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REACTIONS OF ORGANOSILYLMETALLIC COMPOUNDS WITH SOME HALIDES

by

Dan Kazumi Aoki

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Approved:

Signature was redacted for privacy.

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Signature was redacted for privacy.

Head of Major Department

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Dean of Graduate College

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Of Science and Technology
Ames, Iowa

1961

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I. INTRODUCTION

Since organosilyllithium compounds became readily accessible as relatively stable solutions in tetrahydrofuran,[1, 2] their chemistry and application in organic synthesis have been studied intensively and extensively. Recently, certain aspects of the subject have been reviewed and summarized.[3, 4, 5, 6, 7]

It has been found that these highly reactive organosilyllithium compounds react with a variety of compounds forming new bonds between silicon and many other elements. In general, they react with functional groups in a manner similar to other organometallic compounds such as

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

[2] H. Gilman, D. J. Peterson, and D. Wittenberg, Chemistry and Industry, 1958, 1479.

[3] D. Wittenberg and H. Gilman, Quart. Rev., 13, 116 (1959).

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

[5] G. D. Lichtenwalter. Organosilylmetallic compounds and derivations. Unpublished Ph.D. Thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1958.

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 Unpublished Ph.D. Thesis.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

[7] W. J. Trepka. Aryloxy and related organosilicon chemistry. Unpublished Ph.D. Thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1960.

Grignard reagents and organolithium compounds. However, perhaps owing in part to large electronegativity differences between silicon and other more electronegative elements than the differences between carbon and the corresponding elements, organosilyllithium compounds often exhibit dissimilarities in their mode of reaction. The fact that this has shown to be particularly true of their reactions with organic halides[8, 9] has led to the present investigation.

The reactions studied were those of triphenylsilyllithium with aliphatic mono- and polyhalides and vinyl-type halides. During the course of the investigation it was learned that the resulting silanes having unsaturated linkages on the side-chain close to a silicon atom undergo metalation quite readily. This fact has led to the synthesis of several stable triphenylsilyl substituted allenes. Other functional silanes of particular interest, which were synthesized and studied for their reactions with organometallic compounds, are halotriphenylsilylacetylenes.

The scope of the reaction is unlimited. It is particularly interesting to study more thoroughly the mechanisms involved in many of the reactions presented in this thesis and many other reactions which one can easily conceive.

---

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

[9] H. Gilman and D. Aoki, J. Org. Chem., 24, 426 (1959).

II. HISTORICAL

A. Reactions of Grignard Reagents with Organic Halides[10]

The reaction of benzyl chloride and methylmagnesium iodide may illustrate the development of the understanding of the reaction mechanism of Grignard reagents with organic halides in general.

In 1903 Houben[11] first reported the reaction just cited above. He isolated ethylbenzene, the "normal" condensation product, in a yield of 25% and some dibenzyl, the "coupling" product. Ten years later Späth[12] reported the reaction. He obtained ethylbenzene (37%), dibenzyl (large amount), and a compound he called 1,2,3-triphenylpropane. Fuson[13, 14, 15] was led to a more detailed study of the reaction when he obtained _s_-bis(_o_-cyanophenyl)ethane as an only product (43%) from the reaction of methylmagnesium iodide with _o_-cyanobenzyl bromide.[13] He obtained the "normal" product, ethylbenzene, in a yield of 23-27%; the "coupling" product, dibenzyl, in a yield of 31-33%; and a gaseous material (33-35%)

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[10] For a comprehensive discussion and accompanying bibliography on reactions of Grignard reagents with organic halides, see M. S. Kharasch and O. Reinmuth. Grignard Reactions of Nonmetallic Substances. New York, N.Y., Prentice-Hall, Inc. 1954. pp. 1046-1132.

[11] J. Houben, _Ber._, _36_, 3083 (1903).

[12] Späth, _Monatsh._, _34_, 1965 (1913).

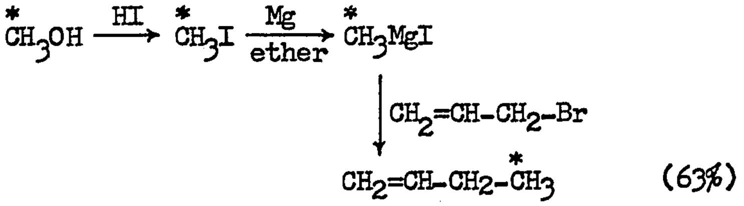
[13] R. C. Fuson, _J. Am. Chem. Soc._, _48_, 830 (1926).

[14] R. C. Fuson, _ibid._, _48_, 2681 (1926).

[15] R. C. Fuson, _ibid._, _48_, 2937 (1926).

which he characterized as ethane.[14] Kharasch et al.[16] made a more thorough investigation of the gaseous products obtained when various organic halides were reacted with phenylmagnesium bromide in the presence of cobaltous chloride. It is now an accepted view that the "coupling" reaction is free-radical in nature. The methyl radical in ether solution, Kharasch observed, does not couple to give ethane; instead it either abstracts hydrogen from the solvent to give methane or reacts with diethyl ether, attacking the oxygen atom and yielding methyl ethyl ether and ethyl radicals, which disproportionate to give ethane and ethylene. Therefore, he concluded that the gaseous product, which Fuson called ethane, was in reality a mixture of methane, ethane, and ethylene.[10]

The course of the reaction is influenced by various factors. Generally speaking, the "normal" condensation reaction occurs with relatively reactive halides. Thus, alkyl halides do not react appreciably with Grignard reagents at room temperature.[17] Allyl halides, on the other hand, give the "normal" product in high yield under mild conditions. Regier and Blue[18] applied this reaction to synthesize 1-butene



$$\begin{tikzcd} \overset{*}{C}H_3OH \arrow[r, "HI"] & \overset{*}{C}H_3I \arrow[r, "Mg", "ether"'] & \overset{*}{C}H_3MgI \arrow[d, "CH_2{=}CH{-}CH_2{-}Br"] \\ & & CH_2{=}CH{-}CH_2{-}\overset{*}{C}H_3 \qquad (63\%) \end{tikzcd}$$

---

[16] M. S. Kharasch, D. W. Lewis, and W. B. Reynolds, ibid., 65, 493 (1943).

[17] M. S. Kharasch, F. L. Lambert, and W. H. Urry, J. Org. Chem., 10, 298 (1945).

[18] R. B. Regier and R. W. Blue, ibid., 14, 505 (1949).

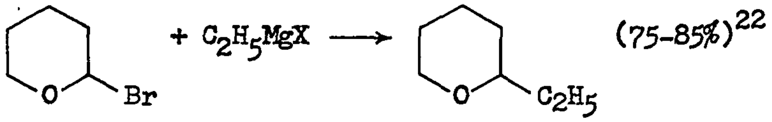
labelled with C^{14} in the 4-position. Bert[19] reported the reaction of 1,3-dichloropropene with phenylmagnesium bromide which gave an almost quantitative yield of 1-chloro-3-phenylpropene.

α-Haloethers give the "normal" products in many cases.

$$C_2H_5\text{-O-}CH_2\text{-Cl} + \text{Ph-}CH_2\text{-MgCl} \longrightarrow \text{Ph-}CH_2\text{-O-}C_2H_5\ (53\text{-}92\%)$$

$$+\ 2\text{-}CH_3\text{-Ph-}CH_2\text{-O-}C_2H_5\ (16\text{-}2\%)$$

$$+\ 4\text{-}CH_2\text{-Ph-}CH_2\text{-O-}C_2H_5\ (31\text{-}6\%)^{20,\ 21}$$



Diphenylmethyl bromide gave the "normal" condensation product in a yield of 85% with methylmagnesium bromide, but with ethylmagnesium iodide the "coupling" product, s-tetraphenylethane, was the major product.[12] The reaction of triphenylmethyl chloride with methylmagnesium bromide also resulted in a high yield (95%) of 1,1,1-triphenylethane.[12]

Grignard et al.[23] reported that ethynylmagnesium bromide reacted with n-butyl bromide to give the "normal" product.

$$n\text{-}C_4H_9Br + H\text{-}C{\equiv}C\text{-MgBr} \longrightarrow n\text{-}C_4H_9\text{-}C{\equiv}C\text{-H}\ (72\%)$$

---

[19] M. L. Bert, Compt. rend., 180, 1504 (1925).

[20] H. Gilman and J. E. Kirby, J. Am. Chem. Soc., 54, 345 (1932).

[21] L. Malm and L. Summers, ibid., 73, 362 (1951).

[22] R. Paul, Compt. rend., 198, 1246 (1934).

[23] V. Grignard, L. Lapayre, and Tchéou Faki, Compt. rend. 187, 517 (1928); Bull. soc. chim., Series 4, 43, 931 (1928).

Binaghi and Oddo[24, 25, 26] reported the reactions of ethylmagnesium bromide and phenylmagnesium bromide with haloforms and carbon tetrachloride. The reactions were very complex, except in the case of the reaction of phenylmagnesium bromide with chloroform, where triphenylmethane was the only product.[27] When phenylmagnesium bromide was reacted with iodoform and carbon tetrachloride, there were obtained, among other products, s-tetraphenylethane and hexaphenylethane, respectively. Apparently, in these reactions the "normal" reaction was followed by the "coupling" reaction.

Although the halogen-metal interconversion reaction is often observed in the reactions of organolithium and organosilyllithium compounds with organic halides, the analogous reaction of Grignard reagents is a rather rare phenomenon. Indeed, Gilman and Jones[28] found that no such interconversion occurs when the following Grignard reagents and organic halides are heated together.

---

[24] B. Oddo and R. Binaghi, Gazz. chem. ital., 51, No. 2, 330 (1921). (Original available but not translated; abstracted in C. A., 16, 1392 (1922)).

[25] R. Binaghi, ibid., 52, No. 2, 132 (1922). (Original available but not translated; abstracted in C. A., 17, 1425 (1923)).

[26] R. Binaghi, ibid., 53, 879 (1923). (Original available but not translated; abstracted in C. A., 18, 1488 (1924)).

[27] This reaction was reported earlier by Reychler, who obtained triphenylmethane in a yield of 70-80%. A. Reychler, Bull. soc. chim., Series 3, 35, 737 (1906).

[28] H. Gilman and H. L. Jones, J. Am. Chem. Soc., 51, 2840 (1929).

(a) $PhCH_2MgBr + PhBr$

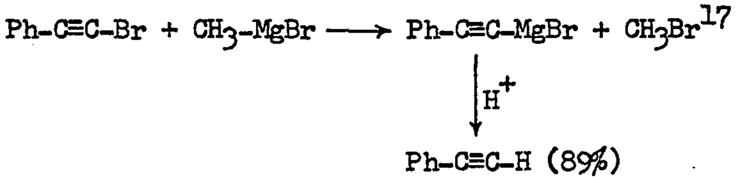
(b) $Ph_3CMgCl + PhBr$

(c) $PhMgBr + PhCH_2Cl$

(d) $PhMgBr + Ph_3CCl$

(e) $PhCH_2MgBr + Ph_3CCl$

Later Kharasch *et al.*[29] confirmed their finding. One exception is found in the reaction of Grignard reagents with ethynyl halides.



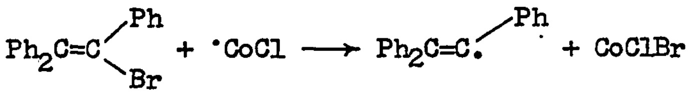
$$Ph\text{-}C{\equiv}C\text{-}Br + CH_3\text{-}MgBr \longrightarrow Ph\text{-}C{\equiv}C\text{-}MgBr + CH_3Br^{17} \xrightarrow{H^+} Ph\text{-}C{\equiv}C\text{-}H\ (89\%)$$

It is of interest that the presence of a small amount of cobaltous chloride induced the functional interchange reactions in many cases.[29] Kharasch suggested that the mechanism in such cases is different from that of the normal interchange reactions and is free-radical in nature.

(1) $\underline{n}\text{-}C_4H_9MgBr + CoCl_2 \longrightarrow \underline{n}\text{-}C_4H_9CoCl + MgBrCl$

(2) $2\ \underline{n}\text{-}C_4H_9CoCl \longrightarrow C_4H_{10} + C_4H_8 + 2\ {}^{\cdot}CoCl$

(3)



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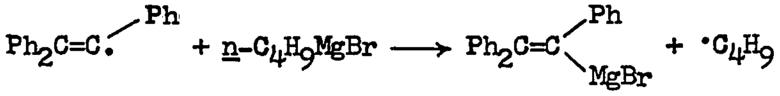
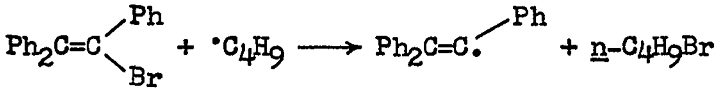
[29] M. S. Kharasch and C. F. Fuchs, *J. Org. Chem.*, 10, 292 (1945).

(4) 

$$Ph_2C{=}\dot{C}{-}Ph + \underline{n}\text{-}C_4H_9MgBr \longrightarrow Ph_2C{=}C\begin{matrix}Ph\\ MgBr\end{matrix} + \cdot C_4H_9$$

(5) 

$$Ph_2C{=}C\begin{matrix}Ph\\ Br\end{matrix} + \cdot C_4H_9 \longrightarrow Ph_2C{=}\dot{C}{-}Ph + \underline{n}\text{-}C_4H_9Br$$

Metallic halides affect the reactions of Grignard reagents with organic halides in a number of ways. The "coupling" reaction is greatly enhanced in their presence.[30, 31] Functional exchange reactions occur in some cases as cited above. Another important effect some of the metallic halides have upon Grignard reactions is that some Grignard reagents condense with vinyl halides and also with ethynyl halides. Thus, phenylmagnesium bromide reacts with vinyl chloride in the presence of a small amount of cobaltous chloride to give styrene in 50-75% yield.[32]

$$PhMgBr + CH_2{=}CHCl \xrightarrow{\text{no cat.}} \text{no reaction}$$

$$PhMgBr + CH_2{=}CHCl \xrightarrow{CoCl_2} Ph{-}CH{=}CH_2\ (50\text{-}75\%) + MgBrCl$$

When bromophenylacetylene was treated with methylmagnesium bromide in the presence of cobaltous chloride, 1-phenylpropyne was obtained in a yield of 41%.[33]

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[30] H. Gilman and M. Lichtenwalter, *J. Am. Chem. Soc.*, *61*, 957 (1939).

[31] M. S. Kharasch and E. K. Fields, *ibid.*, *63*, 2316 (1941).

[32] M. S. Kharasch and C. F. Fuchs, *ibid.*, *65*, 504 (1943).

[33] H. K. Black, H. S. Horn, and B. C. L. Weedon, *J. Chem. Soc.*, *1954*, 1704.

$$\text{Ph-C}\equiv\text{C-Br} + \text{CH}_3\text{MgBr} \xrightarrow{\text{CoCl}_2} \text{Ph-C}\equiv\text{C-H (34\%)}$$

$$+ \text{Ph-C}\equiv\text{C-CH}_3 \text{ (41\%)} + \text{Ph-C}\equiv\text{C-C}\equiv\text{C-Ph}$$

Armitage et al.[34] synthesized dodeca-3,5,7,9-tetrayne in a 47% yield by refluxing in ether the acetylenic Grignard reagent of hexa-1,3-diyne in the presence of cupric bromide.

A few cases of condensation reactions of acetylenic Grignard reagents with ethynyl halides without any catalyst are reported in the literature.

$$\text{Ph-C}\equiv\text{C-MgI} + \text{Ph-C}\equiv\text{C-I} \longrightarrow \text{Ph-C}\equiv\text{C-C}\equiv\text{C-Ph} + \text{MgI}_2{}^{35}$$

$$\underline{n}\text{-C}_5\text{H}_{11}\text{C}\equiv\text{C-MgI} + \underline{n}\text{-C}_5\text{H}_{11}\text{C}\equiv\text{C-I} \longrightarrow (\underline{n}\text{-C}_5\text{H}_{11}\text{C}\equiv\text{C-})_2 + \text{MgI}_2{}^{35}$$

$$\text{Ph-C}\equiv\text{C-MgCl} + \text{Cl-C}\equiv\text{C-Cl} \longrightarrow \text{Ph-C}\equiv\text{C-C}\equiv\text{C-Cl} + \text{MgCl}_2{}^{36}$$

B. Reactions of Organolithium Compounds with Organic Halides

The reactions of organolithium compounds with organic halides may be divided into three main types: the condensation reaction; the halogen-metal interconversion reaction; and the metalation reaction.

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[34] J. B. Armitage, E. R. H. Jones, and M. C. Whiting, ibid., 1952, 2014.

[35] V. Grignard and Tchéon Faki, Bull. soc. chim., Series 4, 43, 42 (1928).

[36] H. G. Viehe, Ber., 92, 3064 (1959).

1. The condensation reaction

A division of the "normal" reaction and the "coupling" reaction, which is so important with Grignard reactions, has little significance in the reactions of organolithium compounds with organic halides.

Under ordinary conditions organolithium compounds do not undergo "coupling" reactions. However, Kharasch *et al.*[37, 38] demonstrated that in the presence of catalytic amounts of cobaltous halide the "coupling" reaction does take place. When *n*-butyllithium was allowed to react with bromobenzene for 44 hours in the absence of a catalyst, *n*-butylbenzene was obtained in 52% yield. In the presence of cobaltous chloride, however, the products were benzene (10%), biphenyl (50%), *n*-butylbenzene (4%), bromobenzene (20%), a mixture of butane and 1-butene (35%), and *n*-octane (27%). In the case of the reaction of phenyllithium with *n*-butyl bromide, the condensation product was obtained in 55% yield in the absence of the catalyst; biphenyl (67%) and *n*-octane (40%) were the major products when a catalyst was present.

The question of whether the reactions of organolithium compounds with organic halides proceeds *via* an ionic or a free radical mechanism has received considerable attention.[39]

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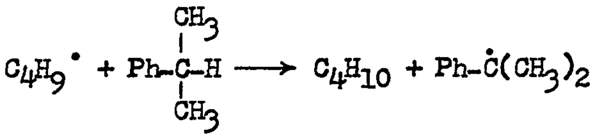
[37] M. S. Kharasch, D. W. Lewis, and W. B. Reynolds, *J. Am. Chem. Soc.*, *65*, 498 (1943).

[38] M. S. Kharasch and W. B. Reynolds, *ibid.*, *63*, 3239 (1941).

[39] For a general discussion of the subject, see E. A. Braude. Organic compounds of lithium. In J. W. Cook, ed. Progress in Organic Chemistry. Vol. 3, pp. 172-217. New York, N.Y., Academic Press, Inc., Publishers. 1955.

Evidence for both mechansims has accumulated. Several workers[40, 41, 42, 43] favor the ionic mechanism in view of their studies, done either kinetically or using optically active halides. Bryce-Smith,[44] on the other hand, has concluded that the condensation reaction proceeds largely by a free radical path. He demonstrated this fact by capturing free radicals with isopropylbenzene. In a typical run, *n*-butyllithium and *n*-butyl halide were allowed to react in isopropylbenzene at 95°. The major products obtained were 2,3-dimethyl-2,3-diphenylbutane (9-18%), and octane (29-50%). He postulated the following mechanism for the formation of 2,3-dimethyl-2,3-diphenylbutane.



$$C_4H_9^{\bullet} + Ph\text{-}\overset{CH_3}{\underset{CH_3}{C}}\text{-}H \longrightarrow C_4H_{10} + Ph\text{-}\dot{C}(CH_3)_2$$

$$2\ Ph\text{-}\dot{C}(CH_3)_2 \longrightarrow Ph\text{-}C(CH_3)_2\text{-}C(CH_3)_2\text{-}Ph$$

2. The halogen-metal interconversion reaction

The halogen-metal interconversion reaction was discovered

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[40] R. L. Letsinger, *J. Am. Chem. Soc.*, *72*, 4842 (1950).

