.398	0.393	0.99
4. $(\underline{p}\text{-}C_6H_5C_6H_4)_2Si(OH)_2$	0.272	0.483	1.78[b]
5. $(C_6H_5)_2(\underline{p}\text{-}CH_3C_6H_4)SiOH$	0.690	0.680	0.99
6. $\underline{p}\text{-}[(CH_3)_2NC_6H_4]_3SiOH$	0.358	0.356	0.99
7. $(C_6H_5)_3SiOH$	1.60	1.60	1.00
8. $(\underline{p}\text{-}ClC_6H_4)_3SiOH$	0.375	0.377	1.00

[a]Compound 2 was prepared by H. N. Benedict and compounds 3, 4, 5, and 6 were prepared by G. E. Dunn. Compound 7 was obtained from the Anderson Laboratories, Adrian, Michigan.

[b]This silanediol presumably contained some condensation products.

Tri-p-xenylmethoxysilane. The solution remaining after
the titration of tri-p-xenylsilanol (m.p. 200-201°) was
diluted with water and filtered. The residue, 0.19 g. (91%),
after washing with water and drying one hour at 120°, melted
at 157-158°. This material would not react with the Fischer
reagent. A portion of this residue was warmed with a solution
of potassium hydroxide in ethanol-dioxane for five minutes,
diluted with water, and filtered. The residue from this
latter filtration melted at 200-202° and its mixed melting
point with tri-p-xenylsilanol showed no depression. A sample
of tri-p-xenylmethoxysilane was prepared by refluxing 0.23 g.
of tri-p-xenylsilanol with 2.0 g. of anhydrous zinc chloride
in 10 ml. of methanol for forty hours. The product was
filtered and the residue was washed with methanol and acetone
to leave 0.1 g. (42%) of white needles, m.p. 158°. A mixed
melting point with the above compound isolated from the Fischer
titration showed no depression.

Anal. Calcd. for $C_{37}H_{30}OSi$: Si, 5.42. Found: Si, 5.49.

Titrations of Triphenyllead Hydroxide, Triphenyltin
Hydroxide, Phenylboric Oxide, and Phenylboric Acid. The samples
of triphenyltin hydroxide, m.p. 122-124°, and triphenyllead
hydroxide, and phenylboric oxide, m.p. 219°, had been prepared
by C. E. Arntzen, R. K. Abbott and B. A. Hunter, respectively.
A sample of the phenylboric oxide was recrystallized from water
and the product was dried overnight at 70°. Titration of

0.120 g. (0.00115 mole) of the dried material required 18.94 ml.
of Fischer reagent equivalent to 0.001144 mole of water or
99 mole percent calculated as $(C_6H_5BO)_3$. Another sample of
the oxide was crystallized from water and dried thirty
minutes at room temperature and 20 mm. pressure. Titration
of 0.00755 mole of this product took 24.60 ml. of Fischer
reagent, equivalent to 0.00148 mole or 98 mole percent
calculated as phenylboric acid, $C_6H_5B(OH)_2$. Samples of the
triphenyltin hydroxide and triphenyllead hydroxide, on titration,
gave 1.01 and 1.02 moles of apparent water found per mole
hydroxide, respectively. Both compounds decolorized additional
reagent on standing several hours.

Triphenyl-t-butoxysilane. A Fischer-type reagent was
prepared in which the methanol was replaced by t-butyl
alcohol. This reagent was made up from 10 ml. of pyridine,
3.15 g. of iodine, 1.67 ml. of liquid sulfur dioxide, and
24.8 ml. of t-butyl alcohol. The iodine color of this reagant
was not destroyed by the addition of triphenylsilanol at room
temperature although water decolorized the reagent instantly.
A 0.26 g. (0.00095 mole) sample of triphenylsilanol was added
to 25 ml. of this reagent and the mixture was heated in a
glass-stoppered flask at 90° for fourteen hours. The reaction
mixture was then hydrolyzed in dilute hydrochloric acid and
filtered to give 0.23 g. (73%) of a light solid melting from

99° to 101°. Two crystallizations of this material from methanol gave clear crystals melting at 104°.

Anal. Calcd. for $C_{22}H_{24}OSi$: Si, 8.45. Found: Si, 8.64.

This compound was also prepared by refluxing a mixture of 2.0 g. (0.0068 mole) of triphenylchlorosilane and 2 ml. of dimethylaniline in 15 ml. of t-butyl alcohol for two hours. The product was recovered and purified as above to yield 0.52 g. (23%) of material identical with the above (mixed melting point).