[41] S. J. Cristol, J. W. Ragsdale, and J. S. Meek, *ibid.*, *73*, 810 (1951).

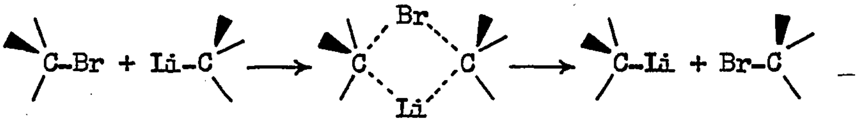
[42] S. J. Cristol, W. C. Overhults, and J. S. Meek, *ibid.*, *73*, 813 (1951).

[43] H. D. Zook and R. N. Goldey, *ibid.*, *75*, 3975 (1953).

[44] D. Bryce-Smith, *J. Chem. Soc.*, *1956*, 1603.

independently by Gilman and co-workers[45, 46] and by Wittig and his associates.[47] Since then it has been studied extensively and was reviewed by Gilman and Jones.[48]

The mechanism of the reaction is generally viewed as a nucleophilic attack by the anion of the organometallic compound on the positively polarized halogen atom.[48] The fact that the exchange occurred with some retention of the configuration at the carbon atom originally linked to halogen[40, 49] suggests the following transition state.[39]



Since the interconversion reaction depends largely on the polarizability of the halogen atoms, it is most often observed with iodides and bromides, less often with chlorides, and not at all with fluorides.[48]

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[45] H. Gilman, W. Langham, and A. L. Jacoby, J. Am. Chem. Soc., 61, 106 (1939).

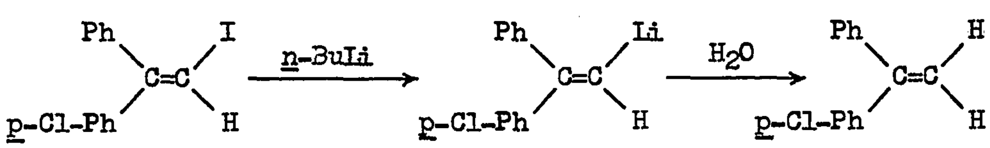
[46] H. Gilman and A. L. Jacoby, J. Org. Chem., 3, 108 (1938).

[47] G. Wittig, U. Pockels, and H. Dröge, Ber., 71, 1903 (1938).

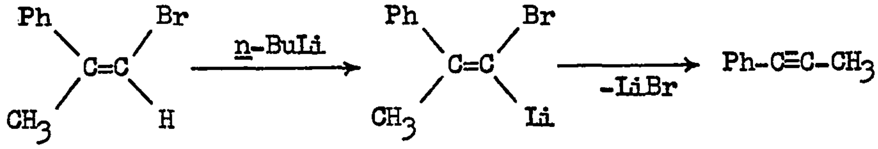
[48] R. G. Jones and H. Gilman. The halogen-metal interconversion reaction with organolithium compounds. In R. Adams, ed. Organic Reactions. Vol. 6, pp. 339-366. New York, N.Y., John Wiley and Sons, Inc. 1951.

[49] H. M. Walborsky and F. J. Impastato, J. Am. Chem. Soc., 81, 5835 (1959).

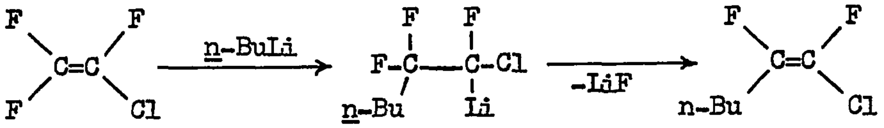
Where vinyl halides are concerned, metalation and addition reactions compete with halogen metal interconversion reactions, depending on the nature of halogen.



[50]



[51]



[52]

With polyhalomethanes and related compounds, metalation seems to occur more readily than halogen-metal interconversion when α-hydrogen is present. When no active hydrogen is available, however, such a compound undergoes the interconversion reaction.

Thus, Miller and Kim[53] demonstrated the formation of

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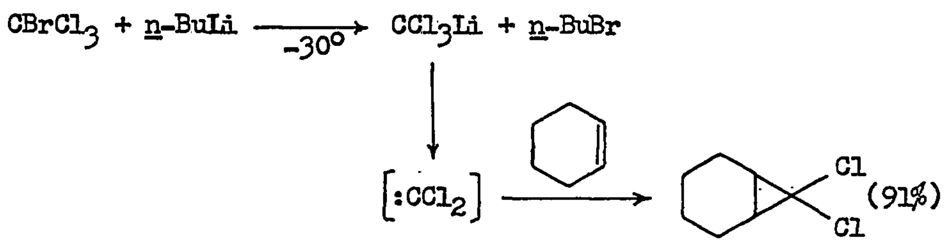
[50] J. W. Crump, Dissertation Abstract, 17, 977 (1957).

[51] D. Y. Curtin and J. W. Crump, J. Am. Chem. Soc., 80, 1922 (1958).

[52] S. Dixon, J. Org. Chem., 21, 400 (1956).

[53] W. T. Miller, Jr. and C. S. Y. Kim, J. Am. Chem. Soc. 81, 5008 (1959).

dihalocarbenes[54, 55] from tetrahalomethanes upon treatment with methyl- or *n*-butyllithium.



The reaction of iodotrifluoromethane with methyllithium at -74° resulted in the formation of tetrafluoroethylene.[56]

$$\begin{tikzcd}
CF_3I + CH_3Li \arrow[r, "-74^\circ"'] & CF_3Li + CH_3I \arrow[d] & \\
& {[:CF_2]} \arrow[r, "{[:CF_2]}"] & F_2C{=}CF_2
\end{tikzcd}$$

When heptafluoro-1-iodopropane was treated with organolithium compounds at -74° in ether, heptafluopropyllithium was formed.[56] Acid hydrolysis at 0° gave heptafluoropropane in 64% yield. When the solution was refluxed for half an hour, lithium fluoride was eliminated to form hexafluoropropene (77%).

Moore and Ward[57] reported the synthesis of various allenes by

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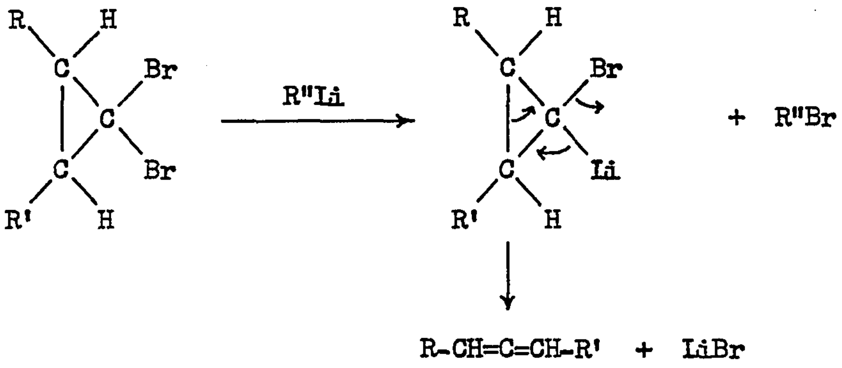
[54] J. Hine, *ibid.*, *72*, 2438 (1950).

[55] W. von E. Doering and A. K. Hoffman, *ibid.*, *76*, 6162 (1954).

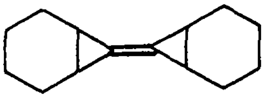
[56] O. R. Pierce, E. T. McBee, and G. F. Judd, *ibid.*, *76*, 474 (1954).

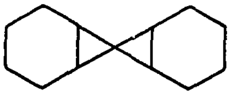
[57] W. R. Moore and H. R. Ward, *J. Org. Chem.*, *25*, 2073 (1960).

treating gem-dibromocyclopropanes with methyl- or n-butyllithium in ether at 0° to -80°.[58]



In these reactions no evidence of a carbene intermediate has been found in experiments employing cyclohexene as a trapping agent. When, however, 7,7-dibromobicyclo [4.1.0] -heptane was treated in an ether-cyclohexene mixture at -80°, three products were isolated.[57] The structures, 7,7'-{bicyclo [4.1.0] heptylidene} (I) and 7,7'-spirobi-{bicyclo [4.1.0] heptane} (II), were assigned to two of them. In the absence of cyclohexene, (I) was obtained, but the other two compounds were not formed.


(I)


(II)

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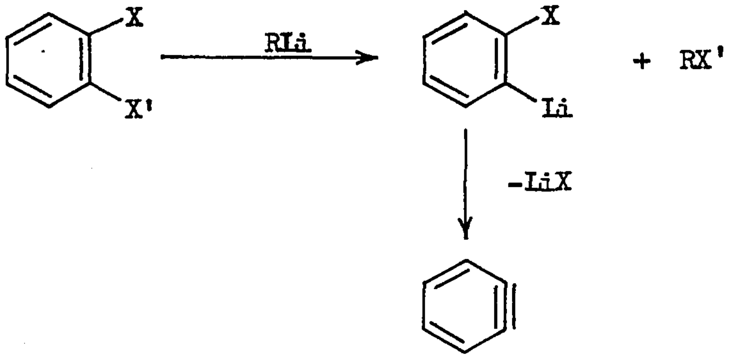
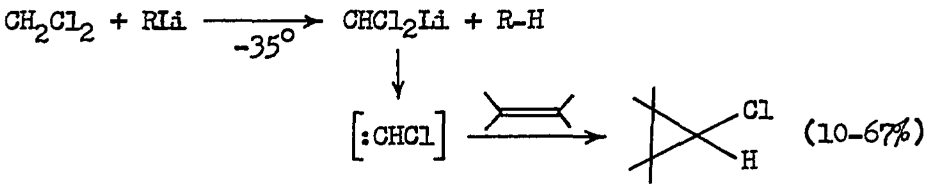
[58] Analogous reactions are brought about by the use of an active metal such as sodium. See W. von E. Doering and P. M. LaFlamme, Tetrahedron, 2, 75 (1958).

The formation of benzyne[59] is often brought about by halogen-metal interconversion as the first step with o-dihalobenzenes.



3. The metalation reaction

The success of Closs and Closs in the synthesis of various chlorocyclopropanes[60, 61] rests on the fact that metalation rather than halogen-metal interconversion occurs when methylene chloride is treated with organolithium compounds. With methylene bromide, carbene is formed after an initial halogen-metal interconversion.[53]



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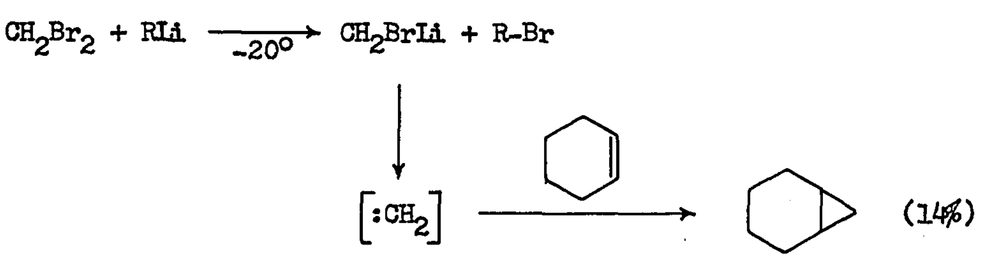
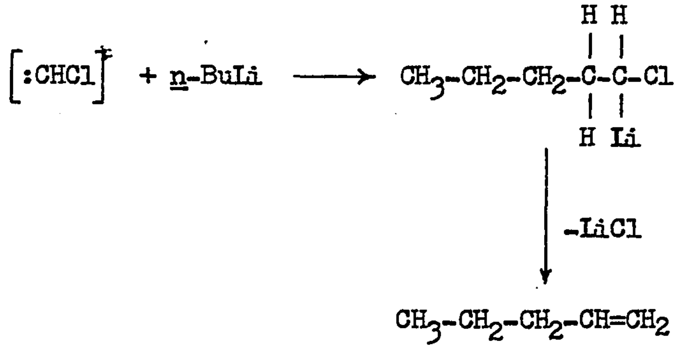
[59] For a comprehensive review of benzyne chemistry see R. Huisgen. Benzyne chemistry. In H. Zeiss, ed. Organometallic Chemistry. pp. 36-87. New York, N.Y., Reinhold Publishing Corporation. 1960.

[60] G. L. Closs and L. E. Closs, J. Am. Chem. Soc., 81, 4996 (1959).

[61] G. L. Closs and L. E. Closs, ibid., 82, 5723 (1960).



In the absence of an olefin, chlorocarbene reacted with n-butyllithium to give 1-pentene in 82% yield.[60]



$$[:CHCl]^{\ddagger} + \underline{n}\text{-BuLi} \longrightarrow CH_3-CH_2-CH_2-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{Li}{C}}-Cl \xrightarrow{-LiCl} CH_3-CH_2-CH_2-CH{=}CH_2$$

The reaction of n-butyllithium with 1-chloro-2,3-dimethyl-2-butene in tetrahydrofuran at -15° gave 1,3,3-trimethylcyclopropene in 16% yield.[62] The same compound was obtained from the reaction of 1,2-dimethylpropenyllithium with methylene chloride[63] and also from the action of sodium methoxide on the tosylhydrazone of 2,3-dimethyl-2-butenal.[62] A common intermediate, an alkenylcarbene, was postulated for these reactions.[62]

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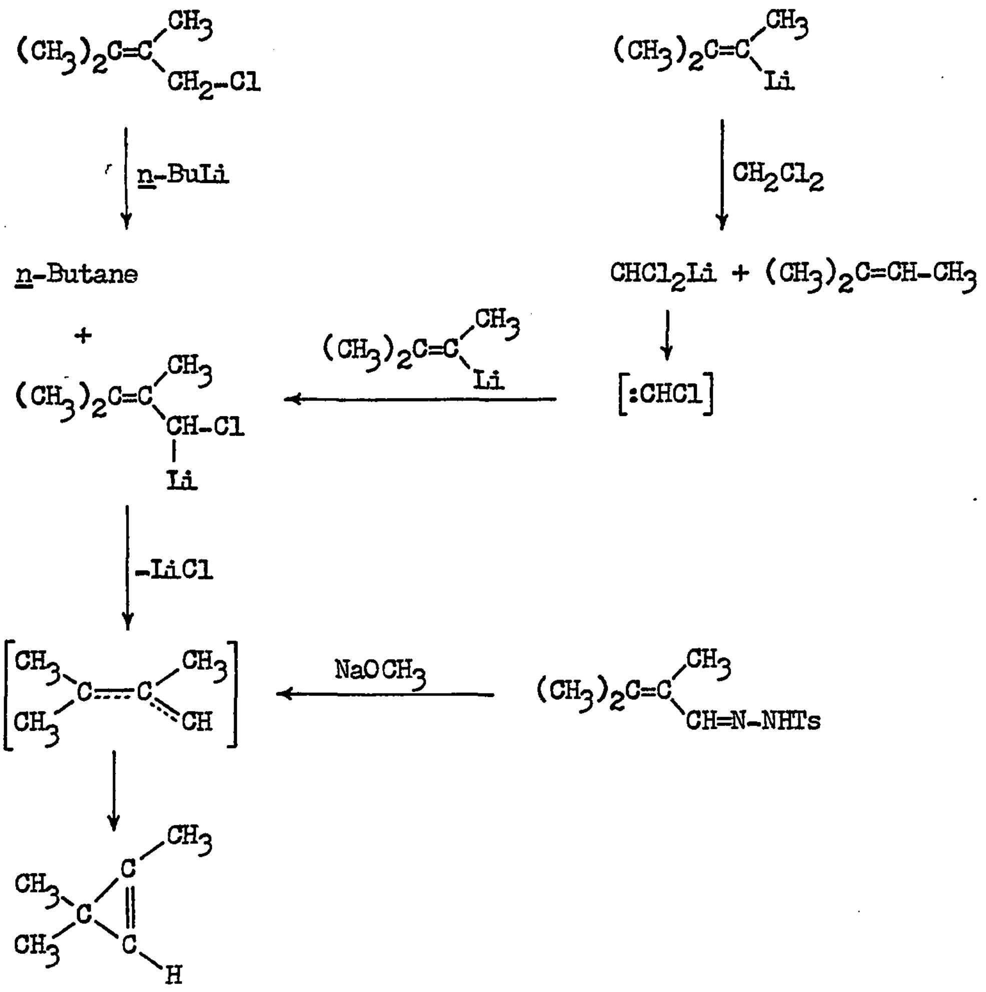
[62] G. L. Closs and L. E. Closs, ibid., 83, 2015 (1961).

[63] G. L. Closs and L. E. Closs, ibid., 83, 1003 (1961).



It was pointed out earlier that some vinyl halides undergo metalation and a subsequent elimination of lithium halides, giving rise to acetylenes.

Cristol and Helmreich[64] proposed the abstraction of α-hydrogen by

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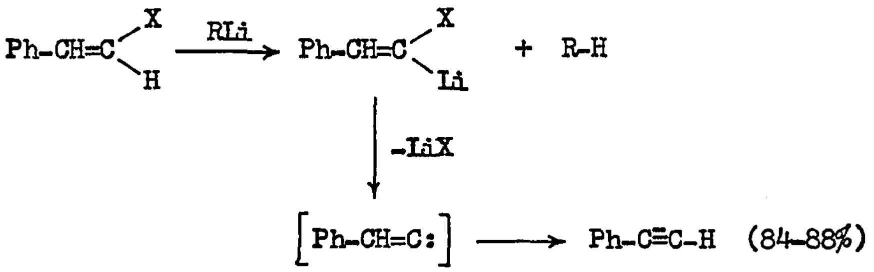
[64] S. J. Cristol and R. F. Helmreich, *ibid.*, *77*, 5034 (1955).

organolithium compounds as the first step for the reactions of *cis*- and *trans*- β -halostyrenes.



When 1-bromopropene was allowed to react with *n*-butyllithium, 1-phenyl-2-butyn-1-ol was obtained in 75% yield after treatment with benzaldehyde.[51]

The low reactivity of 2-chloro-1-phenyl-1-propene with phenyllithium[65] lends some support to Cristol's α-elimination mechanism;[64] however, 1-chlorocyclohexene is more reactive toward organolithium compounds.[66, 67] In this case a highly strained intermediate, cyclohexyne,[67] may be responsible for the greater reactivity.

In the aromatic system, the *ortho*-hydrogens, activated by the presence of electronegative halogens, may undergo metalation reactions readily. This fact is particularly true of fluoro compounds. The intermediates, *o*-lithiohalobenzenes, may eliminate lithium halides to form benzyne.[59]

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[65] G. Wittig and G. Harborth, *Ber.*, *77B*, 315 (1944).

[66] G. Wittig and G. Harborth, *ibid.*, *77B*, 306 (1944).

[67] F. Scardiglia and J. D. Roberts, *Tetrahedron*, *1*, 343 (1957).

C. Reactions of R_3ELi[68] Compounds with Organic Halides

1. Reactions of triphenylsilyllithium with aryl halides[4, 69]

Huisgen and Sauer[59, 70] made kinetic studies of benzyne formation from halobenzenes with phenyllithium and found that the rate constant for fluorobenzene is ten times greater than for chloro-, bromo-, and iodobenzenes, the latter three compounds having rate constants of approximately the same magnitude.

The reaction of triphenylsilyllithium with fluorobenzene resulted in the formation of tetraphenylsilane in a 50% yield with no hexaphenyldisilane being obtained. The reactions with chloro-, bromo-, and iodobenzenes under similar conditions, however, yielded hexaphenyldisilane (66-76%), the product resulting from a prior halogen-metal interconversion reaction, and tetraphenylsilane (12-20%), the apparent coupling product.