DISCUSSION

Organosilicon Compounds

The group of silanes containing the p-chlorophenyl

group were prepared in order to ascertain their toxicity as

insecticides compared to related carbon analogues. The

investigations[152] which were made during the development of

DDT, $(p-ClC_6H_4)_2CHCCl_3$, disclosed that many compounds contain-

ing the p-chlorophenyl group showed some contact-type insect-

icidal activity, the contact insecticides being those which

cause death to the insect by being absorbed on contact,

usually through the tracheal tract or at the base of the

hair. In order to penetrate the waxy outer layer of the

insect's body, this type of insecticide should have relatively

high lipid solubility and this may be one of the chief functions

imparted by the p-chlorophenyl group in its derivatives. In

addition, Lauger and his coworkers[152] postulated that the

molecule of a contact insecticide should contain one or more

groups related to the molecule of an anesthetic. Thus in

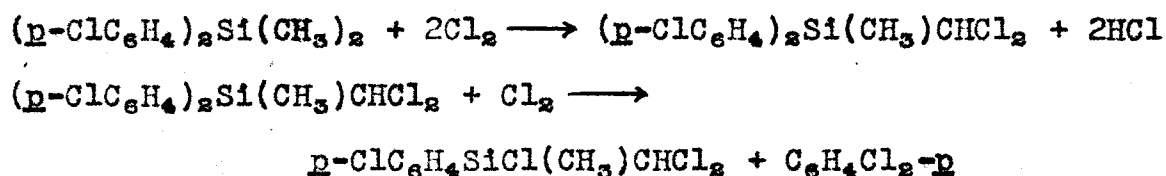DDT, the trichloromethyl group is related to chloroform and

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[152] Lauger, Martin and Muller, Helv. Chim. Acta., 27, 892
(1944).

also the p-chlorophenyl group is related to chlorobenzene or to p-dichlorobenzene. The p-chlorophenyl group may therefore be considered to impart both lipid solubility and aneathetizing ability to an insecticide.

The preparation of an exact analogue of DDT containing one central silicon atom, i.e. the compound $(p\text{-}ClC_6H_4)_2SiH(CCl_3)$, appeared to be somewhat impractical since such a compound would contain a hydrogen atom bonded directly to silicon, and this hydrogen-to-silicon bond would be expected to be hydrolyzed on contact with water (containing traces of alkali). Instead, various related compounds, as described in the experimental section, were made.

The preparation of the near-analogue of DDT, methyl-(trichloromethyl)-bis-(p-chlorophenyl)-silane, $(p\text{-}ClC_6H_4)_2$ $Si(CH_3)CCl_3$, was attempted by the treatment of dimethyl-bis-(p-chlorophenyl)-silane with chlorine directly, both with and without carbon tetrachloride as a solvent, and with sulfuryl chloride in the presence of benzoyl peroxide, and also by the reaction of p-chlorophenyllithium with methyl-(trichloro-methyl)-dichlorosilane. None of these three methods led to the desired compound, although by the first two procedures the corresponding dichloromethyl derivative, $(p\text{-}ClC_6H_4)_2$ $Si(CH_3)CHCl_2$, was isolated. The conditions necessary for the preparation and/or isolation of the desired compound apparently led to cleavage of one of the p-chlorophenyl groups, since in all three of the above methods, the cleavage product, p-dichloro-

benzene, was isolated, either during the chlorination, or
on attempted distillation of the products. A model of the
desired trichloromethyl compound above could not be constructed
without interference among the groups substituted on the
silicon atom, so that it is probable that steric considerations
make the substitution of the third chlorine atom in this
molecule difficult and therefore the side reactions, such
as cleavage of an aryl group, would be expected to become
relatively important. Such a cleavage reaction could be
formulated as follows:

$$(\underline{p}\text{-}ClC_6H_4)_2Si(CH_3)_2 + 2Cl_2 \longrightarrow (\underline{p}\text{-}ClC_6H_4)_2Si(CH_3)CHCl_2 + 2HCl$$
$$(\underline{p}\text{-}ClC_6H_4)_2Si(CH_3)CHCl_2 + Cl_2 \longrightarrow$$
$$\underline{p}\text{-}ClC_6H_4SiCl(CH_3)CHCl_2 + C_6H_4Cl_2\text{-}\underline{p}$$

The chlorine atoms in the above dichloromethyl derivative
are assumed to be substituted on the same carbon atom on the
basis of similar chlorination studies carried out by Krieble
and Elliott[23] in which they showed that in the case of dimethyl-
dichlorosilane, substitution of up to three chlorine atoms
proceeded on the methyl group first attacked.

An attempt to prepare the silicon analogue of another
important insecticide, DMC, methyl-bis-(p-chlorophenyl)-
carbinol, in which the central carbon atom is replaced by
silicon, i.e. methyl-bis-(p-chlorophenyl)-silanol, resulted
in the formation of the corresponding condensation product,

$\sqrt{}$ CH$_3$(p-ClC$_6$H$_4$)$_2$Si $\sqrt{}$$_2$O. The condensation apparently took
place during the hydrolysis of the intermediate CH$_3$(p-ClC$_6$H$_4$)$_2$SiCl
with dilute hydrochloric acid (1:20) since none of the liquid
products recovered from this reaction was capable of decolor-
izing the Fischer reagent.(a reaction shown by compounds
containing the Si-OH group).