These results are in accordance with Huisgen's findings as stated above and Gilman's generalization[48] as to the nature of halogens for the halogen-metal interconversion reactions with organolithium compounds.

2. Reactions of triphenylgermyllithium with organic halides

Very little work has been done on the reactions of

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[68] E = Si, Ge, Sn, Pb.

[69] G. Dappen, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Information concerning reactions of triphenylsilyllithium with halobenzenes. Private communication. 1960.

[70] R. Huisgen and J. Sauer, Ber., 92, 192 (1959).

organogermyllithium compounds with organic halides. Gerow[71] treated triphenylgermyllithium with methyl iodide and ethyl bromide to obtain the coupling products, methyltriphenylgermane (27%) and ethyltriphenylgermane (40%), respectively.

3. Reactions of triaryl- and trialkyltin-lithium with organic halides

Gilman and Rosenberg[72] reported the preparation of triphenyltin-lithium from stannous chloride and phenyllithium. The reactions of triphenyltin-lithium so prepared with benzyl chloride and ethyl iodide yielded fairly large amounts (60 and 27%, respectively) of tetraphenyltin, as well as some coupling products, benzyltriphenyltin (21.7%) and ethyltriphenyltin (36.4%).

Recently, however, triphenyltin-lithium was prepared from the reaction of triphenyltin chloride with lithium in tetrahydrofuran[73] and by lithium cleavage of hexaphenylditin in tetrahydrofuran.[73] Triphenyltin-lithium prepared by these methods reacted with benzyl chloride to give benzyltriphenyltin in a 72.5% yield with no tetraphenyltin formation.[74]

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

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

[73] O. Marrs, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Information concerning preparation of triphenyltin-lithium. Private communication. 1961.

[74] S. Y. Sim, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Information concerning reactions of triphenyltin-lithium with some organic halides. Private communication. 1961.

Reactions with allyl chloride and allyl bromide yielded allyltriphenyltin (70 and 43%, respectively) and hexaphenylditin (4.4 and 9.1%, respectively).[74]

The formation of tetraphenyltin in the reactions employing triphenyltin-lithium prepared by the earlier method[71, 75, 76] may be inherent in the preparative process.

The halogen-metal interconversion was observed in the reactions of triphenyltin-lithium with o-substituted iodobenzenes.[74] Thus, when the mixture of triphenyltin-lithium and 2,6-dimethyliodobenzene was carbonated after ten minutes of stirring, 2,6-dimethylbenzoic acid was obtained in a 18.7% yield. When the reaction mixture was stirred for 18 hours, some hexaphenylditin, as well as 2,6-dimethylphenyltriphenyltin (34.1%), was isolated. Hexaphenylditin undoubtedly resulted from the reaction of triphenyltin-lithium with triphenyltin chloride which was formed as a result of halogen-metal interconversion.

Gilman and Rosenberg[77] also prepared trialkyltin-lithium compounds from stannous chloride and phenyllithium. Some tetraalkyltin compounds were isolated in the reactions employing trialkyltin-lithium prepared in this way. When tri-n-butyltin-lithium was refluxed with iodobenzene in ether for 24 hours, tri-n-butylphenyltin (27.6%) and tetra-n-butyltin (27.8%) were obtained.

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

[76] H. Gilman and S. D. Rosenberg, ibid., 18, 1554 (1953).

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

4. Reactions of triphenyllead-lithium with organic halides

Triphenyllead-lithium was prepared by Gilman *et al.*[78] from phenyllithium and lead dichloride in ether and recently by Marrs[79] from the reaction of triphenyllead chloride with lithium in tetrahydrofuran. The reactions with alkyl halides resulted in the coupling products in good yields.

$$\mathrm{Ph_3PbLi + Ph\text{-}CH_2\text{-}Cl \longrightarrow Ph_3Pb\text{-}CH_2\text{-}Ph}\ (69 \text{ and } 78\%)^{78,\ 79}$$

$$\mathrm{Ph_3PbLi + CH_3\text{-}CH_2\text{-}CH_2\text{-}Br \longrightarrow Ph_3Pb\text{-}CH_2\text{-}CH_2\text{-}CH_3}\ (58\%)^{78}$$

$$\mathrm{2Ph_3PbLi + Br\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}Br \longrightarrow Ph_3Pb\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}PbPh_3}\ (58\%)^{80}$$

Triphenyltin-lithium and triphenyllead-lithium which are prepared from phenyllithium with stannous chloride and lead dichloride are believed to exist in equilibrium with phenyllithium and diphenyltin and diphenyllead, respectively.[78, 81]

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

[79] O. Marrs, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Information concerning preparation and reaction of triphenyllead-lithium. Private communication. 1961.

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

[81] J. d'Ans, H. Zimmer, E. Endrulat, and K. Lubke, Naturwiss., 39, 450 (1952).

III. EXPERIMENTAL

A. General Considerations

Triphenylsilyllithium was prepared from hexaphenyldisilane by lithium cleavage in tetrahydrofuran (THF)[82] according to a published procedure.[1] Common Grignard reagents and organolithium compounds were prepared by standard methods.

Reactions involving organosilylmetallic or organometallic compounds in general were carried out in oven-dried glassware under an atmosphere of dried, oxygen-free nitrogen. The equipment was assembled while hot and the apparatus was swept with a brisk stream of nitrogen while cooling.

Diethyl ether, when employed as a solvent for organometallic reactions, was sodium dried. The tetrahydrofuran used in the same capacity was dried and purified by refluxing it over sodium wire for at least 24 hours, followed by distillation into a refluxing suspension of lithium aluminum hydride under dry, nitrogen atmosphere. The solvent was distilled from this suspension immediately before use.

The reaction mixture was worked up in general according to the procedure described below. It was hydrolyzed with dilute sulfuric acid in a separatory funnel. Some ether was added. The water layer was drawn out and the organic layer was washed twice with water. Drying of the organic layer was performed by shaking it with anhydrous sodium sulfate. The

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[82] Tetrahydrofuran will be abbreviated as THF for the remainder of the dissertation.

organic layer was transferred to an Erlenmeyer flask and the solvent was evaporated on a steam bath with the aid of an air-jet.

The residue was treated with petroleum ether (b.p. 60-70°) and poured onto a well-packed alumina (80-200 mesh) column for a chromatographic separation. Eluants used after petroleum ether (b.p. 60-70°) were, in order, carbon tetrachloride, acetone, and methanol.

Melting points and boiling points are in degrees centigrade and are uncorrected. Generally, melting points less than 300° were taken in an electrically heated oil-bath, while those above 300° were determined using a copper block which was heated by a gas flame.

The infrared spectra were taken usually in carbon disulfide solution, but for compounds containing double bonds chloroform solution was used in the region of 6-7μ, and for those containing triple bonds carbon tetrachloride solution was used in the region of 4-5μ.

Silicon analysis was carried out by an improved procedure which is described in detail below.

A sample weighing between 0.10 g. and 0.15 g. is placed in a platinum crucible. The lid of the crucible is so fitted that a very small opening may be formed. This is best done by lowering one side of the lid a few millimeters below the edge of the crucible. Acids are introduced through this opening drop by drop from a medicine dropper. During the addition the lid should never be opened.

The crucible is placed on a ring burner. Ten to fifteen drops of concentrated sulfuric acid are now introduced into the crucible. Then, three to five drops of concentrated nitric acid are cautiously added through the opening. In most cases, the reaction occurs in a fraction of a minute. If not, the crucible is heated gently. After the reaction has started, the crucible is heated until all of the nitric acid evaporates and white fumes start coming off, usually about a minute. As soon as the crucible is cooled, about one milliliter of concentrated nitric acid is added drop by drop, and the crucible is heated again. This is the critical stage. Heating must be controlled so that no foaming occurs and yet a reasonable rate of evaporation of nitric acid is maintained. Only a small amount of sulfuric acid is allowed to evaporate at this time. The crucible is cooled again and another milliliter of nitric acid is added. The nitric acid and some of the sulfuric acid are again evaporated. If there is no danger of foaming, relatively strong heat can be applied. After the fourth or fifth addition of nitric acid, almost all of the sulfuric acid is evaporated. In most cases, the residue is gray or almost white by this time. Addition of nitric acid and its evaporation are repeated until the residue becomes pure white. In the later stages, addition of as much as two milliliters of nitric acid is not harmful.

The above process takes about twenty minutes to one hour. After the residue becomes white, the crucible is blasted as usual.

With this procedure the author experienced only one minor foaming case. The use of fuming nitric acid is contraindicated.

B. Reactions of Triphenylsilyllithium with Alkyl Halides

1. Reaction of triphenylsilyllithium with n-butyl chloride

A solution of triphenylsilyllithium (0.05 mole) was added dropwise to 4.65 g. (0.05 mole) of n-butyl chloride. The reaction was exothermic and Color Test I[83] was negative immediately after the addition. A work-up of the reaction mixture by the general procedure gave a solid residue which was crystallized from methanol, yielding 11.8 g. (75%) of n-butyltriphenylsilane, m.p. 89-90°; this compound was identified by a mixed melting point determination with an authentic sample and by comparison of infrared spectra.

2. Reaction of triphenylsilyllithium with n-butyl bromide

A solution of triphenylsilyllithium (0.02 mole) was added dropwise to 2.74 g. (0.02 mole) of n-butyl bromide in 70 ml. of THF at room temperature. Color Test I was negative immediately after the addition. Subsequent to hydrolysis with dilute acid, hexaphenyldisilane, 3.00 g. (57.9%), was separated by filtration. The organic layer was worked up in the usual manner, followed by chromatography on alumina. Elution with petroleum ether (b.p. 60-70°) gave 1.75 g. (27.5%) of n-butyltriphenylsilane, m.p. 90-91° (mixed m.p.).

3. Reaction of triphenylsilyllithium with n-dodecyl chloride

A solution of triphenylsilyllithium (0.026 mole) was added dropwise

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

to 5.30 g. (0.026 mole) of n-dodecyl chloride. Color Test I was negative immediately after the addition. Work-up of the reaction mixture in the usual manner gave a solid residue which was recrystallized twice from methanol to yield 3.20 g. (28.7%) of n-dodecyltriphenylsilane, m.p. 65-67°. A mixed melting point with an authentic sample was not depressed.

4. Reaction of triphenylsilyllithium with allyl chloride

A solution of triphenylsilyllithium (0.025 mole) was added dropwise to 1.91 g. (0.025 mole) of allyl chloride. The reaction was exothermic and Color Test I was negative immediately after the addition. The solid residue obtained after the usual work-up was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave 4.20 g. (56%) of allyltriphenylsilane, m.p. 90-91°, after recrystallization from petroleum ether (b.p. 60-70°). This compound was identified by a mixed melting point determination with an authentic sample and by comparison of infrared spectra.

5. Reaction of triphenylsilyllithium with cyclopentyl chloride

A solution of triphenylsilyllithium (0.05 mole) was added to 5.23 g. (0.05 mole) of cyclopentyl chloride. The reaction was exothermic, but to a lesser extent than with primary halides. Color Test I was positive when the addition was completed. The reaction mixture was refluxed for 18 hours, at which time Color Test I became negative. Subsequent to hydrolysis, hexaphenyldisilane, 1.2 g. (9.3%), was separated by filtration. The organic layer was worked up by the general procedure and the residue was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave 6.50 g. (40%) of cyclopentyltriphenylsilane, m.p. 112-116°, after recrystallization from ethanol. A mixed melting point with an authentic sample was not depressed and the infrared spectra were identical.

6. Reaction of triphenylsilyllithium with 1,3-dichloropropane

A solution of triphenylsilyllithium (0.05 mole) was added dropwise to 2.83 g. (0.025 mole) of 1,3-dichloropropane. Color Test I was negative immediately after the addition. Work-up of the reaction mixture in the usual manner gave a solid which was recrystallized from petroleum ether (b.p. 60-70°), yielding 10.25 g. (73%) of 1,3-bis(triphenylsilyl)propane, m.p. 132-133.5°. Recrystallization from the same solvent raised the melting point to 133-134°. The infrared spectrum supported the proposed structure of the compound.

Anal. Calcd. for $C_{39}H_{36}Si_2$: Si, 10.02. Found: Si, 10.00, 9.92.

7. Reaction of triphenylsilyllithium with 1,3-dibromopropane

A solution of triphenylsilyllithium (0.04 mole) was added dropwise to 4.04 g. (0.02 mole) of 1,3-dibromopropane. The reaction was exothermic and Color Test I was negative immediately after the addition. Subsequent to hydrolysis, 7.4 g. (71.5%) of hexaphenyldisilane was separated by filtration. A very small amount of the residue, which was obtained after work-up of the organic layer, failed to give any pure product.

8. Reaction of triphenylsilyllithium with methylene chloride

a. Normal addition

(1) Run 1 (1:1) A solution of triphenylsilyllithium (0.08 mole) was added dropwise to 6.8 g. (0.08 mole) of methylene chloride at -60°. The reaction mixture was stirred at this temperature for 2 hours after the addition. It was black and formed a tar-like material. Subsequent to hydrolysis with dilute acid, hexaphenyldisilane, 11.7 g. (56.4%), was separated by filtration. The organic layer was worked up by the general procedure and the residue was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave in the first fraction 5.70 g. (26.0%) of methyltriphenylsilane, m.p. 68-70°, after recrystallization from petroleum ether (b.p. 60-70°). A mixed melting point with an authentic sample was not depressed and the two infrared spectra were superimposable. Further elution with the same solvent gave in the second fraction 0.90 g. (3.6%) of chloromethyltriphenylsilane, m.p. 116-118°, after recrystallization from petroleum ether (b.p. 60-70°). Another recrystallization from the same solvent raised the melting point to 120-122°. Elution with carbon tetrachloride gave 1.10 g. (5.2%) of bis(triphenylsilyl)methane, m.p. 141-142°, after recrystallization from petroleum ether (b.p. 60-70°).

Anal. Calcd. for $C_{37}H_{32}Si_2$: Si, 10.54. Found: Si, 10.49, 10.39.

(2) Run 2 (2:1) A solution of triphenylsilyllithium (0.08 mole) was added dropwise to 3.40 g. (0.04 mole) of methylene chloride at -60°. Color Test I was negative after the addition. The reaction mixture was black as in the case of Run 1. It was worked up by the same

procedure as in Run 1 and the following compounds were isolated: hexaphenyldisilane, 9.45 g. (45.5%); methyltriphenylsilane, 3.75 g. (34.2%); chloromethyltriphenylsilane, 1.05 g. (8.5%); and bis(triphenylsilyl)-methane, 1.15 g. (5.4%).

(3) Run 3 (2:1, in the presence of cyclohexene) A solution of triphenylsilyllithium (0.08 mole) was added dropwise to a mixture of 3.40 g. (0.04 mole) of methylene chloride and 8.1 g. (0.1 mole) of cyclohexene at -60°. Color Test I was slightly positive when the addition was completed. The reaction mixture was a light brown. It was stirred at this temperature for 2 hours at which time Color Test I became negative. Subsequent to hydrolysis, hexaphenyldisilane, 8.30 g. (40.0%), was separated by filtration. The yellow organic layer was dried with sodium sulfate. The solvent was removed by distillation. The mixture was then subjected to fractional distillation, but no product distilled even at 250°. The residue was chromatographed on alumina. The following compounds were isolated: methyltriphenylsilane, 1.70 g. (15.5%); chloromethyltriphenylsilane, 1.45 g. (11.7%); and bis(triphenylsilyl)-methane, 1.30 g. (6.1%).

(4) Run 4 (5:2) A solution of triphenylsilyllithium was added dropwise to 1.70 g. (0.02 mole) of methylene chloride in 20 ml. of THF at room temperature. When 0.04 mole of triphenylsilyllithium had been added, Color Test I was negative, but the color test became positive when 0.052 mole of triphenylsilyllithium had been added. The reaction mixture was worked up by the same procedure as in Run 1. The compounds isolated were hexaphenyldisilane, 4.50 g. (43.5%); methyltriphenylsilane,

1.20 g. (21.9%); and bis(triphenylsilyl)methane, 1.85 g. (17.4%). In addition, a mixture of triphenylsilane and methyltriphenylsilane (1.35 g.) was obtained. Chloromethyltriphenylsilane was not isolated.

b. Reverse addition A solution of methylene chloride in THF was added dropwise to 0.04 mole of triphenylsilyllithium cooled in an ice bath. When 0.02 mole of methylene chloride had been added, Color Test I became negative. The reaction mixture was a brownish black. A work-up by the same procedure as in Run 1 of the previous section gave hexaphenyldisilane, 3.65 g. (35.2%); methyltriphenylsilane, 1.40 g. (25.6%); and bis(triphenylsilyl)methane, 1.25 g. (11.7%).

9. Reaction of triphenylsilyllithium with methylene bromide

a. Normal addition

(1) Run 1 (2:1) A solution of triphenylsilyllithium (0.08 mole) was added dropwise to 6.96 g. (0.04 mole) of methylene bromide at -60°. The reaction mixture was stirred for 5 hours. Color Test I was negative. Subsequent to hydrolysis with dilute acid, hexaphenyldisilane, 12.30 g. (59.4%), was separated by filtration. The organic layer was worked up by the general procedure and the residue was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave in the first fraction 3.55 g. (32.4% based on methylene bromide) of methyltriphenylsilane, m.p. 64-67° (mixed m.p.). Further elution with the same solvent gave 1.35 g. (6.9%) of bromomethyltriphenylsilane, m.p. 121-122.5°, after recrystallization from petroleum ether (b.p. 60-70°).

Anal. Calcd. for $C_{19}H_{17}SiBr$: C, 64.58; H, 4.58; Si, 7.95. Found: C, 63.10, 63.06; H, 4.77, 4.76; Si, 8.04, 7.96.

(2) Run 2 (2:1, in the presence of cyclohexene) A solution of triphenylsilyllithium (0.08 mole) was added dropwise to a mixture of 6.96 g. (0.04 mole) of methylene bromide and 24 g. (0.3 mole) of cyclohexene at -60°. Color Test I was negative after the addition. A work-up by the same procedure as in Run 1 gave hexaphenyldisilane, 8.90 g. (42.5%), and methyltriphenylsilane, 4.35 g. (40.0%).

b. Reverse addition A solution of methylene bromide in THF was added to 0.08 mole of triphenylsilyllithium at -60°. Color Test I became negative when 0.028 mole of methylene bromide had been added. Subsequent to hydrolysis, hexaphenyldisilane, 11.90 g. (57.5%), was separated by filtration. The organic layer was dried with sodium sulfate. The solvent was removed. The residue was treated with petroleum ether (b.p. 60-70°). An insoluble material was separated by filtration. A part of this material melted at 254-260°. This compound has not been identified. The mother liquor was poured onto an alumina column. Elution with the same solvent gave only a trace amount of methyltriphenylsilane.

10. Reaction of triphenylsilyllithium with methylene iodide

A solution of triphenylsilyllithium (0.08 mole) was added dropwise to 10.7 g. (0.04 mole) of methylene iodide at -60°. After an hour's stirring, Color Test I was only slightly positive. Subsequent to hydrolysis, hexaphenyldisilane, 11.80 g. (57.0%), was separated by filtration. The organic layer was worked up by the general procedure and subsequently chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave in the first fraction 3.10 g. (28.3% based on methylene iodide) of methyltriphenylsilane, which was identified by a mixed melting point determination with an authentic sample. Further elution with the same solvent gave 1.00 g. (6.3% based on methylene iodide) of iodomethyltriphenylsilane, m.p. 117-119°, after recrystallization from ethanol.