The following group of compounds which were prepared are
being tested for insecticidal activity[7]: tetrakis-(p-chloro-
phenyl)-silane, diphenyl-bis-(p-chlorophenyl)-silane, triphenyl-
(p-chlorophenyl)-silane, phenyl-tris-(p-chlorophenyl)-silane,
(trichloromethyl)-tris-(p-chlorophenyl)-silane, and methyl-
(dichloromethyl)-bis-(p-chlorophenyl)-silane.

A group of n-alkyltriphenylsilanes was prepared in
conjunction with studies on the preparation of the correspond-
ing n-alkyllithium compounds and also for possible use in the
cleavage studies. The following melting points were found
or are reported for the series of (C$_6$H$_5$)$_3$SiR compounds where
R is the group indicated: methyl, 67°; ethyl[153], 76°;
n-propyl, 84°; n-butyl[141], 88°; n-amyl, 47°; and n-hexyl, 78°.
The interesting break noted in this series between n-butyl and
n-amyl is somewhat unusual, although Dr. R. E. Rundle[154] has
indicated that small changes in the structures of molecules

[153] Kipping, J. Chem. Soc., 93, 198 (1908).

[154] R. E. Rundle, Private communication (1950).

frequently result in changes in the crystal arrangement of the corresponding solid, so that abrupt changes in the melting point may result. In this regard it is interesting to note that the melting points of the corresponding lead derivatives show no definite trend.

The preparation of silanes containing the triphenylmethyl group was clearly successful only in the case of trimethyl-(triphenylmethyl)-silane. This compound exhibited the properties to be expected of a triphenylmethyl derivative in that it was not cleaved readily by hydrogen chloride (as is predicted by Kharasch and Flenner[155]) but was cleaved readily by base as is expected of this group since its carbanion is stabilized by resonance throughout the three benzene rings as discussed in the section on cleavages. The reaction between triphenylmethyllithium and triphenylchlorosilane, however, gave no compound definitely established as triphenyl-(triphenylmethyl)-silane, but instead gave a complex mixture of products melting between 200° and 335°, from which fairly pure components were isolated melting from 210-215° and at 335°.

The analytical data obtained on the former component were close to that expected for triphenyl-(triphenylmethyl)-silane. However, no sharp melting material could be obtained on repeated precipitation of this component from various solvents, and it

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[155] Kharasch and Flenner, *J. Am. Chem. Soc.*, 54, 674 (1932).

was not cleaved by basic reagents. The analyses determined on the 335° melting material corresponded closely to a bis-(triphenylsilyl)-triphenylmethane for which one probable structure seemed to be bis-/p-(triphenylsilyl)-phenyl_/-phenylmethane. However, this latter compound was prepared and found to melt at 315° and its mixed melting point with the 335° melting material above was 305°. Blocking of the para positions of triphenylmethyllithium with methyl groups by using tri-p-tolylmethyllithium in the reaction with triphenylchlorosilane prevented the formation of any high melting products whatsoever, indicating that the corresponding para positions are involved in the original reaction. It is conceivable that the products obtained are mixtures of triphenylmethane derivatives having both lateral and para triphenylsilyl substituents.

Basic Cleavage Reactions

Basic or nucleophilic cleavage reactions may be classed as a type of displacement reaction of the general form:

$$A + BC \longrightarrow AB + C$$

In the reactions of present interest, A represents the basic or nucleophilic reagent and B is an atom of silicon or a metal. As mentioned previously, the nucleophilic reagents of chief interest are: OH^-, NH_2^-, CN^-, OR^-, R^- (the carbanion, or negative portion of an ion-pair, of an organometallic
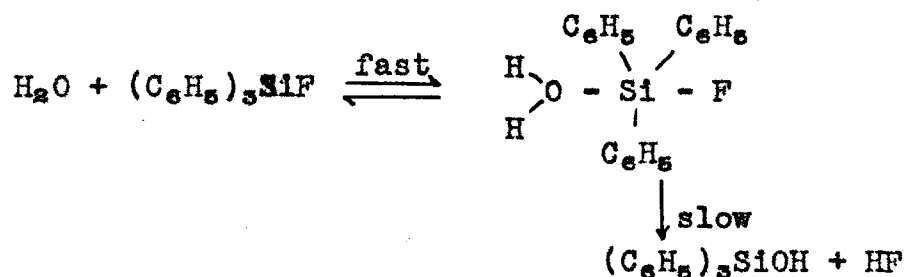
compound), water, alcohols and amines.

Several factors combine to make the silicon atom in a silane more susceptible to nucleophilic attack and resultant cleavage than the carbon atom in its corresponding carbon analogue: (1) Silicon, in contrast to carbon, is capable of expanding its valence shell so that it may accommodate up to six covalent bonds[156]. Thus $SiCl_4 \cdot 6NH_3$ is known to be formed from silicon tetrachloride and ammonia[14]. This property of the silicon atom enables a tetra-substituted silane to form a more or less stable coordination complex with the nucleophilic reagent. Once this complex has formed, any one of the original groups bonded to the silicon atom has a relatively greater chance of being expelled in place of the attacking group than if no such complex was possible. (2) The larger size and extra electron shells of the silicon atom screen its nuclear charge and make it more polarizable than carbon. An electron-attracting group, when bonded to silicon, is therefore able to withdraw electrons from the valence shell of the silicon atom to some extent. The result is a lengthening and weakening of the bond between the silicon atom and this group relative to the length and strength of the other bonds to this silicon atom. (3) In cases where a silicon-to-carbon bond is being broken to form a silicon-to-oxygen bond,

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[156] Sidgwick, "The Electronic Theory of Valency", Oxford University Press, 1927, pp. 159-160.

the relative bond energies, 57.6 and 89.3 kcal.[157], respectively, strongly favor the stability of the silicon-to-oxygen bond.

Recent studies of the rate of hydrolysis of triphenyl-fluorosilane[10] led Swain and his coworkers to the conclusion that the mechanism of this reaction involved a fast formation of a pentacovalent intermediate followed by slow cleavage of the fluoride ion:

$$H_2O + (C_6H_5)_3SiF \xrightleftharpoons{fast} \begin{array}{c} C_6H_5 \quad C_6H_5 \\ H{\searrow} \quad \backslash \quad / \\ O - Si - F \\ H{\nearrow} \quad | \\ C_6H_5 \end{array}$$

$$\downarrow slow$$
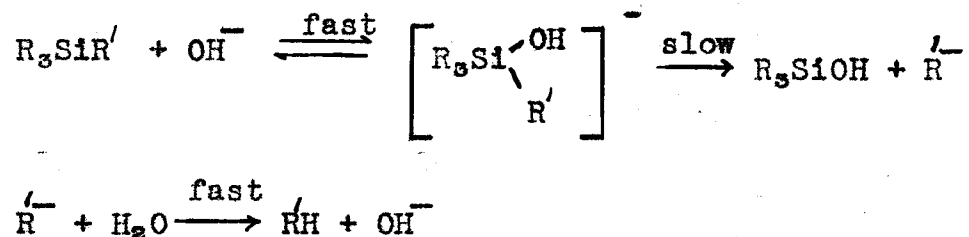
$$(C_6H_5)_3SiOH + HF$$

(Steps involving solvation of the fluorine atom are omitted for clarity.) Thus experimental evidence was obtained to substantiate the importance of the ability of the silicon atom to expand its valence shell with respect to nucleophilic displacements on silicon.

In the case of the cleavage of R_3SiR' types by potassium hydroxide, a similar mechanism can be postulated in which the hydroxyl ion rapidly forms a pentacovalent intermediate. The

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[157] Pauling, "The Nature of the Chemical Bond", Cornell University Press, Ithaca, N. Y., 1945.

slow step then becomes the splitting of the R' group:

$$R_3SiR' + OH^- \underset{\text{fast}}{\rightleftharpoons} \left[R_3Si \overset{OH}{\underset{R'}{\diagup}} \right]^- \xrightarrow{\text{slow}} R_3SiOH + R'^-$$

$$R'^- + H_2O \xrightarrow{\text{fast}} R'H + OH^-$$

Although the first equilibrium is attained rapidly, the position of this equilibrium determines the concentration of the intermediate and therefore affects the over-all rate of cleavage. The position of this equilibrium is determined both by the type of nucleophilic reagent and by the nature of the R and R' groups. Swain[10] and his coworkers conclude (on the basis of solvent effects and the retarding action of para methyl substituents on the hydrolysis of triphenyl-fluorosilane) that the silicon atom is less positive in the transition state and in the pentacovalent intermediate state than in the ground state. It follows therefore that any group which tends to attract electrons will shift the above equilibrium to the right, and therefore increase the rate of cleavage. This interpretation of the mechanism fits in with the observations of Krieble and Elliott[23] that negative Y substituents in a compound of the type Y_3SiCX_3 will increase the ease of cleavage of the CX_3 group.
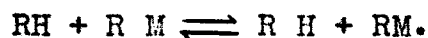
Where four somewhat similar R groups are involved in an R_4Si compound having four carbon-to-silicon bonds, it is