Anal. Calcd. for $C_{19}H_{17}SiI$: Si, 7.02. Found: Si, 7.07, 6.97. Elution with carbon tetrachloride gave 1.20 g. (5.6%) of bis(triphenylsilyl)methane, m.p. 138-140°. A mixed melting point with a sample obtained from the reaction of triphenylsilyllithium with methylene chloride was not depressed and the two infrared spectra were superimposable.

In another run under similar conditions the products isolated were hexaphenyldisilane (50.0%), methyltriphenylsilane (16.4%), and iodomethyltriphenylsilane (23.0%).

In still another run, when the reaction was carried out at room temperature, the yield of hexaphenyldisilane increased (65.1%), while only small amounts of other products were obtained.

11. Reaction of triphenylsilyllithium with chloroform

a. Normal addition

(1) Run 1 (1:1, room temperature) A solution of triphenylsilyllithium (0.08 mole) was added dropwise to 9.55 g. (0.08 mole) of chloroform at room temperature. The reaction was exothermic and Color Test I was negative immediately after the addition. The mixture was black. Subsequent to hydrolysis with dilute acid, hexaphenyldisilane, 10.7 g. (51.6%), was separated by filtration. The residue obtained after

a work-up of the organic layer in the usual manner was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave in the first fraction 2.35 g. (11.3%) of triphenylsilane. Further elution with the same solvent gave in the second fraction 0.80 g. (3.2%) of chloromethyltriphenylsilane, m.p. 119-120° (mixed m.p.). Elution with carbon tetrachloride gave 0.70 g. (1.7%) of bis(triphenylsilyl)methane, m.p. 137-139° (mixed m.p.).

(2) Run 2 (2:1, -60°) A solution of triphenylsilyllithium (0.08 mole) was added dropwise to 4.78 g. (0.04 mole) of chloroform at -60°. This reaction mixture was stirred for 3 hours at this temperature, during which time Color Test I became negative. It was black and formed a tar-like material. Subsequent to hydrolysis, hexaphenyldisilane, 11.0 g. (53.0%), was separated by filtration. The residue after work-up was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave a mixture of compounds from which 1.60 g. (11.7%) of dichloromethyltriphenylsilane, m.p. 147-148°, was separated by crystallization from petroleum ether (b.p. 60-70°). A mixed melting point with the product obtained from the reaction of triphenylsilyllithium with carbon tetrachloride was not depressed. The mother liquor was poured onto an alumina column to be rechromatographed. Elution with petroleum ether (b.p. 60-70°) gave 0.55 g. (5.3%) of triphenylsilane and 0.08 g. (6.5%) of chloromethyltriphenylsilane. Elution with carbon tetrachloride gave 0.60 g. (2.8%) of bis(triphenylsilyl)methane, m.p. 140-141.5° (mixed m.p.).

b. Reverse addition A solution of 4.78 g. (0.04 mole) of chloroform in 20 ml. of THF was added to 0.08 mole of triphenylsilyllithium at -60°. Color Test I was negative at the end of the addition and the reaction mixture was black. Subsequent to hydrolysis, hexaphenyldisilane, 12.55 g. (60.5%), was separated by filtration. The organic layer was worked up in the usual manner and the residue was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave in the first fraction 1.35 g. (13.0%) of triphenylsilane. Further elution with the same solvent gave in the second fraction 1.60 g. of a mixture of chloro- and dichloromethyltriphenylsilane, m.p. 130-140°. No attempt was made to separate these two. The combined yield was approximately 12%. Further elution with carbon tetrachloride gave 2.20 g. (10.3%) of bis(triphenylsilyl)methane, m.p. 140-141° (mixed m.p.).

12. Reaction of triphenylsilyllithium with bromoform

a. Normal addition

(1) Run 1 (2:1) A solution of triphenylsilyllithium (0.08 mole) was added dropwise over a period of 40 minutes to 10.1 g. (0.04 mole) of bromoform at -60°. Color Test I was negative immediately after the addition. Subsequent to hydrolysis with dilute acid, hexaphenyldisilane, 12.55 g. (60.5%), was separated by filtration. The black organic layer was dried with sodium sulfate. The solvent was removed and the residue was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave 0.35 g. (3.3%) of methyltriphenylsilane which was identified by a comparison of its infrared spectrum with that of an

authentic sample. Elution with carbon tetrachloride gave an oily material in two fractions. The first fraction was treated with petroleum ether (b.p. 60-70°) to give 2.90 g. (20.5% based on bromoform) of bromomethyltriphenylsilane, m.p. 122-123.5°, after recrystallization from the same solvent. A mixed melting point with a sample obtained from the reaction of triphenylsilyllithium with methylene bromide was not depressed. The second fraction was also treated with petroleum ether (b.p. 60-70°) to produce a solid with a wide melting point range, 128-140°. This solid was recrystallized from the same solvent to give 0.70 g. (4.0%) of a compound, possibly dibromomethyltriphenylsilane, m.p. 137-140°. Two more recrystallizations from the same solvent raised the melting point to 150-152°.

Anal. Calcd. for $C_{19}H_{16}SiBr_2$: Si, 6.51. Found: Si, 6.77, 6.69.

In another run under identical conditions the following products were isolated: hexaphenyldisilane (54%); methyltriphenylsilane (0.9%); bromomethyltriphenylsilane (34.0%); and triphenylsilane (0.5%). Dibromomethyltriphenylsilane, however, was not isolated.

(2) Run 2 (8:3) A solution of triphenylsilyllithium (0.08 mole) was added slowly to 7.6 g. (0.03 mole) of bromoform in 50 ml. of ether at -60°. Color Test I was slightly positive at the end of the addition. The reaction mixture, however, was hydrolyzed immediately with dilute acid. Hexaphenyldisilane, 10.1 g. (48.7%), was separated by filtration. The straw colored organic layer was worked up by the same procedure as in Run 1. The products isolated were: methyltriphenylsilane, 0.80 g. (9.7%), m.p. 66-67° (mixed m.p.);

bromomethyltriphenylsilane, 2.60 g. (24.5%), m.p. 121-122.5° (mixed m.p.); and dibromomethyltriphenylsilane, 1.80 g. (13.9%), m.p. 150-152° (mixed m.p.).

b. Reverse addition An ethereal solution of bromoform was added dropwise to 0.08 mole of triphenylsilyllithium at -60°. When 0.03 mole of bromoform had been added, Color Test I became negative. Subsequent to hydrolysis, hexaphenyldisilane, 12.9 g. (62.5%), was separated by filtration. The organic layer was worked up by the same procedure as in Run 1 to give 0.15 g. (1.9%) of triphenylsilane, which was identified from its infrared spectrum; 0.85 g. (10.3%) of methyltriphenylsilane, m.p. 65-67° (mixed m.p.); and 2.55 g. (24.0%) of bromomethyltriphenylsilane, m.p. 122.5-123.5° (mixed m.p.).

13. Reaction of triphenylsilyllithium with iodoform

a. Normal addition

(1) Run 1 (until positive with Color Test I) A solution of triphenylsilyllithium was added dropwise to 7.88 g. (0.02 mole) of iodoform in 50 ml. of ether at room temperature. Slight heat was evolved during this addition. When 0.069 mole of triphenylsilyllithium had been added, Color Test I became positive. The reaction mixture was stirred for 2 hours, at which time Color Test I became negative. The reaction mixture was hydrolyzed with dilute acid. Hexaphenyldisilane, 10.80 g. (60.5% based on the silyllithium compound), was separated by filtration. The dark organic layer was dried with sodium sulfate. The solvent was removed and the residue was chromatographed on alumina. Elution with

petroleum ether (b.p. 60-70°) gave 1.30 g. (23.7% based on iodoform) of methyltriphenylsilane, which was identified by a mixed melting point determination with an authentic sample. Further elution with carbon tetrachloride gave 2.10 g. (19.7% based on iodoform) of bis(triphenylsilyl)methane, m.p. 137-140° (mixed m.p.).

(2) Run 2 (2:1, in the presence of triphenylsilane) A solution of 0.08 mole of triphenylsilyllithium was added dropwise to a mixture of 15.8 g. (0.04 mole) of iodoform and 5.20 g. (0.02 mole) of triphenylsilane dissolved in 50 ml. of THF. The reaction mixture was cooled to -60° by means of a Dry Ice-acetone bath when one-third of the silyllithium compound had been added. Color Test I was negative when the addition was completed. A work-up of the reaction mixture as in Run 1 gave 12.40 g. (60.0%) of hexaphenyldisilane and an oil, which was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave in the first fraction 4.50 g. (86.5% recovery) of triphenylsilane. Further elution with the same solvent gave in the second fraction 2.50 g. (15.6%) of iodomethyltriphenylsilane, m.p. 117.5-119° (mixed m.p.), after recrystallization from petroleum ether (b.p. 60-70°). Elution with carbon tetrachloride gave 3.05 g. (14.5%) of crude diiodomethyltriphenylsilane. Three recrystallizations from petroleum ether (b.p. 60-70°) gave a sample with a melting point of 151.0-152.5°.

Anal. Calcd. for $C_{19}H_{16}SiI_2$: C, 43.36; H, 3.07; Si, 5.34. Found: C, 44.00, 43.97; H, 3.31, 3.10; Si, 5.41, 5.33.

b. Reverse addition A solution of 11.82 g. (0.03 mole) of iodoform in THF was added dropwise to 0.08 mole of triphenylsilyllithium at room temperature. When 0.026 mole of iodoform had been added, Color Test I became negative. The reaction mixture was hydrolyzed with dilute acid. Hexaphenyldisilane, 13.40 g. (64.7%), was separated by filtration. The residue after a work-up of the organic layer was chromatographed on alumina. Elution with petroleum ether gave 0.90 g. (11.0%) of methyltriphenylsilane, m.p. 67-68° (mixed m.p.). Further elution with carbon tetrachloride gave a solid, which was treated with petroleum ether (b.p. 60-70°). The insoluble material was filtered off. There was no attempt made to purify this compound, m.p. 185-205°, (0.20 g., 2.4%). Its infrared spectrum was identical with that of 1,2-bis(triphenylsilyl)-ethane, m.p. 211-212°. From the mother liquor there was isolated 0.50 g. (3.1%) of bis(triphenylsilyl)methane, m.p. 140.5-142° (mixed m.p.).

14. Reaction of triphenylsilyllithium with carbon tetrachloride

a. Normal addition A solution of triphenylsilyllithium was added dropwise to 3.19 g. (0.021 mole) of carbon tetrachloride in 50 ml. of ether at -60°. When 0.04 mole of triphenylsilyllithium had been added, Color Test I was negative, but it became positive when 0.054 mole of the silyllithium compound had been added. The reaction mixture was black. Subsequent to hydrolysis, hexaphenyldisilane, 8.0 g. (57.2%), was separated by filtration. The organic layer was dried with sodium sulfate. The solvent was removed and the residue was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave a trace amount of triphenylsilane. Further elution with carbon tetrachloride gave 3.0 g. (42.2% based on carbon tetrachloride) of dichloromethyltriphenylsilane, m.p. 147-148.5°, after recrystallization from petroleum ether (b.p. 60-70°).

Anal. Calcd. for $C_{19}H_{16}SiCl_2$: C, 66.46; H, 4.70; Si, 8.18. Found: C, 66.54, 66.50; H, 4.95, 4.72; Si, 8.04, 7.95.

In another run 0.06 mole of triphenylsilyllithium was reacted with 0.03 mole of carbon tetrachloride under the same conditions to give hexaphenyldisilane, 8.8 g. (56.6%) and dichloromethyltriphenylsilane, 1.35 g. (13.0%).

b. Reverse addition A solution of carbon tetrachloride in THF was added dropwise to 0.08 mole of triphenylsilyllithium at -60°. When 0.026 mole of carbon tetrachloride had been added, Color Test I became negative. The reaction mixture was black. Subsequent to hydrolysis with dilute acid, hexaphenyldisilane, 15.25 g. (73.6%), was separated by filtration. The organic layer was worked up as in the case of the normal addition. The only product isolated and identified was dichloromethyltriphenylsilane, m.p. 147-148.5° (mixed m.p.), 1.0 g. (11.2%).

15. Reaction of triphenylsilyllithium with carbon tetrabromide

a. Normal addition A solution of triphenylsilyllithium (0.08 mole) was added over a period of 55 minutes to 13.3 g. (0.04 mole) of carbon tetrabromide in 50 ml. of ether at -60°. The color of the reaction mixture changed from yellow to gray as the addition proceeded. Color Test I was slightly positive at the end of the addition. The mixture was allowed to warm to room temperature. After an hour's stirring, Color Test I was negative. By this time the mixture was black.

Subsequent to hydrolysis with dilute acid, hexaphenyldisilane, 11.0 g. (53.1%), was separated by filtration. The organic layer was dried with sodium sulfate. The solvent was removed and the residue was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave only a trace amount of a material which was not identified. The following elution with carbon tetrachloride gave an oily material which was treated with petroleum ether (b.p. 60-70°). A material which crystallized out first was separated by filtration. It was recrystallized from the same solvent and was identified as dibromomethyltriphenylsilane, m.p. 148-150° (mixed m.p.). The mother liquor was concentrated and a second compound, m.p. 154-157.5°, was crystallized out. This compound was identified as bis(triphenylsilyl)acetylene by a mixed melting point determination with an authentic sample prepared from dilithium acetylide and chlorotriphenylsilane. The yields of dibromomethyltriphenylsilane and bis(triphenylsilyl)acetylene were 0.30 g. (1.7%) and 0.50 g. (4.6%) respectively.

b. <u>Reverse addition</u> An ethereal solution of carbon tetrabromide was added slowly to 0.08 mole of triphenylsilyllithium at -60°. When 0.03 mole of carbon tetrabromide had been added, the color of the reaction mixture changed from yellow to pale green and Color Test I was negative. An excess of carbon tetrabromide was added, making a total of 0.08 mole. The reaction mixture was stirred at -60° for one hour; then it was allowed to warm to room temperature. Its color changed to gray, but Color Test I remained negative. It was stirred at room temperature for 2.5 hours before it was worked up. Subsequent to hydrolysis, hexaphenyldisilane, 15.3 g. (73.9%), was separated by filtration. The black organic layer was dried with sodium sulfate. The solvent was removed and the residue was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave 0.22 g. (2.0%) of bromotriphenylsilylacetylene, m.p. 108-110°, after recrystallization from ethanol. This compound was identified by a mixed melting point determination with an authentic sample prepared from bromoethynyllithium and chlorotriphenylsilane and by a comparison of infrared spectra. Further elution with carbon tetrachloride gave an oil in two fractions. The first fraction was treated with petroleum ether (b.p. 60-70°). Most of the oil dissolved, leaving a small amount of solid, m.p. 168-250, which was obtained by filtration. This solid was recrystallized from the same solvent to give 0.07 g. of a compound with a melting point of 185-190°. Its infrared spectrum was very similar to that of bis(triphenylsilyl)-acetylene. The mother liquor was concentrated and a second compound, m.p. 119-122°, crystallized out. A mixed melting point with bromomethyltriphenylsilane was not depressed. The yield was 0.03 g. (2.8%). The second fraction was treated with petroleum ether (b.p. 60-70°) to give 0.70 g. (4.3%) of bis(triphenylsilyl)acetylene, which was identified by a mixed melting point determination with an authentic sample and a comparison of infrared spectra.

16. Reaction of triphenylsilyllithium with chloromethyltriphenylsilane

A solution of triphenylsilyllithium was added dropwise to 0.90 g. (0.0029 mole) of chloromethyltriphenylsilane in 25 ml. of THF at room temperature. Color Test I was negative when 0.004 mole of triphenylsilyllithium had been added, but it became positive upon the addition of another 0.001 mole. The reaction mixture was hydrolyzed with dilute acid after a stirring of 30 minutes. Hexaphenyldisilane, 0.55 g. (36.8%), was separated out by filtration. The organic layer was worked up in the usual manner and the residue was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave only a trace amount of triphenylsilane. Further elution with carbon tetrachloride gave 0.50 g. (32.4%) of pure bis(triphenylsilyl)methane, m.p. 140.5-142° (mixed m.p.).

17. Reaction of triphenylsilyllithium with dichloromethyltriphenylsilane

A solution of triphenylsilyllithium was added dropwise to 1.40 g. (0.0041 mole) of dichloromethyltriphenylsilane in 45 ml. of THF at -60°. The reaction appeared to be slow at this low temperature; therefore, the cooling bath was removed and the reaction mixture was allowed to reach room temperature. When 0.0125 mole of triphenylsilyllithium had been added, Color Test I was found to be slightly positive. The reaction mixture was hydrolyzed with dilute acid after 10 minutes of stirring. Hexaphenyldisilane, 1.50 g. (46.4%), was separated by filtration. The residue after a work-up of the organic layer was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave a trace amount of methyltriphenylsilane, identified from its infrared spectrum. Further elution with carbon tetrachloride gave 0.75 g. (34.3%) of bis(triphenylsilyl)methane, m.p. 140.5-142° (mixed m.p.).

18. Reaction of triphenylsilyllithium with chloromethyltrimethylsilane

A solution of triphenylsilyllithium (0.08 mole) was added to 13.0 g. (0.12 mole) of chloromethyltrimethylsilane. The reaction mixture was cooled in an ice-bath during the addition. Color Test I was negative when the addition was completed. A work-up by general procedure gave an oily residue which was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave 22.7 g. (82%) of an oil. Upon distillation under reduced pressure it solidified immediately, m.p. 70-71°, after recrystallization from a mixture of petroleum ether (b.p. 60-70°) and ethanol.

Anal. Calcd. for $C_{22}H_{26}Si_2$: Si, 16.21. Found: Si, 16.09, 16.02.

19. Reaction of triphenylsilyllithium with chloromethyldimethylvinylsilane

A solution of triphenylsilyllithium (0.08 mole) was added to 10.8 g. (0.08 mole) of chloromethyldimethylvinylsilane at an ice bath temperature. Color Test I was negative immediately after the addition. A work-up by the general procedure, followed by chromatography on alumina, gave an oil, 18.2 g. (63.5%), which was distilled under reduced pressure, b.p. 158-159°/0.01 mm., $n_D^{21.8}$ 1.5890.

Anal. Calcd. for $C_{23}H_{26}Si_2$: Si, 15.67. Found: Si, 15.43, 15.38.

20. Reduction of dichloromethyltriphenylsilane with lithium aluminum hydride

A solution of 0.70 g. (0.002 mole) of dichloromethyltriphenylsilane in 25 ml. of THF was added to 0.70 g. (0.018 mole) of lithium aluminum hydride in 25 ml. of THF at room temperature. The reaction mixture became slightly warm during the addition. It was stirred for 35 minutes before the excess lithium aluminum hydride was destroyed by adding dropwise 25 ml. of ethyl acetate.

The reaction mixture was worked up by the general procedure, followed by chromatography on alumina. Elution with petroleum ether (b.p. 60-70°) gave 0.08 g. (14.6%) of methyltriphenylsilane, m.p. 69-70° (mixed m.p.). Further elution with carbon tetrachloride gave 0.40 g. (64.6%) of chloromethyltriphenylsilane, m.p. 117.5-119° (mixed m.p.).

21. Reduction of diiodomethyltriphenylsilane with lithium aluminum hydride

This reduction was carried out essentially in the same manner as the reduction of dichloromethyltriphenylsilane. Using 1.10 g. (0.0021 mole) of diiodomethyltriphenylsilane, there was obtained 0.45 g. (78.5%) of methyltriphenylsilane, m.p. 70-71° (mixed m.p.).

22. Reaction of bromomethyltriphenylsilane with lithium in THF

To bromomethyltriphenylsilane, 2.0 g. (0.00566 mole), and finely cut lithium wire, 1.2 g. (0.17 mole), was added tetrahydrofuran (45 ml.) in small portions at room temperature. An immediate reaction occurred evolving some heat, and the reaction mixture turned black. Color Test I was positive. The reaction mixture was worked up by the general procedure after 20 minutes of stirring. The residue obtained was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave 0.15 g. (9.7%) of methyltriphenylsilane. Further elution with carbon tetrachloride gave 0.60 g. (38.8%) of 1,2-bis(triphenylsilyl)ethane, which was identified by a mixed melting point determination with an authentic sample, m.p. 210-211°, and by comparison of infrared spectra.

23. Reaction of triphenylsilyllithium with 1,1-dichlorobutane

a. Normal addition A solution of triphenylsilyllithium was added dropwise to 3.81 g. (0.03 mole) of 1,1-dichlorobutane in 50 ml. of ether at -60°. When 0.051 mole of triphenylsilyllithium had been added, Color Test I became positive. The reaction mixture was stirred at -60° for 20 minutes. Then it was allowed to warm to room temperature. Color Test I was found to be negative 30 minutes later. The reaction mixture was hydrolyzed with dilute acid. Hexaphenyldisilane, 9.0 g. (58.0%), was separated by filtration. A work-up of the organic layer in the usual manner gave a solid residue which was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave 3.70 g. (39.0%) of n-butyltriphenylsilane, m.p. 90-91°, after recrystallization from methanol. A mixed melting point with an authentic sample was not depressed.

b. Reverse addition An ethereal solution of 1,1-dichlorobutane was added to 0.028 mole of triphenylsilyllithium at room temperature. The rate of addition was such that only slight warming was allowed. When 0.014 mole of 1,1-dichlorobutane had been added, Color Test I became negative. The reaction mixture was worked up by the same procedure as in (a) above to give 4.95 g. (68.2%) of hexaphenyldisilane and 1.20 g. (27.1%) of n-butyltriphenylsilane.

24. Reaction of triphenylsilyllithium with 1,1-dibromoethane

A solution of triphenylsilyllithium (0.08 mole) was added dropwise to 7.52 g. (0.04 mole) of 1,1-dibromoethane in 50 ml. of ether at -60°. Color Test I was weakly positive after the addition was completed. The reaction mixture was stirred for 15 minutes before it was hydrolyzed. Hexaphenyldisilane, 12.30 g. (59.4%), was separated by filtration. A work-up of the organic layer left a solid which was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave 3.83 g. (33.2%) of ethyltriphenylsilane, m.p. 74-75.5°, after recrystallization from ethanol. It was identified by a mixed melting point determination with an authentic sample. Further elution with carbon tetrachloride gave 1.35 g. (4.6%) of 1-bromo-1-triphenylsilylethane, m.p. 131-132.5°, after recrystallization from petroleum ether (b.p. 60-70°).

Anal. Calcd. for $C_{20}H_{19}SiBr$: Si, 7.65. Found: Si, 7.66, 7.69.

C. Reactions of Triphenylsilyllithium with Alkenyl Halides

1. Reaction of triphenylsilyllithium with 1-chloropropene

a. 1:1 ratio A solution of triphenylsilyllithium (0.08 mole) was added dropwise to 6.1 g. (0.08 mole) of 1-chloropropene at -60°. The reaction appeared to be slow at this temperature; therefore, the reaction mixture was allowed to warm to room temperature after 0.05 mole of triphenylsilyllithium had been added. The mixture was cooled again and the rest of the silyllithium compound was added. When the reaction mixture reached room temperature for the second time, Color Test I was positive. The reaction mixture was stirred for one hour, at which time Color Test I was only faintly positive. Subsequent to hydrolysis with dilute acid, hexaphenyldisilane, 2.80 g. (13.5%), was separated by filtration. The organic layer was worked up by the general procedure, followed by chromatography on alumina. Elution with petroleum ether (b.p. 60-70°) gave 10.20 g. (45.5%) of 1,2-bis(triphenylsilyl)propane, m.p. 147.5-148.5°, after recrystallization from a benzene-petroleum ether (b.p. 60-70°) mixture. A mixed melting point with a sample obtained from the reaction of triphenylsilyllithium with 1-triphenylsilylpropene was not depressed and the infrared spectra were superimposable.

Anal. Calcd. for $C_{39}H_{36}Si_2$: C, 83.51; H, 6.47; Si, 10.02. Found: C, 83.89; H, 6.31; Si, 10.03, 9.97.

b. <u>2:1 ratio, followed by addition of chlorotriphenylsilane</u> A solution of triphenylsilyllithium (0.08 mole) was added dropwise to 3.1 g. (0.04 mole) of 1-chloropropene. The reaction mixture was cooled in an ice-salt bath during the addition and for an hour thereafter. Then it was allowed to come to room temperature. After a total of 2.5 hours of reaction time, there was added 12 g. (0.04 mole) of chlorotriphenylsilane in 50 ml. of THF. The reaction mixture was worked up by the same procedure as in (a) above after one hour of stirring. The following compounds were obtained: hexaphenyldisilane, 7.10 g., and 1,2-bis(triphenylsilyl)propane, m.p. 148-148.5° (mixed m.p.), 10.55 g. (47%).

c. <u>Reaction of triphenylsilyllithium with 1-triphenylsilylpropene</u> A solution of triphenylsilyllithium (0.008 mole) was added to 1.90 g. (0.007 mole) of 1-triphenylsilylpropene, which was prepared from propenyllithium and chlorotriphenylsilane. Color Test I was positive when the addition was completed. The reaction mixture was stirred for 22 hours at room temperature and then for 2 hours at reflux. It was worked up in the same manner as in (a) to give 1.50 g. (38.4%) of 1,2-bis(triphenylsilyl)propane, m.p. 148-148.5°, after recrystallization from a benzene-petroleum ether (b.p. 60-70°) mixture.

d. Reaction of propenyllithium with triphenylsilane Propenyllithium was prepared from 1-bromopropene with excess lithium in ether, stirring at room temperature overnight. Acid titration showed the yield to be 87.5%.

A solution of propenyllithium (0.035 mole) was added to 9.10 g. (0.035 mole) of triphenylsilane. Color Test I was positive at the end of the addition. It became negative after 4.5 hours of stirring at room temperature. The reaction mixture was worked up to give a solid, which was then treated with methanol. Some insoluble material was separated by filtration. The mother liquor was cooled with ice to crystallize out 9.60 g. (91.5%) of 1-triphenylsilylpropene, m.p. 55-60°. Several recrystallizations from methanol raised the melting point to 90.5-92°. The infrared spectra of the crude and pure products were identical, both showing characteristic double bond absorption bands at 6.20 μ (in chloroform) and 10.19 μ (in carbon disulfide).

e. Reaction of propenyllithium with chlorotriphenylsilane A solution of propenyllithium (0.035 mole) prepared as above was added to 12 g. (0.04 mole) of chlorotriphenylsilane in 50 ml. of ether. The reaction was exothermic, but Color Test I was positive at the end of the addition. Color Test I became negative after 40 minutes of stirring. The reaction mixture was worked up to give a solid, which was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave 6.15 g. (58.5%) of crude 1-triphenylsilylpropene, m.p. 60-70°. Several recrystallizations from methanol gave a sample with a melting point of 87-90°. A mixed melting point with a sample obtained in (d) above was not depressed and the infrared spectra were superimposable. In addition, a small amount of 1-triphenylsilylpropyne was isolated.

2. Reaction of triphenylsilyllithium with 1-chloro-1-butene

a. 1:1 ratio at room temperature A solution of triphenylsilyllithium (0.04 mole) was added over a period of 30 minutes to 2.23 g. (0.04 mole) of 1-chloro-1-butene at room temperature. Color Test I was positive when the addition was completed. It remained positive at the end of 28 hours of stirring at room temperature. The reaction mixture was worked up by the general procedure and the oily residue was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave an oil which solidified after two weeks of standing. The solid was recrystallized from petroleum ether (b.p. 60-70°) to give 2.55 g. (22.2%) of a product, possibly 1,2-bis(triphenylsilyl)butane, m.p. 137-139°.

Anal. Calcd. for $C_{40}H_{38}Si_2$: C, 83.56; H, 6.67; Si, 9.77. Found: C, 83.69, 83.50; H, 6.44, 6.29; Si, 9.75, 9.64.

Elution with carbon tetrachloride gave 1.55 g. of a glassy polymeric material which failed to crystallize.

b. 1:1 ratio at reflux A solution of triphenylsilyllithium

(0.04 mole) was added over a period of 30 minutes to 2.23 g. (0.04 mole) of 1-chloro-1-butene. The color of the reaction mixture was a dark reddish-brown. The reaction mixture was refluxed for 1.5 hours. It was worked up by the same procedure as in (a) above. 1,2-bis(triphenylsilyl)butane was obtained in a yield of 3.00 g. (26.0%), m.p. 136-137° (mixed m.p.). In addition, 1.70 g. of a glassy polymeric material was isolated.

c. <u>1:1 ratio at room temperature, followed by addition of chlorotriphenylsilane</u> A solution of triphenylsilyllithium (0.037 mole) was added to 2.23 g. (0.04 mole) of 1-chloro-1-butene in 100 ml. of THF. The reaction mixture was stirred at room temperature for 16 hours before 6.5 g. (0.022 mole) of chlorotriphenylsilane in 60 ml. of THF was added. The reaction mixture changed from a deep reddish-brown to colorless within one hour after the addition of chlorotriphenylsilane. Subsequent to hydrolysis, hexaphenyldisilane, 3.00 g. (15.6%), was separated by filtration. The organic layer was worked up by the general procedure and subsequently chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave in the first fraction a mixture of triphenylsilane and 1-triphenylsilyl-1-butyne. The mixture was treated with ethanol to give 0.85 g. (7.4%) of 1-triphenylsilyl-1-butyne, m.p. 86-88°. A mixed melting point with an authentic sample prepared from butynyllithium and chlorotriphenylsilane was not depressed. From the mother liquor there was obtained 1.25 g. (13.0%) of triphenylsilane, n_D^{20} 1.6142. Further elution with the same solvent gave an oil, which was treated with petroleum ether (b.p. 60-70°) to give 2.55 g. of

1,2-bis(triphenylsilyl)butane, m.p. 138-140° (mixed m.p.). Elution with carbon tetrachloride gave 1.55 g. of an oil from which 0.60 g. more of the same compound was obtained. The total yield of 1,2-bis(triphenylsilyl)butane was 3.15 g. (29.6%).

3. Reaction of triphenylsilyllithium with 1-bromopropene

a. 1:1 ratio A solution of triphenylsilyllithium (0.05 mole) was added dropwise over a period of 50 minutes to 6.06 g. (0.05 mole) of 1-bromopropene in 100 ml. of ether at room temperature. Color Test I was negative after the addition. The reaction mixture was stirred for 4 hours. Subsequent to hydrolysis with dilute acid, hexaphenyldisilane, 8.90 g. (68.7%), was separated by filtration. The organic layer was worked up in the usual manner and the residue was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave in the first fraction 1.65 g. (11.0%) of 1-triphenylsilylpropene, m.p. 90.5-92°, after recrystallization from methanol. A mixed melting point with an authentic sample prepared from propenyllithium and chlorotriphenylsilane was not depressed and the infrared spectra were superimposable. Further elution with the same solvent gave in the second fraction 1.05 g. (7.1%) of 1-triphenylsilylpropyne, m.p. 115.5-116°, after recrystallization from methanol. A mixed melting point with an authentic sample was not depressed. Elution with carbon tetrachloride gave 0.25 g. (1.8%) of 1,3-bis(triphenylsilyl)propene, identified by a mixed melting point determination with a sample obtained from the reaction of triphenylsilyllithium with 1,3-dichloropropene and by a comparison of infrared spectra, as well as a trace amount of tris(triphenylsilyl)propadiene, identified by a comparison of its infrared spectrum with that of the sample obtained from the reaction of triphenylsilyllithium with 1-triphenylsilylpropyne.

b. <u>4:3 ratio, followed by addition of chlorotriphenylsilane</u> A solution of triphenylsilyllithium (0.08 mole) was added dropwise over a period of 2 hours to 7.28 g. (0.06 mole) of 1-bromopropene in 200 ml. of ether. Color Test I was faintly positive when the addition was completed. After one hour of stirring there was added 15 g. (0.05 mole) of chlorotriphenylsilane in 150 ml. of ether. The reaction mixture was stirred for 2.5 hours before it was worked up by the same procedure as in (a) above. The following compounds were isolated: hexaphenyldisilane, 15.0 g. (72.5%); triphenylsilane, 1.35 g. (6.5% based on triphenylsilyllithium); 1-triphenylsilylpropyne, 2.75 g. (15.3% based on 1-bromopropene); 1-triphenylsilylpropene, 1.20 g. (6.7% based on 1-bromopropene); 1,2-bis(triphenylsilyl)propane, 0.10 g. (0.3%), identified by comparison of its infrared spectrum with that of an authentic sample; and tris(triphenylsilyl)propadiene, 1.80 g. (3.7%), m.p. 186.5-188.5° (mixed m.p.).

c. <u>8:5 ratio, followed by addition of chlorotriphenylsilane</u> A solution of triphenylsilyllithium (0.08 mole) was added to 6.06 g. (0.05 mole) of 1-bromopropene in 100 ml. of ether at room temperature. Color Test I was positive even after 5 hours of stirring. Chlorotriphenylsilane was added until the color test became negative. This process required about 0.02 mole of chlorotriphenylsilane. An excess of 0.01 mole of chlorotriphenylsilane was added. The reaction mixture was worked up by the same procedure as in (a). The following compounds were isolated: hexaphenyldisilane, 15.20 g.; a mixture of triphenylsilane and 1-triphenylsilylpropene, 1.75 g.; 1-triphenylsilylpropyne, 1.0 g. (6.6%); 1,2-bis(triphenylsilyl)propane, 2.15 g. (7.7%); 1,3-bis(triphenylsilyl)propene, 0.40 g. (1.4%); 1,3-bis(triphenylsilyl)propyne, 0.30 g. (1.1%); and tris(triphenylsilyl)propadiene, 2.60 g. (6.4%).

d. 3:1 ratio A solution of triphenylsilyllithium (0.08 mole) was added dropwise over a period of one hour to 3.03 g. (0.025 mole) of 1-bromopropene in 100 ml. of ether at 30-35°. Color Test I was positive at the end of this addition. It remained positive after 2 hours of stirring. Subsequent to hydrolysis, hexaphenyldisilane, 1.90 g. (9.2%), was separated by filtration. The organic layer was worked up by the general procedure and the residue was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave in the first fraction 10.45 g. (50.2%) of triphenylsilane, which was identified by its infrared spectrum. Further elution with the same solvent gave in the second fraction 0.95 g. (6.8%) of 1,2-bis(triphenylsilyl)propane, m.p. 148-150° (mixed m.p.). Elution with carbon tetrachloride gave 1.00 g. (7.2%) of 1,3-bis(triphenylsilyl)propyne, m.p. 133.5-135.5°, after recrystallization from petroleum ether (b.p. 60-70°). A mixed melting point with a sample obtained from the reaction of triphenylsilyllithium with 1-triphenylsilylpropyne was not depressed and the infrared spectra were superimposable.

In another run, chlorotriphenylsilane (10.2 g., 0.034 mole) was added after the mixture was stirred for one hour and forty minutes. The yield of hexaphenyldisilane was 19.50 g. The other products were triphenylsilane, 2.35 g. (36.2% based on 1-bromopropene); 1,2-bis(triphenylsilyl)propane, 0.45 g. (3.2%); 1,3-bis(triphenysilyl)propene, 0.30 g. (2.2%); 1,3-bis(triphenylsilyl)propyne, 0.60 g. (4.3%); and a compound with a melting point of 186-189°. The last compound has not been identified, but the infrared spectrum indicated the presence of a double bond.

4. Reaction of triphenylsilyllithium with 1-bromo-1-butene

A solution of triphenylsilyllithium (0.08 mole) was added dropwise to 3.38 g. (0.025 mole) of 1-bromo-1-butene in 100 ml. of ether. Slight heat was evolved during the addition of the first two-thirds of the triphenylsilyllithium and the color of the reaction mixture was yellowish-brown. The last one-third was added rapidly. The color of the mixture became dark brown. Color Test I was positive. The reaction mixture was stirred for 2 hours at room temperature, during which time Color Test I remained positive. Subsequent to hydrolysis with dilute acid, hexaphenyldisilane, 4.53 g. (33.6% based on 1-bromo-1-butene), was separated by filtration. The organic layer was worked up by the general procedure, followed by chromatography on alumina. Elution with petroleum ether (b.p. 60-70°) gave in the first fraction 11.10 g. (53.4%) of triphenylsilane, identified by its infrared spectrum. Further elution with the same solvent yielded a solid material which was recrystallized from a mixture of ethyl acetate and petroleum ether (b.p. 60-70°) to give 0.30 g. of a compound with a melting point of 223.5-225°. From the mother liquor there was isolated 0.40 g. of a material which melted at

198-202°. Neither compound has been identified.

5. Reaction of triphenylsilyllithium with 2-bromo-1-butene, followed by addition of chlorotriphenylsilane

A solution of triphenylsilyllithium was added dropwise to 5.40 g. (0.04 mole) of 2-bromo-1-butene in 100 ml. of ether at room temperature. The rate of addition was such that only slight warming was allowed. When 0.047 mole of triphenylsilyllithium had been added, the color of the reaction mixture deepened to a reddish-brown and Color Test I was positive. An ethereal solution of chlorotriphenylsilane (0.02 mole) was added. The reaction mixture was stirred for 1.5 hours, during which time it became colorless. Subsequent to hydrolysis, hexaphenyldisilane, 7.25 g. (35.0% based on 2-bromo-1-butene), was separated by filtration. The organic layer was worked up in the usual manner and the residue was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave in the first fraction 2.60 g. of a mixture, which upon recrystallization from a mixture of petroleum ether (b.p. 60-70°) and methanol yielded 1.45 g. (11.5%) of 2-triphenylsilyl-1-butene, m.p. 95.5-97°. Part of an oily residue, 0.20 g. (1.7%), was identified as triphenylsilane by its infrared spectrum. A structure of 2-triphenylsilyl-1-butene was proposed for the compound above on the basis of its infrared and n.m.r. spectra (see Tables 3 and 4). Further elution with the same solvent gave in the second fraction 1.10 g. (8.8%) of 1-triphenylsilyl-1-butyne, m.p. 90-91, after recrystallization from ethanol. This compound was identified by a mixed melting point determination with a sample prepared from a reaction of butynyllithium with chlorotriphenylsilane.

Elution with carbon tetrachloride gave an oil, which upon treatment with petroleum ether (b.p. 60-70°) yielded 0.75 g. (2.3%) of 1,1,3-tris(triphenylsilyl)-1,2-butadiene, m.p. 195.5-197°, after two recrystallizations from petroleum ether (b.p. 60-70°). A mixed melting point with a sample prepared from the reaction of methyl iodide with metalated tris(triphenylsilyl)propadiene was not depressed and the infrared spectra were superimposable.

6. Reaction of triphenylsilyllithium with 1,1-dichloropropene

a. At -60°

(1) Run 1 (2:1) A solution of triphenylsilyllithium (0.08 mole) was added over a period of one hour to 4.45 g. (0.04 mole) of 1,1-dichloropropene in 50 ml. of ether at -60°. The reaction mixture was allowed to warm to room temperature, whereupon Color Test I was negative. Subsequent to hydrolysis with dilute acid, hexaphenyldisilane, 14.5 g. (70.0%), was separated by filtration. The organic layer was worked up in the usual manner and the residue was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave a trace amount of triphenylsilane and 1-triphenylsilylpropene, both of which were identified by comparison of their infrared spectra with those of authentic samples. Elution with carbon tetrachloride gave also a trace amount of 2-chloro-3-triphenylsilylpropene and tris(triphenylsilyl)propadiene. These two compounds were also identified by their infrared spectra.