reasonable to expect that the R group which will split preferentially from the pentacovalent intermediate will be that group which draws the pair of electrons contained in its carbon-to-silicon bond most strongly away from the silicon atom. In other words, the most electron-attracting group will cleave most readily upon nucleophilic attack in cases where only carbon-to-silicon bonds are being considered. According to Pauling's[157] use of the word electronegative (as referring to electron-attracting ability), this group would also be considered the most electronegative group. However, the term electronegative, as used by Kharasch[158] with regard to the cleavage of unsymmetrical mercury compounds by hydrogen chloride, does not necessarily refer to the electron-attracting ability of the group, but rather to the ability of the group to cleave more readily from mercury on electrophilic attack. The ortho-para directing nature of the radicals which are high in Kharasch's series, such as p-anisyl or 2-thienyl leads one to postulate that these groups are actually predominately electron-releasing in nature, and that this type of cleavage reaction may be initiated by an attack of the hydrogen chloride ion-pair (or by a proton) on that carbon atom (attached to the metal) which has the highest electron density. These groups would therefore

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[158] Kharasch and Grafflin, J. Am. Chem. Soc., 47, 1948 (1925).

actually be those which are most capable of electron-release toward this carbon on attack by the hydrogen ion.

In predicting the groups which are capable of attracting electrons the most readily, a knowledge of the acidity of the acid formed by replacing the metal of the organometallic compound by hydrogen should be of value since the more electron attracting radical should form the stronger acid, providing secondary mechanisms are not involved. An acid strength series for hydrocarbon acids, was obtained[6] by measuring the position of the equilibrium in the reaction:

$$RH + R'M \rightleftharpoons R'H + RM.$$

The weaker acid was considered to be the one whose R-group held the proton to the greater extent. The series obtained, listed according to decreasing acid strength included: (9-phenylfluorene, α-naphthyfluorene, phenylacetylene, indene), fluorene, diphenylbiphenylmethane, triphenylmethane, diphenyl-α-naphthylmethane, diphenylmethane, diphenylmethylmethane and cumene. From studies on relative ease of metalation[1a], this series may be extended in a general way to include the following still more weakly acidic types (listed according to decreasing acid strength): toluene (lateral hydrogen), benzene and its derivatives (nuclear hydrogen), and the alkanes.

The data in Table I tend to substantiate the above interpretation, the following being the order of decreasing ease of cleavage of the radicals from the corresponding $(C_6H_5)_3SiR$

compounds by potassium hydroxide: (phenylethynyl, 1-indenyl, 9-fluorenyl), benzohydryl, benzyl, (m-trifluoromethylphenyl, p-chlorophenyl), ∝-naphthyl, and (phenyl, β-phenylethyl, methyl, hexyl). In addition, the very strongly electron-attracting trichloromethyl group cleaved at least as readily as the first group of radicals above.

The data previously cited in the literature (see pp. 26-34 of this thesis) on cleavages of carbon-to-silicon bonds by base can be summarized approximately by the following series (listed according to decreasing ease of cleavage of radicals by base): (trichloromethyl, phenylethynyl, ethynyl), (β-chloroethyl, β-oxygen-substituted-ethyl groups, p-amino-phenyl), dichloromethyl, (chloromethyl, γ-chloro-n-propyl), β-chlorovinyl, (p-nitrophenyl, m-nitrophenyl, benzyl, m-amino-phenyl), phenyl, and alkyl groups. This series appears to correspond closely to the estimated decreasing order of electron attracting ability of these groups. The possibility of elim-ination of an unsaturated molecule from the groups containing a negative substituent in the beta position enhances their electron-attracting ability.

It is not surprising that the p- and m-nitrophenyl groups were found to cleave quite readily since the nitro group is generally considered to be electron attracting in nature, and this property would be transmitted by resonance and inductive effects through the benzene ring. An interpretation of the

ease of cleavage of the p-aminophenyl group is not so obvious.
In reactions involving electrophilic attack on a p-aminophenyl-
substituted silane the amine hydrochloride would first be
formed, and the resulting positive charge would increase the
electron-attracting nature of the group so that it would be
cleaved readily on attack of the silicon atom by water or
hydrogen chloride. It is therefore not surprising that the
p-aminophenyl group is cleaved easily from silicon by acids.
In nucleophilic attack where the electron-attracting ability,
not the electron-releasing ability of this group is brought
into play, the inductive effect of the electronegative nitrogen
atom increases this former ability as compared with the un-
substituted phenyl group so that cleavage again takes place
relatively easily. Since the p-aminophenyl group is cleaved
very readily from silicon both by dilute acids and dilute bases,
future preparations of these derivatives will probably be
more successful if a recovery method is devised which eliminates
any hydrolysis of the reaction products. p-Aminophenyltri-
ethoxysilane, the only p-aminophenyl-substituted silane described
in the literature, has been prepared successfully by filtration
and direct distillation of the reaction product of p-amino-
phenyllithium (as its lithium salt) and tetraethoxysilane[159].

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[159] Fleming, U. S. Patent 2,386,452, Oct. 9, 1945 /C.A.
40, 603 (1946)_/; Clark, Doctoral Dissertation, Iowa State
College (1946).

Nobis[160] found a similar instability of p-hydroxyphenyl-substituted silanes to hydrolysis on attempted recovery of the product from the reaction of the lithium salt of p-hydroxyphenyllithium with trimethylchlorosilane. None of the desired trimethyl-(p-hydroxyphenyl)-silane could be isolated.

The series of silanes of the type $(C_6H_5)_3SiR$ was chosen for the cleavage studies using potassium hydroxide for several reasons. These silanes could be readily prepared by the reaction of organometallic compounds on the commercially available triphenylchlorosilane. They were all solids which could, in most cases, be readily purified and analyzed, and they could usually be recovered conveniently from the cleavage mixture by simple extraction. For this reason, the amount of recovered silane was used to calculate the extent of cleavage in most of the reactions. Using reagent (D) (Table I) the cleavage products formed were the corresponding hydrocarbon and triphenylsilanol. The triphenylsilanol was readily separated from the starting silane by extraction with 90% aqueous methanol and this silanol could be readily characterized.

The silicon atom was considered to be large enough so that for most of the substituted triphenylsilanes considered, no great steric interference with nucleophilic attack on silicon was expected. The validity of this assumption was

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[160] Nobis, Doctoral Dissertation, Iowa State College (1948).

confirmed by the ready cleavage of the relatively large 9-fluorenyl and benzohydryl groups from their triphenyl-silyl derivatives. Even the α-naphthyl group in triphenyl-α-naphthyl silane was cleaved to an appreciable extent. This is in contrast to the lack of cleavage observed on treatment of tri-α-naphthylsilanol with n-butyllithium. Since cleavage of the α-naphthyl group has generally been found to take place more readily than cleavage of the phenyl group, both with base (Table I) and with n-butyllithium on various α-naphthyl derivatives of metals, it is probable that steric interference of nucleophilic attack prevents cleavage in the case of tri-α-naphthylsilanol. A similar low extent of cleavage in the case of tri-α-naphthylbismuth[97] was explained as being due to the low solubility of this compound in ether, although steric factors may be involved here also.

It is possible that the product obtained from the reaction of triphenylchlorosilane on triphenylmethyllithium, which melted at 210-215° and gave approximately the correct silicon analysis, may be the desired triphenyl-(triphenylmethyl)-silane even though it could not be cleaved on treatment by base. Here, again, steric factors and low solubility might combine to make cleavage difficult.

Initial experiments with basic reagents for the cleavages of the silanes indicated that the most effective reagents were those which remained homogeneous and were good solvents for

the silanes, and yet contained a small concentration of water
so that the polarity of the medium was relatively high. These
properties were combined quite successfully in reagent (D).
The dioxane was an excellent solvent for a majority of the
silanes and the alcohol was necessary in order to make the
medium remain homogeneous after the addition of water and
alkali. If a much higher concentration of water was employed,
or if a solvent less miscible in water was used, it was found
that a second layer of concentrated aqueous alkali often formed
on extended heating, with a resultant lowering of the effective-
ness of the reagent.

Further studies with reagents containing lower concen-
trations of alkali are needed to distinguish between the ease
of removal of the readily cleavable radicals such as phenyl-
ethynyl, 9-fluorenyl and chloromethyl. On the other hand, a
still more effective reagent is needed for the cleavage of
the various substituted phenyl derivatives.

The data covered in the historical section indicate that
organometallic compounds are generally stable to attack by
the hydroxyl ion providing they are stable in water itself,
although there was no report of an organometallic compound
containing an easily cleavable group having been tested for
this specific property. Since a metal-hydroxyl bond tends
to be more ionic as the metal becomes more metallic in character,
it is reasonable to expect that the ability of the hydroxyl ion

to displace a relatively covalent metal-to-carbon bond would become lower in the same order.

The metal-metal interconversion type reaction, however, involves only the replacement of one metal-to-carbon bond by another so that the position of the resultant equilibrium should be determined by the relative electron-attracting ability of the radicals involved and upon the relative electronegativities and polarizabilities of the two metals. The rate at which the interconversion reaction takes place will be dependent on the polarity of the solvent, the solubility of the products and reactants, and possible steric interference with the nucleophilic attack of the carbanion, as well as by the above factors affecting the equilibrium.