In a second experiment reverse addition was employed. The work-up gave hexaphenyldisilane (77.6%), triphenylsilane (4.8%), 1-triphenylsilylpropene (0.5%), and 2-chloro-3-triphenylsilylpropene (0.7%).

(2) Run 2 (3:1) A solution of triphenylsilyllithium was added dropwise for 1.25 hours to 2.78 g. (0.025 mole) of 1,1-dichloropropene in 50 ml. of ether at -60°. When 0.06 mole of triphenylsilyllithium had been added, Color Test I became positive. The reaction mixture was allowed to warm to room temperature and an additional 0.02 mole of triphenylsilyllithium was added. Color Test I remained positive after 3 hours of stirring. Chlorotriphenylsilane in ether was added dropwise. When 0.01 mole had been added, Color Test I became negative. The reaction mixture was worked up by the same procedure as in Run 1. The following compounds were isolated: hexaphenyldisilane, 13.5 g.; triphenylsilane, 1.50 g. (23.1% based on 1,1-dichloropropene); and 1-triphenylsilylpropyne, 0.30 g. (4.0%). The last compound was identified by a mixed melting point determination with an authentic sample.

b. At room temperature

(1) Run 1 (1:2) A solution of triphenylsilyllithium (0.05 mole) was added dropwise over a period of one hour to 11.1 g. (0.10 mole) of 1,1-dichloropropene in 150 ml. of ether at room temperature. After being stirred for one-half hour, the reaction mixture was hydrolyzed with dilute acid. Hexaphenyldisilane, 8.90 g. (68.7%), was separated by filtration. The organic layer was worked up in the usual manner and the residue was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave in the first fraction 0.45 g. (3.5%) of triphenylsilane. Further elution with the same solvent gave in the second

fraction 0.70 g. (4.2%) of 2-chloro-3-triphenylsilylpropene, m.p. 97-99°, after recrystallization from methanol. A mixed melting point with a sample obtained from the reaction of triphenylsilyllithium with 2,3-dichloropropene was not depressed. The infrared and n.m.r. spectra were identical. Elution was continued with petroleum ether (b.p. 60-70°), whereupon 1-triphenylsilylpropyne, 0.85 g. (5.7%), m.p. 115.5-116.5° (mixed m.p.), was isolated as the last product.

(2) Run 2 (2:1) A solution of triphenylsilyllithium (0.08 mole) was added dropwise over a period of 2 hours and 20 minutes to 5.34 g. (0.048 mole) of 1,1-dichloropropene in 125 ml. of ether. Color Test I was negative when the addition was complete. The reaction mixture was worked up by the same procedure as in Run 1 to give hexaphenyldisilane, 11.80 g. (57.0%); triphenylsilane, 2.10 g. (16.9% based on 1,1-dichloropropene); and 1-triphenylsilylpropyne, 2.85 g. (20.0% based on 1,1-dichloropropene).

In a second experiment the addition of chlorotriphenylsilane, 9.4 g. (0.032 mole), followed after the reaction mixture had been stirred for 4 hours. Hexaphenyldisilane was obtained in a yield of 14.5 g. (70%), but the yield of the other two products remained essentially the same: triphenylsilane, 2.20 g. (18.8%); and 1-triphenylsilylpropyne, 2.35 g. (18.5%). Chlorotriphenylsilane was recovered as triphenylsilanol in an 81.5% yield.

(3) Run 3 (2.5:1) A solution of triphenylsilyllithium was added dropwise to 3.34 g. (0.03 mole) of 1,1-dichloropropene in 100 ml. of ether. When 0.07 mole of triphenylsilyllithium had been added, Color

Test I was negative, but it became positive when 0.075 mole had been added. After being stirred for half an hour, the reaction mixture was worked up by the same procedure as in Run 1. The following compounds were isolated: hexaphenyldisilane, 10.2 g (52.5%); triphenylsilane, 3.20 g. (16.4% based on 1,1-dichloropropene); 1-triphenylsilylpropyne, 2.35 g. (26.2% based on 1,1-dichloropropene).

(4) <u>Run 4 (3:1, followed by addition of chlorotriphenylsilane)</u> A solution of triphenylsilyllithium (0.08 mole) was added dropwise over a period of 3 hours to 2.78 g. (0.025 mole) of 1,1-dichloropropene in 100 ml. of THF. The color of the reaction mixture changed from white to a reddish-brown during the last third of the addition. After 3 hours of stirring chlorotriphenylsilane (10.0 g., 0.033 mole) in 30 ml. of THF was added. The reaction mixture was stirred for 1.5 hours before it was worked up by the general procedure. The following compounds were isolated: hexaphenyldisilane, 12.50 g. (60.2%); triphenylsilane, 5.05 g. (77.7% based on 1,1-dichloropropene, 24.3% based on triphenylsilyllithium); 1-triphenylsilylpropyne, 3.10 g. (41.6% based on 1,1-dichloropropene); 1,2-bis(triphenylsilyl)propene, 0.75 g. (5.4%); and tris(triphenylsilyl)propadiene, 1.20 g. (5.9%). In addition, there was 1.05 g. of a material with a melting range of 145-200° which was mainly a mixture of the last two compounds. 1,2-bis(triphenylsilyl)propene and tris(triphenylsilyl)propadiene were identified by mixed melting points and a comparison of infrared spectra with those of the samples obtained from the reaction of triphenylsilyllithium with 1-triphenylsilylpropyne.

7. Reaction of triphenylsilyllithium with 1,2-dichloropropene

A solution of triphenylsilyllithium (0.08 mole) was added to 4.44 g. (0.04 mole) of 1,2-dichloropropene. The reaction was exothermic and Color Test I was negative after the addition. Subsequent to hydrolysis, there was isolated 12.8 g. (61.8%) of hexaphenyldisilane. The organic layer was worked up by the usual procedure and the residue was chromatographed on alumina. Elution with petroleum ether gave 0.20 g. (2%) of 1-triphenylsilylpropyne, which was identified by a mixed melting point determination.

In another run, 3 equivalents of triphenylsilyllithium were added and hexaphenyldisilane was obtained in a 92% yield (based on 1,2-dichloropropene). The other product was triphenylsilane (36.5%). Color Test I was negative prior to work-up.

8. Reaction of phenyllithium with 1,2-dichloropropene

a. <u>1:1 ratio, followed by addition of triphenylsilyllithium</u> An ethereal solution of phenyllithium (0.04 mole) was added dropwise to 4.44 g. (0.04 mole) of 1,2-dichloropropene in 100 ml. of THF at room temperature. The rate of addition was such that only slight warming was allowed. Color Test I was negative when the addition was complete. A solution of triphenylsilyllithium (0.04 mole) was then added dropwise. A white precipitate was formed. The solution, however, gave a positive Color Test I. Subsequent to hydrolysis, hexaphenyldisilane, 7.65 g. (73.9%), was separated by filtration. The organic layer was worked up in the usual manner and the residue was chromatographed on alumina.

Elution with petroleum ether (b.p. 60-70°) gave 1.40 g. (11.7%) of 1-triphenylsilylpropyne, m.p. 116-118° (mixed m.p.).

b. <u>2:1 ratio, followed by addition of chlorotriphenylsilane</u> An ethereal solution of phenyllithium (0.04 mole) was added dropwise over a period of one hour to 2.22 g. (0.02 mole) of 1,2-dichloropropene in 100 ml. of THF at room temperature. Color Test I was positive when the addition was complete. A solution of chlorotriphenylsilane, 6.0 g. (0.02 mole), in ether was added. Color Test I became negative immediately. A work-up by the general procedure, followed by chromatograph on alumina, gave 4.40 g. (74.0%) of 1-triphenylsilylpropyne, m.p. 116-117.5° (mixed m.p.).

9. <u>Reaction of phenyllithium with trichloroethylene</u>

a. <u>1:1 ratio, followed by addition of chlorotriphenylsilane</u> An ethereal solution of phenyllithium (0.02 mole) was added to 2.63 g. (0.02 mole) of trichloroethylene in 50 ml. of ether at -60°. Color Test I was very weakly positive. A THF solution of chlorotriphenylsilane, 6.0 g. (0.02 mole), was added. A work-up by the general procedure gave a solid residue, which was treated with petroleum ether (b.p. 60-70°). An insoluble material was filtered off. It was identified as triphenylsilanol by a mixed melting point determination with an authentic sample, m.p. 148-152.5°. The mother liquor was poured onto an alumina column. Elution with petroleum ether (b.p. 60-70°) gave 0.60 g. (9.4%) of chlorotriphenylsilylacetylene, m.p. 99-101° (mixed m.p.). Further elution with carbon tetrachloride gave 0.15 g. (2.8%) of bis(triphenylsilyl)acetylene, m.p. 154-156° (mixed m.p.).

b. 1:1 ratio, followed by addition of triphenylsilyllithium An ethereal solution of phenyllithium (0.04 mole) was added to 5.25 g. (0.04 mole) of trichloroethylene in 100 ml. of ether at -60°. When the addition was completed, the reaction mixture was allowed to warm to room temperature. A solution of triphenylsilyllithium (0.04 mole) was added dropwise over a period of one hour. The reaction mixture was black. After being stirred for 1.5 hours, it was hydrolyzed with dilute acid. Hexaphenyldisilane, 5.50 g. (53.1%), was separated by filtration. The organic layer was worked up in the usual manner, followed by chromatography on alumina. Elution with petroleum ether (b.p. 60-70°) gave 2.17 g. (17%) of chlorotriphenylsilylacetylene, m.p. 99-102° (mixed m.p.). Further elution with carbon tetrachloride yielded 0.45 g. (4.2%) of bis(triphenylsilyl)acetylene, m.p. 152-155°, which was identified by a comparison of infrared spectra.

10. Reaction of triphenylsilyllithium with 1,3-dichloropropene

a. 1:1 ratio A solution of triphenylsilyllithium (0.04 mole) was added dropwise over a period of 2.5 hours to 4.45 g. (0.04 mole) of 1,3-dichloropropene in 100 ml. of THF. Color Test I was negative immediately after this addition. After one hour of stirring the reaction mixture was hydrolyzed with dilute acid. Hexaphenyldisilane, 1.00 g. (9.7%), was separated by filtration. The organic layer was worked up by the general procedure and subsequently chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave 10.05 g. (75.0%) of a mixture of two isomers, possibly 1-triphenylsilyl-3-chloropropene and 1-chloro-3-triphenylsilylpropene.

Anal. Calcd. for $C_{21}H_{19}SiCl$: Si, 8.39. Found: Si, 8.41, 8.33.

Separation of the two isomers proved to be very difficult. Recrystallization of the mixture from ethanol afforded a sample with a melting point of 87-89°. When the mixture was chromatographed on alumina, the first fraction eluted with petroleum ether (b.p. 60-70°) gave a sample with a melting point of 87-96°. Repeated recrystallizations from n-propanol gave a small amount (less than 0.1 g.) of a compound (I) with a melting point of 105-107.5°.

The very last fractions eluted with petroleum ether (b.p. 60-70°), after 1000 ml. of the eluant, gave a sample which was rich in the other component, m.p. 89-106°. Repeated recrystallizations from n-propanol gave a compound (II) (less than 0.1 g.), m.p. 112.5-115.5°.

When the infrared spectra of compound (I) and compound (II) were combined, the resulting spectrum was superimposable with that of a typical mixture. Thus, the mixture consisted of these two isomers. (For their infrared spectra data, see Table 4.)

The n.m.r. spectra of compound (I) and compound (II) were very similar, both indicating the presence of a methylene group and olefinic hydrogens (see Table 3).

The combined information of the infrared and n.m.r. spectra suggested compound (I) to be 1-triphenylsilyl-3-chloropropene and compound (II) to be 1-chloro-3-triphenylsilylpropene.

b. 2:1 ratio A solution of triphenylsilyllithium (0.08 mole) was added dropwise to 4.45 g. (0.04 mole) of 1,3-dichloropropene in 100 ml. of THF. The reaction mixture was cooled by an ice bath during the addition. Color Test I was slightly positive when the addition was completed. Subsequent to hydrolysis, hexaphenyldisilane, 2.60 g. (12.5%), was separated by filtration. The residue obtained after the work-up of the organic layer was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave 6.90 g. (31.0%) of 1,3-bis(triphenylsilyl)-propene, m.p. 157-158.5°, after recrystallization from an ethyl acetate-ethanol mixture. A mixed melting point with a dehydrated product of 1,3-bis(triphenylsilyl)propan-2-ol was not depressed.

c. <u>3:1 ratio</u> A solution of triphenylsilyllithium (0.08 mole) was added dropwise over a period of 2 hours to 2.78 g. (0.025 mole) of 1,3-dichloropropene in 100 ml. of THF. The reaction mixture was a deep reddish-black. Color Test I was positive when the addition was complete. It became only weakly positive after 4 hours of stirring. Subsequent to hydrolysis, hexaphenyldisilane, 0.87 g. (6.7%), was separated by filtration. The residue obtained after a work-up of the organic layer was chromatographed on alumina. The early fractions eluted with petroleum ether (b.p. 60-70°) were rechromatographed to give 5.00 g. (77.0% of theoretical) of triphenylsilane, 0.15 g. (1.8%) of tetraphenylsilane, m.p. 228-234° (mixed m.p.), and 0.40 g. of 1,3-bis(triphenylsilyl)propene, m.p. 156-158° (mixed m.p.).

The original chromatography was continued. Elution with petroleum ether (b.p. 60-70°) gave 3.25 g. of 1,3-bis(triphenylsilyl)propene. Elution with carbon tetrachloride gave 3.40 g. of the same compound and a fair amount of non-crystallizing polymeric oil. The combined yield of 1,3-bis(triphenylsilyl)propene was 7.05 g. (50.5%).

d. <u>Reaction of triphenylsilyllithium with a mixture of compounds (I) and (II)</u> A solution of triphenylsilyllithium (0.04 mole) was added dropwise over a period of one hour to 6.70 g. (0.02 mole) of the mixture obtained in (a) above in 70 ml. of THF. The solution immediately turned a reddish-brown, indicating that metalation was taking place as soon as the coupling product was formed. The color became a deep reddish-black at the end of the addition. Color Test I was positive. After an hour's stirring the reaction mixture was hydrolyzed with dilute acid. No hexaphenyldisilane was obtained. The organic layer was worked up by the general procedure employed above. The compounds isolated were: triphenylsilane, 5.00 g. (96.2% of theoretical); and 1,3-bis(triphenylsilyl)propene, 6.45 g. (57.7%), m.p. 155.5-159.5° (mixed m.p.). In addition, there was some non-crystallizing, glassy, polymeric material.

e. <u>Reaction of phenyllithium with a mixture of compounds (I) and (II)</u> An ethereal solution of phenyllithium was added to 6.70 g. (0.02 mole) of a mixture of compounds (I) and (II) in 50 ml. of THF. Immediately a purple color developed with evolution of some heat. Color Test I was negative after the addition was completed. The reaction mixture was worked up by the general procedure after one hour of stirring, followed by chromatography on alumina. Elution with petroleum ether (b.p. 60-70°) gave the following compounds: the starting material, 1.85 g. (27.6% recovery); tetraphenylsilane, 0.15 g. (2.2%); and 3-triphenylsilylpropyne, 0.64 g. (10.7%), m.p. 89-91°, after recrystallization from n-propanol. The latter compound was identified by its infrared spectrum (see Table 6). Elution with carbon tetrachloride gave a fair amount of non-crystallizing polymeric oil.

f. Reaction of triphenylsilyllithium with 1,3-bis(triphenylsilyl)-propene, followed by addition of chlorotriphenylsilane A solution of triphenylsilyllithium (0.02 mole) was added over a period of 15 minutes to 5.35 g. (0.0096 mole) of 1,3-bis(triphenylsilyl)propene in 50 ml. of THF. A deep reddish color developed. After stirring for 24 hours there was added 7.20 g. (0.024 mole) of chlorotriphenylsilane in 50 ml. of ether. The color of the reaction mixture faded gradually and completely over a period of 11 hours. The mixture was hydrolyzed with dilute acid. Hexaphenyldisilane, 3.45 g. (33.3%), was separated by filtration. The residue obtained after a work-up of the organic layer was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave 1.80 g. (34.6%) of triphenylsilane. Further elution with carbon tetrachloride gave an oil, which was treated with a mixture of petroleum ether (b.p. 60-70°) and methanol to give 5.65 g. (34.6%) of 1,3,3-tris(triphenylsilyl)propene, m.p. 165-166.5°, after two recrystallizations from an ethyl acetate-methanol mixture.

Anal. Calcd. for $C_{57}H_{48}Si_3$: C, 83.78; H, 5.92; Si, 10.31. Found: C, 83.91, 83.81; H, 5.80, 5.74; Si, 10.29, 10.27.

The n.m.r. spectrum supports the proposed structure (see Table 3).

11. Reaction of triphenylsilyllithium with 2,3-dichloropropene

a. 1:1 ratio A solution of triphenylsilyllithium (0.03 mole) was added dropwise over a period of one and one quarter hours to 3.30 g. (0.03 mole) of 2,3-dichloropropene in 100 ml. of THF. The reaction mixture was a light brown. It was stirred for 3 hours. Subsequent to hydrolysis with dilute acid, hexaphenyldisilane, 2.20 g. (28.3%), was separated by filtration. The organic layer was worked up by the general procedure and subsequently chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave in the first fraction 0.85 g. (10.9%) of triphenylsilane, which was identified by its infrared spectrum. Further elution with the same solvent gave a partially solidified oil, which was treated with a petroleum ether (b.p. 60-70°)-methanol mixture. A compound (III), m.p. 99-100°, crystallized out. The mother liquor was concentrated and more of compound (III) was isolated. The filtrate was again concentrated to give a material with a melting range of 78-95°. It was recrystallized twice from methanol to give pure compound (III). The total yield of compound (III) was 1.95 g. (19.5%). From the third filtrate there was obtained 0.10 g. of 1-triphenylsilylpropyne, m.p. 114-115° (mixed m.p.). Further elution with the same solvent gave 0.60 g. of 1-triphenylsilylpropyne. The combined yield was 0.70 g. (7.8%).

The melting point of compound (III) was raised to 101-102° after two recrystallizations from methanol. The infrared spectrum (see Table 4) showed the characteristic absorption bands for a double bond at 6.18 μ and 10.72 μ. Other characteristic bands for the compound were: 11.64 μ (a possible chlorine bond attached to an unsaturated carbon) and 12.95 μ (a possible methylene group).

The n.m.r. spectrum indicated the presence of a methylene group and terminal vinyl hydrogens (see Table 3).

A possible structure is 2-chloro-3-triphenylsilylpropene.

b. <u>2:1 ratio, followed by addition of chlorotriphenylsilane</u> A solution of triphenylsilyllithium (0.05 mole) was added dropwise over a period of 30 minutes to 2.75 g. (0.025 mole) of 2,3-dichloropropene in 100 ml. of ether. Color Test I was slightly positive and the color of the reaction mixture was a reddish-brown. After 20 minutes of stirring, 7.5 g. (0.025 mole) of chlorotriphenylsilane in ether was added. The reaction mixture was stirred for one hour. It was worked up by the same procedure as in (a) above. The compounds isolated were: hexaphenyldisilane, 4.50 g. (34.7%); triphenylsilane, 3.10 g. (47.7%); 1-triphenylsilylpropyne, 1.55 g. (20.8%); a mixture of 1-triphenylsilylpropyne and compound (III), 1.0 g.; and tris(triphenylsilyl)propadiene, 0.55 g. (2.7%). The last compound was identified by a mixed melting point determination with the compound obtained from the reaction of triphenylsilyllithium with 1-triphenylsilylpropyne followed by addition of chlorotriphenylsilane.

c. <u>8:3 ratio, followed by addition of chlorotriphenylsilane</u> A solution of triphenylsilyllithium (0.08 mole) was added dropwise over a period of three and one quarter hours to 3.30 g. (0.03 mole) of 2,3-dichloropropene in 100 ml. of THF. Color Test I was weakly positive and the color of the reaction mixture was a dark reddish-brown. After two and three quarter hours of stirring, 10.4 g. (0.035 mole) of chlorotriphenylsilane in 30 ml. of THF was added. The stirring was continued for another hour before the reaction mixture was worked up by the same procedure as in (a). The compounds isolated were: hexaphenyldisilane, 0.25 g. (3.3%); triphenylsilane, 9.65 g. (46.4%); 1-triphenylsilylpropyne, 0.85 g. (9.5%); 1,2-bis(triphenylsilyl)propene, 0.90 g. (5.4%); 1,3-bis(triphenylsilyl)propyne, 0.75 g. (4.5%); and tris(triphenylsilyl)propadiene, 4.40 g. (18.0%). The last three compounds were identified by mixed melting points and a comparison of their infrared spectra with those of the respective compounds obtained from the reaction of triphenylsilyllithium with 1-triphenylsilylpropyne followed by the addition of chlorotriphenylsilane.

d. Reaction of triphenylsilyllithium with compound (III) A solution of triphenylsilyllithium (0.005 mole) was added dropwise over a period of 15 minutes to 1.60 g. (0.0048 mole) of compound (III) in 50 ml. of THF. A purple color developed immediately. During the first few hours of stirring the purple color faded to light orange. After stirring for a total of 7.5 hours the reaction mixture was worked up by the same procedure as in (a). The compounds isolated were: triphenylsilane, 0.80 g. (64.1%), and 1-triphenylsilylpropyne, 0.90 g. (62.9%).

D. Reactions of Triphenylsilyllithium with 1-Triphenylsilylpropyne and Related Reactions

1. Reaction of triphenylsilyllithium with 1-triphenylsilylpropyne

a. Without addition of chlorotriphenylsilane A solution of triphenylsilyllithium (0.03 mole) was added dropwise over a period of 20 minutes to 9.25 g. (0.031 mole) of 1-triphenylsilylpropyne in 70 ml. of THF. The reaction mixture was stirred for 5 hours at room temperature during which time Color Test I remained positive. A work-up by the general procedure gave a solid residue which was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave in the first fraction 4.0 g. (51.3%) of triphenylsilane, which was identified by its infrared spectrum. Further elution with the same solvent gave in the second fraction 1.70 g. (18.4% recovery) of the starting material. Still further elution with the same solvent gave in the third fraction 3.20 g. (18.5%) of 1,2-bis(triphenylsilyl)propene, m.p. 147-149°, after several recrystallizations from an ethyl acetate-methanol mixture.

Anal. Calcd. for $C_{39}H_{34}Si_2$: C, 83.81; H, 6.13; Si, 10.05. Found: C, 83.89, 83.77; H, 6.23, 6.43; Si, 10.05, 9.84. The n.m.r. spectrum (see Table 3) was in agreement with the proposed structure. The infrared spectrum, however, did not show any absorption band corresponding to a double bond.

Elution with carbon tetrachloride gave an oil which was treated with petroleum ether (b.p. 60-70°) to give 4.10 g. of 1,3-bis(triphenylsilyl)propyne, m.p. 127-128.5°, after recrystallization from an ethyl acetate-methanol mixture. The mother liquor was concentrated and an additional 1.05 g. of the same compound crystallized out. The total yield was 5.15 g. (29.9%).

Anal. Calcd. for $C_{39}H_{32}Si_2$: C, 84.12; H, 5.79; Si, 10.09. Found: C, 84.35, 84.31; H, 5.91, 5.77; Si, 9.97, 9.95.

The infrared spectrum showed a characteristic triple bond absorption band at 4.60 μ (see Table 6).

b. Followed by addition of chlorotriphenylsilane

(1) Run 1 (in a mixture of ether and THF) A solution of triphenylsilyllithium (0.03 mole) was added dropwise to 9.0 g. (0.03 mole) of 1-triphenylsilylpropyne in 70 ml. of ether at room temperature. A deep reddish-brown color developed. After 5 hours of stirring there was added 9.0 g. (0.03 mole) of chlorotriphenylsilane in ether. The color of the reaction mixture faded to light yellow. The reaction mixture was hydrolyzed with dilute acid after one hour of stirring. Hexaphenyldisilane, 2.45 g. (15.8%), was separated by filtration. The organic layer was worked up in the usual manner and the residue was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave the following compounds: triphenylsilane, 4.25 g. (54.5%); 1-triphenylsilylpropyne, 2.55 g. (28.6% recovery); and 1,2-bis(triphenylsilyl)propene, 2.45 g. (14.6%).

Elution with carbon tetrachloride gave an oil which upon treatment with petroleum ether (b.p. 60-70°) yielded 5.65 g. (23.1%) of crude tris(triphenylsilyl)propadiene, m.p. 181-184°. The melting point was raised to 188-189.5° after two recrystallizations from an ethyl acetate-methanol mixture.

Anal. Calcd. for $C_{57}H_{46}Si_3$: C, 83.97; H, 5.69; Si, 10.34; mol. wt., 815.21. Found: C, 84.09, 84.01; H, 5.86, 5.73; Si, 10.21, 10.20; mol. wt., 764 (Rast). The infrared spectrum showed a characteristic allenic absorption band at 5.30 μ (see Table 5). The n.m.r. spectrum supported the proposed structure showing a single peak at 5.75 τ (see Table 3).

From the mother liquor after separation of tris(triphenylsilyl)-propadiene there was obtained 0.90 g. (5.4%) of 1,3-bis(triphenylsilyl)-propyne, m.p. 126-127.5° (mixed m.p.).

(2) Run 2 (in THF) A solution of triphenylsilyllithium (0.03 mole) was added dropwise to 9.10 g. (0.03 mole) of 1-triphenylsilylpropyne in 50 ml. of THF. After 5.5 hours of stirring there was added 10.0 g. (0.033 mole) of chlorotriphenylsilane in 50 ml. of THF. Color Test I was positive prior to this addition. The reaction mixture was hydrolyzed with dilute acid after one hour of stirring. The organic layer was dried with sodium sulfate. The solvent was removed. When the oily residue was treated with petroleum ether (b.p. 60-70°) there appeared a fairly large amount (6.10 g.) of precipitate which was filtered off. The melting point of this precipitate was 177-182°. It was raised to 186-188° after recrystallization from an ethyl acetate-methanol mixture. A mixed melting point with tris(triphenylsilyl)propadiene was not depressed.

The mother liquor was poured onto an alumina column for chromatography. The following compounds were isolated: triphenylsilane, 2.00 g. (25.2%); 1-triphenylsilylpropyne, 0.90 g. (9.9% recovery); 1,2-bis(triphenylsilyl)propene, 3.00 g. (18.0%); tris(triphenylsilyl)-propadiene, 1.85 g.; and 1,3-bis(triphenylsilyl)propyne, 1.60 g. (9.5%). The combined yield of tris(triphenylsilyl)propadiene was 7.95 g. (32.1%).

2. Reaction of phenyllithium with 1-triphenylsilylpropyne

a. Followed by addition of triphenylsilane

(1) Run 1 (5 hours) A solution of phenyllithium (0.03 mole) was added dropwise over a period of 15 minutes to 9.0 g. (0.03 mole) of 1-triphenylsilylpropyne in 50 ml. of THF. The reaction mixture became slightly warm during this addition. After 5 hours of stirring at room temperature, during which time Color Test I became negative, there was added 7.8 g. (0.03 mole) of triphenylsilane in 60 ml. of THF. The reaction mixture was stirred for another 5 hours. The solution was a dark reddish-brown. A work-up by the general procedure left an oily residue which was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave in the first fraction 5.45 g. (69.9% recovery) of triphenylsilane, which was identified by its infrared spectrum. Further elution with the same solvent gave in the second fraction a mixture of tetraphenylsilane and 1-triphenylsilylpropyne. Fractional recrystallization of this mixture from petroleum ether (b.p. 60-70°) gave 0.75 g. (9.6%) of tetraphenylsilane and 1.25 g. (13.9% recovery) of 1-triphenylsilylpropyne. Both compounds were identified by mixed melting points with authentic samples.

Further elution with carbon tetrachloride gave an oil which upon treatment with petroleum ether (b.p. 60-70°) yielded 4.55 g. (27.2%) of 1,3-bis(triphenylsilyl)propyne, m.p. 126-127.5° (mixed m.p.).

(2) Run 2 (24 hours) A solution of phenyllithium (0.03 mole) was added to 9.0 g. (0.03 mole) of 1-triphenylsilylpropyne in 70 ml. of THF. After 16 hours of stirring at room temperature there was

added 8.50 g. (0.0326 mole) of triphenylsilane in 30 ml. of THF. The reaction mixture was stirred for another 24 hours. It was worked up by the same procedure as in Run 1 to give triphenylsilane, 4.60 g. (54.1% recovery); tetraphenylsilane, 1.11 g. (11.0%); 1-triphenylsilylpropyne, 1.45 g. (17.2% recovery); and 1,3-bis(triphenylsilyl)propyne, 5.30 g. (31.7%).

b. Followed by addition of chlorotriphenylsilane A solution of phenyllithium (0.02 mole) was added slowly to 6.0 g. (0.02 mole) of 1-triphenylsilylpropyne in 50 ml. of THF. After stirring for 7 hours there was added 6.30 g. (0.021 mole) of chlorotriphenylsilane in 50 ml. of ether. The reaction mixture was stirred for another 1.5 hours. It was worked up in the usual manner and subsequently chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave 0.77 g. (11.5%) of tetraphenylsilane and 1.95 g. (32.5% recovery) of 1-triphenylsilylpropyne. Further elution with carbon tetrachloride gave an oil which upon treatment with petroleum ether (b.p. 60-70°) yielded 3.67 g. (22.5%) of tris(triphenylsilyl)propadiene, m.p. 186-188° (mixed m.p.). The mother liquor was concentrated and there crystallized out 1.40 g. (12.6%) of 1,3-bis(triphenylsilyl)propyne, m.p. 127-128° (mixed m.p.).

3. Reaction of triphenylsilyllithium with tris(triphenylsilyl)propadiene

a. Without addition of chlorotriphenylsilane A solution of triphenylsilyllithium (0.013 mole) was added to 5.8 g. (0.0071 mole) of tris(triphenylsilyl)propadiene in a mixture of 50 ml. of ether and 50 ml. of THF at room temperature. After 3 hours of stirring Color Test I was only faintly positive. The reaction mixture was worked up by the usual procedure after a total stirring of 5 hours. The residue obtained was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave 2.35 g. (69.5%) of triphenylsilane, which was identified by its infrared spectrum. Further elution with carbon tetrachloride gave an oil which was treated with petroleum ether (b.p. 60-70°) to yield 5.15 g. (88.8%) of the starting material, tris(triphenylsilyl)propadiene.

b. <u>Followed by addition of chlorotriphenylsilane</u> A solution of triphenylsilyllithium (0.0135 mole) was added slowly to 5.6 g. (0.0069 mole) of tris(triphenylsilyl)propadiene in 77 ml. of THF at room temperature. Color Test I was positive after 3.5 hours of stirring. The reaction mixture was stirred for a total of 6 hours before 4.0 g. (0.013 mole) of chlorotriphenylsilane in 40 ml. of THF was added. After being stirred for an additional 3.5 hours, the reaction mixture was hydrolyzed with dilute acid. Hexaphenyldisilane, 2.20 g. (31.4%), was separated by filtration. A work-up of the organic layer left a solid residue which was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave 1.85 g. (52.6%) of triphenylsilane. Further elution with carbon tetrachloride gave an oil which upon treatment with petroleum ether (b.p. 60-70°) gave 4.25 g. (76.0%) of the starting material. However, this material contained some tetrakis(triphenylsilyl)propadiene, as evidenced by the presence of an additional absorption band at 5.5μ in its infrared spectrum, although the melting point was 186.5-188.5° (mixed m.p.). From the mother liquor there was isolated 0.20 g. (2.7%) of crude tetrakis(triphenylsilyl)propadiene, m.p. 418-440°.

4. Reaction of phenyllithium with tris(triphenylsilyl)propadiene

a. Followed by addition of chlorotriphenylsilane An ethereal solution of phenyllithium (0.01 mole) was added to 6.0 g. (0.00736 mole) of tris(triphenylsilyl)propadiene in 60 ml. of THF. The reaction mixture became slightly warm. Color Test I was negative after 1.5 hours of stirring. A solution of 3.3 g (0.011 mole) of chlorotriphenylsilane in 30 ml. of THF was added after a total of 4 hours of stirring. The reaction mixture was stirred for another 23 hours, during which time the color of the solution changed from light clear brown to yellow. A work-up by the general procedure gave an oily residue which was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave 0.40 g. (11.9%) of tetraphenylsilane which was identified by a mixed melting point determination with an authentic sample. Further elution with carbon tetrachloride gave an oil in three fractions which were treated separately with petroleum ether (b.p. 60-70°). From the first fraction there was obtained 0.15 g. of pure starting material. When the second fraction was treated with petroleum ether (b.p. 60-70°), there precipitated out 0.55 g. of a material, melting above 305°, which was recrystallized from an ethyl acetate-methanol mixture to give 0.35 g. of tetrakis(triphenylsilyl)propadiene, m.p. 442-448°. The mother liquor was concentrated and some petroleum ether (b.p. 60-70°) was replaced with ethyl acetate. Upon the addition of cold methanol there precipitated out 2.65 g. of a material melting at 183-203°. Fractional recrystallization from an ethyl acetate-methanol mixture gave 0.85 g. of pure starting material and 0.17 g. of tetrakis(triphenylsilyl)propadiene, m.p.

448-452°. The third fraction gave, after similar treatment to the above, 0.55 g. of tetrakis(triphenylsilyl)propadiene, m.p. 448-452°. The total yield of the starting material recovered in pure form was 1.0 g. (16.7%). Tetrakis(triphenylsilyl)propadiene was obtained in a yield of 1.07 g. (13.5%).

Anal. Calcd. for $C_{75}H_{60}Si_4$: C, 83.90; H, 5.63; Si, 10.47; mol. wt., 1073.6. Found: C, 83.25, 83.05; H, 5.67, 5.50; Si, 10.25, 10.25; mol. wt., 1058, 990. The infrared spectrum showed a very intense band at 5.49 μ which was attributable to the allenic bond. Other characteristic bands appeared at 12.00 μ and 12.18 μ (see Table 5). The n.m.r. spectrum showed only the absorption signals of the aromatic hydrogens, thus supporting the structure of a tetra-substituted allene.

b. Followed by addition of methyl iodide A solution of phenyllithium (0.01 mole) was added slowly to 2.20 g. (0.0027 mole) of tris(triphenylsilyl)propadiene in 50 ml. of THF. After a stirring of 3.25 hours at room temperature there was added 1.8 g. (0.0127 mole) of methyl iodide in 10 ml. of THF. Some heat was evolved and the reaction mixture became colorless. After one hour of stirring the reaction mixture was worked up in the usual manner, followed by chromatography on alumina. Elution with petroleum ether (b.p. 60-70°) did not give any product. Elution with carbon tetrachloride gave a solid product which was recrystallized from petroleum ether (b.p. 60-70°) to give 1.70 g. (67%) of 1,1,3-tris(triphenylsilyl)-1,2-butadiene, m.p. 196-198°.

Anal. Calcd. for $C_{58}H_{48}Si_3$: C, 84.00; H, 5.83; Si, 10.16. Found: C, 82.51, 82.34; H, 6.06, 5.97; Si, 10.22, 10.12.

The infrared spectrum showed a very intense allenic absorption band at 5.34μ (see Table 5). A band at 7.36μ was very likely due to the methyl group present.

c. Followed by addition of deuterium oxide[84] A solution of phenyllithium (0.01 mole) was added to 2.0 g. (0.0025 mole) of tris(triphenylsilyl)propadiene in 60 ml. of THF. After a stirring of 3 hours there was added 0.8 ml. (0.04 mole) of deuterium oxide. Some ether was added. The organic layer was washed twice with water and dried with sodium sulfate. The solvent was removed. The residue was treated with petroleum ether (b.p. 60-70°) and methanol to give 1.75 g. (87.5%) of deuterated tris(triphenylsilyl)propadiene, m.p. 187-189°, after recrystallization from an ethyl acetate-methanol mixture. The mixed melting point of the non-deuterated and the deuterated compounds was not depressed. Their infrared spectra were identical, except that a peak at 13.80μ was missing in the spectrum of the deuterated compound. The n.m.r. spectrum showed no signal at 5.75τ, indicating that the compound was deuterated completely.

5. Reaction of triphenylsilyllithium with 1,3-bis(triphenylsilyl)propyne followed by addition of chlorotriphenylsilane

A solution of triphenylsilyllithium (0.01 mole) was added slowly over a period of 15 minutes to 5.2 g. (0.0093 mole) of 1,3-bis(triphenylsilyl)propyne in 50 ml. of THF. A deep reddish-brown color developed

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[84] Deuterium oxide was kindly provided by Dr. R. W. King of Iowa State University.

almost immediately after this addition. After a stirring of 3.5 hours at room temperature there was added 3.5 g. (0.012 mole) of chlorotriphenylsilane in 30 ml. of THF. The solution was decolorized almost immediately without evolving any heat. The reaction mixture was hydrolyzed with dilute acid after an additional stirring of 3 hours. A small amount, 0.15 g. (2.9%), of hexaphenyldisilane was separated by filtration. The organic layer was worked up by the usual procedure and the residue was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave 2.30 g. (88.5%) of triphenylsilane, which was identified by its infrared spectrum. Elution with carbon tetrachloride gave an oil, which upon treatment with petroleum ether (b.p. 60-70°) yielded a total of 3.85 g. (50.8%) of tris(triphenylsilyl)propadiene, m.p. 187-188.5°, after recrystallization from an ethyl acetate-methanol mixture. From the mother liquor there was obtained 0.12 g. of a high melting material, m.p. 444-600°(+), part of which was tetrakis(triphenylsilyl)propadiene, as indicated by the presence of an absorption band at 5.50μ in its infrared spectrum (see Table 5).