Among the group IV-B elements it seems reasonable to expect a regular progression with regard to the ease with which a particular radical will be cleaved from the metals by a reagent such as n-butyllithium. The tetraphenyl derivatives of silicon[57], tin[93] and lead[93] have all been treated with this latter reagent. Tetraphenylsilane did not react in twenty-four hours in refluxing ether. Tetraphenyltin and tetraphenyllead were reported[93] to have given 45% and 30% yields of benzoic acid, respectively, after treatment with n-butyllithium in ether followed by carbonation, but the other experimental data on these reactions were not given. In the experimental section of this same report, the only corresponding data given

listed a 38% yield of benzoic acid on similar treatment of tetraphenyllead in ether for thirty minutes, while tetraphenyltin gave a 36% yield of benzoic acid after refluxing twenty-four hours in an ether-benzene solution with n-butyllithium. Thus there appears to be no definite data in the literature to refute the expected regular progression toward greater ease of cleavage of the lower members of group IV-B by RM compounds.
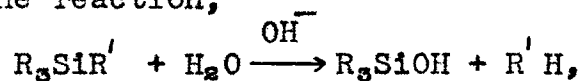
The actual number of radicals involved in the reported metal-metal interconversion reactions is not large. The following order of decreasing ease of cleavage of the particular radicals mentioned appears to be consistent in all reported cases: p-halogenated-phenyl groups, p-tolyl, phenyl, (alkyl, o-tolyl). In the cleavage of bismuth and antimony compounds there was little difference in the labilities of the p-tolyl and phenyl groups, while in other interconversions the p-tolyl group was definitely cleaved somewhat more easily. The α-naphthyl group was generally cleaved more readily than p-tolyl except in the previously mentioned case of tri-α-naphthylbismuth.

The ortho-substituted radicals in general (including mesityl, o-chlorophenyl, o-tolyl, and α-naphthyl) exhibit anomalous behavior in the interconversion reactions probably due to the accentuated steric and field effects involved. These groups, especially when more than one is attached to a single metal, are generally not cleaved readily. However, in

the comparatively less sterically hindered dimesitylmercury, the mesityl group was cleaved more readily than the p-chlorophenyl group by n-butyllithium.
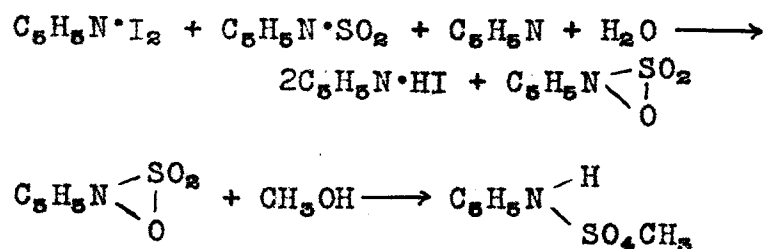
Silanol Titrations with the Fischer Reagent

During some of the early studies of the cleavages of silanes by reagents containing aqueous potassium hydroxide a method was devised by which it was hoped that the extent of the reaction,

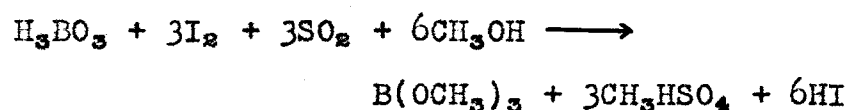$$R_3SiR' + H_2O \xrightarrow{\text{OH}^-} R_3SiOH + R'H,$$

could be followed by titrating aliquots of the reaction mixture for water content with the Fischer reagent. In this manner the order of the reaction and the corresponding rate constant could be determined in a convenient manner. Preliminary experiments showed, however, that the silanols themselves reacted quantitatively with the Fischer reagent so that there was no net change in the titer of the solution during the reaction.

The Fischer reagent, consisting of a solution containing methanol, pyridine, sulfur dioxide and iodine, reacts with water in the following manner[151]:

$$C_5H_5N \cdot I_2 + C_5H_5N \cdot SO_2 + C_5H_5N + H_2O \longrightarrow$$
$$2C_5H_5N \cdot HI + C_5H_5N \diagdown \begin{array}{c} SO_2 \\ | \\ O \end{array}$$

$$C_5H_5N \diagdown \begin{array}{c} SO_2 \\ | \\ O \end{array} + CH_3OH \longrightarrow C_5H_5N \diagdown \begin{array}{c} H \\ SO_4CH_3 \end{array}$$
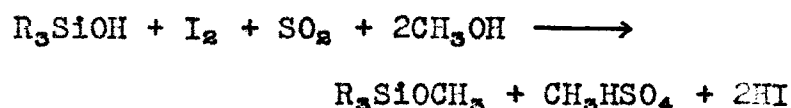
The color change on conversion of iodine to the iodide ion provides an observable endpoint for the titration. The basic hydroxides react quantitatively with the reagent in an analogous manner[151] so that titration of a solution of aqueous base determines the combined concentration of water and base. The water concentration can then be obtained by subtracting the concentration of the base, as determined by an acid titration, from the total concentration of water and base.

The reaction between the Fischer reagent and silanols is analogous to that taking place between other weak acids or oxides and this reagent. For example, the reaction with boric acid has been formulated as follows[151]:

$$H_3BO_3 + 3I_2 + 3SO_2 + 6CH_3OH \longrightarrow$$

$$B(OCH_3)_3 + 3CH_3HSO_4 + 6HI$$

The reaction with silanols may be formulated similarly:

$$R_3SiOH + I_2 + SO_2 + 2CH_3OH \longrightarrow$$

$$R_3SiOCH_3 + CH_3HSO_4 + 2HI$$

In the case of the titration of tri-p-xenylsilanol, where the resulting tri-p-xenylmethoxysilane was stable to hydrolysis by dilute acid, the product from the titration was shown to be the expected methoxy derivative. In such cases where recovery can be made by simple hydrolysis and filtration, this method appears to be an attractive one for the preparation of alkoxysilanes in high yield. As a test of the scope of this method, a reagent was prepared in which the methanol was

replaced by t-butyl alcohol and this reagent reacted with triphenylsilanol on heating to give a 73% yield of triphenyl-t-butoxysilane. This latter reagent, incidentally, does not react with silanols at an appreciable rate at room temperature, so that it might be used, as originally planned for the unmodified Fischer reagent, to follow the course of cleavage reactions with aqueous base.

The Fischer titration method is quite specific for silanols (in the absence of water and bases) since the following compounds do not react with the Fischer reagent at all or do not react rapidly enough to be titrated: hexamethyldisiloxane, hexaphenyldisiloxane, ethyltriethoxysilane, tris-(p-chlorophenyl)-ethoxysilane, triphenylchlorosilane, and tris-(p-dimethylaminophenyl)-silane.

The only silanols which did not react rapidly with the Fischer reagent were the two highly hindered compounds, tri-α-naphthylsilanol[161a] and tri-o-tolylsilanol[161b]. The former silanol would decolorize a slight amount of Fischer reagent on standing several hours.

Evidence of steric hinderance in these and several other silanes has been reported[161a,b,c,20,25]. For example, tri-α-

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[161](a) Gilman and Brannen, J. Am. Chem. Soc., 72, 0000 (1950); (b) Gilman and Smart, J. Org. Chem., 15, 000 (1950); (c) Gilman and Clark, J. Am. Chem. Soc., 69, 1499 (1947); Price, ibid., 69, 2600 (1947); Nebergall and Johnson, ibid., 71, 4022 (1949).

naphthylchlorosilane was found to be quite resistant to hydrolysis by water and relatively forced conditions were required to affect hydrolysis by alcoholic base.

The carbon compounds analogous to the silanols, i.e. tertiary alcohols, do not react with the Fischer reagent. t-Butyl alcohol solutions have been titrated for water content without interference[151] and triphenylcarbinol was tested and found not to decolorize the Fischer reagent. Hydroxy compounds of the heavier group IV-B elements which were available could be titrated with the Fischer reagent, as described in the experimental section.

A sample of phenylboric acid, $C_6H_5B(OH)_2$, which had been freshly crystallized from water gave on titration 1.96 moles apparent water per mole of acid. On standing in the air or drying at 70° for several hours, the oxide $(C_6H_5BO)_3$, was formed which analyzed 0.99 mole apparent water per mole of oxide. Although organic hydroxy derivatives of germanium and arsenic were not tested, it is probable that they, as well as the more basic organometallic hydroxides, can be determined by this method.

SUMMARY

A survey of known reactions involving the splitting
of carbon-to-silicon or carbon-to-metal bonds by basic or
nucleophilic reagents has been presented.

Organolithium reagents have been used extensively in
the preparation of a number of new arylsilanes. One group
of these silanes has been submitted to Dr. C. H. Richardson
of the Department of Entomology, Iowa State College, for
evaluation of their insecticidal activity.

The ease of cleavage of various organic radicals from
the trimethylsilyl or the triphenylsilyl group by various
reagents containing potassium hydroxide has been found to
correspond closely to the reported ease of cleavage of these
radicals from organometallic compounds by organoalkali reagents.
The series giving the relative ease of cleavage of R-radicals,
obtained by the treatment of silanes with potassium hydroxide,
has also been correlated with the acid strengths of the corres-
ponding RH hydrocarbons.

Some reactions of triphenylmethyllithium with trimethyl-
chlorosilane and with triphenylchlorosilane have been described.

A new method for the determination of silanols by titra-
tion with the Fischer reagent has been developed.