6. Reaction of phenyllithium with 1,3-bis(triphenylsilyl)propyne

a. Followed by addition of chlorotriphenylsilane   A solution of phenyllithium (0.01 mole) was added slowly over a period of 15 minutes to 5.60 g. (0.01 mole) of 1,3-bis(triphenylsilyl)propyne in 50 ml. of THF at room temperature. Immediately a reddish color developed and the solution became warm. The reaction mixture was stirred for 3 hours, during which time its color became a very dark reddish-brown. Color Test

I was, however, negative. A solution of 3.30 g. (0.011 mole) of chlorotriphenylsilane in 30 ml. of THF was added. The color of the reaction mixture changed slowly from dark to light orange. After 2 hours of stirring one gram more of chlorotriphenylsilane was added and the stirring was continued for another 3 hours. The reaction mixture was then worked up by the general procedure and the residue was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave 0.40 g. (11.9%) of tetraphenylsilane, which was identified by a mixed melting point determination with an authentic sample. Further elution with carbon tetrachloride gave an oil, which upon treatment with petroleum ether (b.p. 60-70°) yielded 3.45 g. (42.4%) of tris(triphenylsilyl)propadiene, m.p. 187-189°, after recrystallization from an ethyl acetate-methanol mixture. This compound was identified by a mixed melting point determination and by a comparison of the infrared spectra. The mother liquor was concentrated and there was isolated 1.55 g. (27.7%) of the starting material, 1,3-bis(triphenylsilyl)propyne. In addition, a trace amount of tetrakis(triphenylsilyl)propadiene, identified by its infrared spectrum, was formed.

b. Followed by addition of methyl iodide

(1) Run 1 (2:1) A solution of phenyllithium (0.01 mole) was added rapidly to 2.50 g. (0.0045 mole) of 1,3-bis(triphenylsilyl)-propyne in 50 ml. of THF. The solution immediately became reddish-black and evolved some heat. After one hour's stirring there was added 1.80 g. (0.0127 mole) of methyl iodide in 10 ml. of THF. The reaction mixture was worked up by the general procedure after one hour of stirring. The

residue obtained was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave in the first fraction 0.13 g. (8.6%) of tetraphenylsilane. Further elution with the same solvent gave in the second fraction 0.08 g. (3.1%) of a compound with a melting point of 166-167° after recrystallization from petroleum ether (b.p. 60-70°). The infrared spectrum of this compound was very similar to that of 2,4-bis(triphenylsilyl)-2,3-pentadiene, which was obtained from the reaction of phenyllithium with a mixture of 1,3-bis(triphenylsilyl)-1-butyne and 1,3-bis(triphenylsilyl)-1,2-butadiene followed by the addition of methyl iodide. Further elution with carbon tetrachloride gave an oil, which upon treatment with petroleum ether (b.p. 60-70°) gave 0.95 g. of a material with a melting point of 131-135°. Recrystallization from an ethyl acetate-methanol mixture failed to give a pure product. The infrared spectrum showed characteristic bands at 4.65 (strong), 5.25 (weak), 10.75, 11.32, and 12.80μ. The material may have been a mixture of 1,3-bis(triphenylsilyl)-1-butyne and 1,3-bis(triphenylsilyl)-1,2-butadiene. From the mother liquor there was obtained an additional 0.35 g. of the mixture. The total yield of the mixture was 1.30 g. (50.8%).

(2) <u>Run 2 (1:1)</u> A solution of phenyllithium (0.01 mole) was added slowly to 5.10 g. (0.0092 mole) of 1,3-bis(triphenylsilyl)-propyne in 70 ml. of THF. The reaction mixture was stirred for 20 hours at room temperature before 1.80 g. (0.0127 mole) of methyl iodide in 15 ml. of THF was added. After being stirred for 2 hours, the reaction mixture was worked up by the same procedure as in Run 1. Tetraphenylsilane was not isolated. The yield of the mixture was 3.05 g. (58%). The

infrared spectrum of the mixture showed characteristic bands (in carbon disulfide solution) at 5.22, 7.32, 7.36, 10.30, 10.60 (very weak), 10.98, 11.85 (weak), and 13.76μ. The analysis of these bands (see Table 7) indicated that the following compounds were present in the mixture: 1,3-bis(triphenylsilyl)-1-butyne (7.32, 10.30, 10.98); 1,3-bis(triphenylsilyl)-1,2-butadiene (5.22, 7.36, 10.60, 13.76); 1,3-bis(triphenylsilyl)-3-methyl-1-butyne (7.36, 11.84); and possibly the starting material (7.32, 13.76). Three recrystallizations of this mixture gave a material with a melting point of 133-135°. It was predominantly 1,3-bis(triphenylsilyl)-1-butyne, the major contaminant being the starting material (13.33, 13.76). 1,3-Bis(triphenylsilyl)-1-butyne was obtained from the reaction of phenyllithium with 1-triphenylsilyl-1-butyne followed by the addition of triphenylsilane, m.p. 135-136.5°.

7. Reaction of triphenylsilyllithium with 1-triphenylsilyl-1-butyne

A solution of triphenylsilyllithium (0.03 mole) was added to 7.35 g. (0.0235 mole) of 1-triphenylsilyl-1-butyne in 70 ml. of THF. The reaction mixture was stirred for 40.5 hours at room temperature. Its color remained a dark reddish-brown. The reaction mixture was worked up in the usual manner and the black residue obtained was treated with petroleum ether (b.p. 60-70°). A solid material, 0.80 g., m.p. 190-220°, was separated by filtration. It was recrystallized from an ethyl acetate-ethanol mixture, 0.60 g., m.p. 197-225°. The mother liquor was poured onto an alumina column. Elution with petroleum ether (b.p. 60-70°) gave in the first fraction 3.35 g. (43.0%) of triphenylsilane, which was identified by its infrared spectrum. Further elution with the same solvent gave a partially solidified oil in several fractions from which the following compounds were isolated: tetraphenylsilane, 0.35 g. (4.4%), m.p. 230-233° (mixed m.p.); 1-triphenylsilyl-1-butyne, 0.20 g. (2.7% recovery); a compound obtained from the reaction of triphenylsilyllithium with 1-bromo-1-butene, 0.15 g., m.p. 221-223°; and a compound, possibly 1,2-bis(triphenylsilyl)-1-butene, 0.20 g. (2%), m.p. 134-137°, whose infrared spectrum showed a moderately strong absorption band at 6.25μ, suggesting the presence of a double bond. Elution with carbon tetrachloride gave 3.90 g. of an oil from which there was isolated 0.15 g. (1.8%) of crude 1,3-bis(triphenylsilyl)-1-butyne, m.p. 128-133°, which was identified by a comparison of infrared spectra.

8. Reaction of phenyllithium with 1-triphenylsilyl-1-butyne

a. Followed by addition of triphenylsilane An ethereal solution of phenyllithium (0.034 mole) was added slowly to 9.35 g. (0.030 mole) of 1-triphenylsilyl-1-butyne in 100 ml. of THF. The reaction mixture was stirred for 20 hours at room temperature before 9.40 g. (0.036 mole) of triphenylsilane in 30 ml. of THF was added. After being stirred for another 20 hours, the reaction mixture was hydrolyzed with dilute acid. An insoluble material, 3.70 g., was separated by filtration. It was identified as tetraphenylsilane, m.p. 231-233.5° (mixed m.p.). The organic layer was worked up by the general procedure and the residue was treated with petroleum ether (b.p. 60-70°). The precipitate was filtered off. It was identified as tetraphenylsilane, 1.35 g. The mother liquor was poured onto an alumina column. Elution with petroleum ether (b.p. 60-70°) gave 7.65 g. (81.4% recovery) of triphenylsilane, identified by its infrared spectrum, and 0.40 g. of tetraphenylsilane. The combined yield of tetraphenylsilane was 5.45 g. (47.6% based on phenyllithium). In addition, there was isolated 0.20 g. (1.3%) of crude starting material.

Elution with carbon tetrachloride gave an oil in two fractions, both of which were treated separately with a mixture of petroleum ether (b.p. 60-70°) and methanol. The first fraction gave 1.45 g. (11.7%) of a material with a melting range of 128.5-136°. The infrared spectrum showed characteristic absorption bands at 4.64, 5.23, 7.35, 10.30, 10.68, 10.99, and 13.79μ. This material was possibly a mixture of 1,3-bis(triphenylsilyl)-1-butyne and 1,3-bis(triphenylsilyl)-1,2-butadiene. (For a comparison of infrared spectra see Table 7.) The second fraction yielded 0.55 g. (3.2%) of what was possibly 1,3-bis(triphenylsilyl)-1-butyne, m.p. 135-136.5°. The infrared spectrum showed characteristic bands at 4.64 ($-C\equiv C-$), 10.30, and 10.99μ.

Anal. Calcd. for $C_{40}H_{34}Si_2$: C, 84.16; H, 6.00; Si, 9.84. Found: C, 84.44, 84.24; H, 5.86, 5.76; Si, 9.67, 9.64.

b. Followed by addition of methyl iodide An ethereal solution of phenyllithium (0.015 mole) was added to 3.15 g. (0.01 mole) of 1-triphenylsilyl-1-butyne in 50 ml. of THF. The reaction mixture was stirred for 19 hours before 2.25 g. (0.016 mole) of methyl iodide in 30 ml. of ether was added. The reaction mixture went from light brown to colorless with the evolution of some heat. It was hydrolyzed with dilute acid after 1.75 hours of stirring. Tetraphenylsilane, 1.15 g., was separated by filtration. The organic layer was worked up in the usual manner leaving an oily residue, which was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave an oil which was treated with methanol. The insoluble material was filtered off and identified as tetraphenylsilane, 0.25 g., m.p. 231-234° (mixed m.p.). The combined yield of tetraphenylsilane was 1.40 g. (41.6% based on 1-triphenylsilyl-1-butyne). From the mother liquor there was obtained 0.10 g. (3.1%) of what was possibly 1-triphenylsilyl-3-methyl-1-butyne, m.p. 79-81°. The infrared spectrum showed characteristic bands at 4.60 (-C≡C-), 7.65, 10.38, and 12.11 μ (see Table 6).

9. Reaction of phenyllithium with a mixture of 1,3-bis(triphenylsilyl)-1-butyne and 1,3-bis(triphenylsilyl)-1,2-butadiene, followed by addition of methyl iodide

The starting mixture was obtained from two sources: (1) from the reaction of phenyllithium with 1,3-bis(triphenylsilyl) propyne followed by the addition of methyl iodide; (2) from the reaction of phenyllithium with 1-triphenylsilyl-1-butyne followed by the addition of triphenylsilane.

An ethereal solution of phenyllithium (0.01 mole) was added to 3.15 g. (0.0055 mole) of a mixture of 1,3-bis(triphenylsilyl)-1-butyne and 1,3-bis(triphenylsilyl)-1,2-butadiene in 60 ml. of THF. The reaction mixture was stirred for 3 hours before 1.8 g. (0.0127 mole) of methyl iodide in 15 ml. of ether was added. The reaction mixture went from orange-brown to colorless upon the addition of methyl iodide. After 2 hours of stirring the reaction mixture was worked up by the general procedure, followed by chromatography on alumina. Elution with petroleum ether (b.p. 60-70°) gave 0.10 g. of tetraphenylsilane, m.p. 229-232° (mixed m.p.). Elution with carbon tetrachloride gave an oil which was treated with petroleum ether (b.p. 60-70°) to give 1.90 g. of a solid, m.p. 140-162°. Recrystallization from a mixture of ethyl acetate and methanol yielded 1.15 g. (35.8%) of crude 2,4-bis(triphenylsilyl)-2,3-pentadiene, m.p. 165-170°. Another recrystallization from the same solvent mixture produced 0.90 g. (28.0%) and raised the melting point to 174-175°. (See Table 5 for the infrared spectrum.)

Anal. Calcd. for $C_{41}H_{36}Si_2$: C, 84.19; H, 6.20; Si, 9.61. Found: C, 84.51, 84.31; H, 6.00, 5.94; Si, 9.64, 9.64. From the filtrate and from the original mother liquor there was obtained a material, 1.60 g. (50%), which melted in the range of 135-145°. An attempt to purify by recrystallization failed. The infrared spectrum of this material showed characteristic bands at 4.61, 4.68, 5.22, 7.36, 10.10 (?), 10.34 (very weak), 11.00 (broad and very weak), and 11.84μ. Analysis of these bands (see Table 7) indicated that this material was a mixture of 1,3-bis(triphenylsilyl)-1-butyne (trace, 4.61 ? , 10.34, 11.00), 2,4-bis(triphenylsilyl)-2,3-pentadiene (5.22, 7.37, 10.10, 11.03), and possibly 1,3-bis(triphenylsilyl)-3-methyl-1-butyne (4.68, 7.36, 11.84).

10. Reaction of triphenylsilyllithium with allyltriphenylsilane

A solution of triphenylsilyllithium (0.02 mole) was added to 6.0 g. (0.02 mole) of allyltriphenylsilane in 30 ml. of THF. After being stirred for 22 hours at room temperature, the reaction mixture was worked up by the general procedure and the residue obtained was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave in the first fraction 1.50 g. (29%) of triphenylsilane, which was identified by its infrared spectrum. Further elution with the same solvent gave in the second fraction 0.55 g. (9.2%) of allyltriphenylsilane, the starting material. Following elution with carbon tetrachloride there was obtained 4.45 g. (40.0%) of 1,3-bis(triphenylsilyl)propene, m.p. 158-159.5°, after recrystallization from petroleum ether (b.p. 60-70°). This compound was identical with a dehydration product of 1,3-bis(triphenylsilyl)propan-2-ol. It was also identical with a product obtained from a reaction of triphenylsilyllithium with 1,3-dichloropropene in a 2:1 ratio.

E. Reactions of Triphenylsilyllithium with Polyhaloethylenes and Related Reactions

1. Reaction of triphenylsilyllithium with *cis*-1,2-dichloroethylene

A solution of triphenylsilyllithium (0.08 mole) was added dropwise over a period of 45 minutes to 2.42 g. (0.025 mole) of *cis*-1,2-dichloroethylene in 100 ml. of ether at room temperature. Color Test I was negative after the addition was completed. The reaction mixture was stirred for one hour before it was hydrolyzed with dilute acid. Hexaphenyldisilane, 9.60 g. (46.4%), was separated by filtration. The organic layer was dried with sodium sulfate. The solvent was removed and the residue was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave 7.10 g. (34.2%) of triphenylsilane, which was identified by its infrared spectrum. Further elution with carbon tetrachloride gave 0.80 g. of a material with a melting range of 182-194°. Its infrared spectrum was identical with that of an unidentified compound obtained from the reaction of triphenylsilyllithium with carbon tetrabromide.

2. Reaction of triphenylsilyllithium with trichloroethylene

a. 1:1 ratio A solution of triphenylsilyllithium (0.05 mole) was added dropwise over a period of 2 hours to 6.56 g. (0.05 mole) of trichloroethylene in 100 ml. of THF. After being stirred for an additional 3 hours, the reaction mixture was hydrolyzed with dilute acid. Hexaphenyldisilane, 7.60 g. (58.7%), was separated by filtration. The organic layer was worked up in the usual manner and the residue was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave a mixture of triphenylsilane and chlorotriphenylsilylacetylene. Two products were separated by treating the mixture with ethanol. Triphenylsilane was obtained in a yield of 0.80 g. (6.2%) and identified by its infrared spectrum. Chlorotriphenylsilylacetylene was obtained in a yield of 0.80 g. (5.0%) and identified by a mixed melting point determination with an authentic sample prepared from chloroethynyllithium and chlorotriphenylsilane.

Further elution with other solvents did not yield any other compounds in a pure state.

b. 2:1 ratio A solution of triphenylsilyllithium (0.08 mole) was added dropwise over a period of two hours and forty minutes to 5.25 g. (0.04 mole) of trichloroethylene in 100 ml. of ether. The color of the reaction mixture changed from orange to dark brown as the addition proceeded. After stirring for an additional 1.5 hours the reaction mixture was worked up by the same procedure as in the experiment above. The following compounds were isolated: hexaphenyldisilane, 12.40 g. (59.8%); triphenylsilane, 1.05 g. (10.0%); chlorotriphenylsilylacetylene, 1.00 g. (7.8%); and bis(triphenylsilyl)acetylene, 2.40 g. (11.0%), m.p. 155-157° (mixed m.p.).

In another run a temperature of -60° was employed. Triphenylsilane was not isolated. The following compounds were obtained: hexaphenyldisilane, 69.9%; chlorotriphenylsilylacetylene, 8.9%; and bis(triphenylsilyl)acetylene, 7.4%.

In a run using THF alone at room temperature the products were hexaphenyldisilane, 61.5%; triphenylsilane, 7.7%; and chlorotriphenylsilylacetylene, 6.7%. Bis(triphenylsilyl)acetylene was not isolated.

3. Preparation of bis(triphenylsilyl)acetylene

Acetone-free acetylene was bubbled through 130 ml. of THF in a 4-necked flask for 10 minutes. Subsequently there was slowly added over a period of one hour one-tenth mole of phenyllithium prepared from bromobenzene and lithium in 100 ml. of ether, acetylene being passed through the solution continuously. After an additional hour of stirring, there was added over a 20 minute period 29.5 g. (0.10 mole) of chlorotriphenylsilane in 100 ml. of THF, and the reaction mixture was stirred for another two hours. A work-up of the reaction mixture in the usual manner gave a solid residue which was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave 5.05 g. (17.8%) of triphenylsilylacetylene, b.p. 146-149°/0.05 mm., n_D^{20} 1.6180. The infrared spectrum of this compound showed a characteristic ethynyl hydrogen absorption band at 3.07μ and a triple bond absorption band at 4.91μ. Further elution with carbon tetrachloride gave 11.30 g. (41.6%) of bis(triphenylsilyl)-acetylene, m.p. 156-157°, after recrystallization from petroleum ether (b.p. 60-70°). The infrared spectrum of this compound did not show any triple bond absorption band, because of the symmetry of the molecule.

4. Preparation of chlorotriphenylsilylacetylene

a. From trichloroethylene A solution of phenyllithium (0.06 mole) was added over a period of one hour to a solution of 3.94 g. (0.03 mole) of trichloroethylene in 80 ml. of ether at -60°. After the addition was completed, the reaction mixture was allowed to warm to room temperature, whereupon there was added 9.30 g. (0.031 mole) of chlorotriphenylsilane in 70 ml. of ether. The color of the reaction mixture changed from white to black. After an hour's stirring the reaction mixture was worked up in the usual manner, leaving a solid residue which was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave 6.80 g. (71.0%) of crude chlorotriphenylsilylacetylene. This compound was recrystallized from ethanol to give 5.70 g. (59.6%) of the pure product, m.p. 101-102°.

b. From *cis*-1,2-dichloroethylene

(1) Run 1 (in ether) A solution of phenyllithium (0.06 mole) was added dropwise over a period of 18 minutes to 2.91 g.

(0.03 mole) of cis-1,2-dichloroethylene in 100 ml. of ether at -60°. After the addition was completed, the reaction mixture was allowed to warm to room temperature. When it reached room temperature, it became cloudy with the formation of some precipitate. A total of nine grams (0.03 mole) of chlorotriphenylsilane in 50 ml. of ether was added. The reaction mixture was stirred for another 5 hours. It was then worked up in the usual manner. The solid residue was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave 8.15 g. (85.1%) of crude chlorotriphenylsilylacetylene. This compound was recrystallized from ethanol to give 7.20 g. (75.3%) of the pure product, m.p. 101-103°.

(2) Run 2 (in a mixture of ether and THF) An ethereal solution of phenyllithium (0.06 mole) was added dropwise over a period of 30 minutes to 2.91 g. (0.03 mole) of cis-1,2-dichloroethylene in 100 ml. of THF at -60°. After the addition was completed, the reaction mixture was allowed to warm to room temperature. It became black as it reached room temperature. After a total stirring of 3 hours there was added 9.0 g. (0.03 mole) of chlorotriphenylsilane in 70 ml. of ether. The reaction mixture was hydrolyzed with dilute acid after stirring for another 1.5 hours. A trace amount of black solid was isolated by filtration. The organic layer was worked up by the same procedure as in Run 1 to give 7.70 g. (80.5%) of crude chlorotriphenylsilylacetylene. The pure yield was 7.07 g. (74.0%).

5. Preparation of bromotriphenylsilylacetylene

a. From pentabromoethane

(1) Run 1 (in ether at -60°) An ethereal solution of phenyllithium (0.06 mole) was added dropwise over a period of one-half hour to 8.50 g. (0.02 mole) of pentabromoethane in 60 ml. of ether at -60°. The reaction mixture was allowed to warm to room temperature. After two hours of stirring there was added 6.0 g. (0.02 mole) of chlorotriphenylsilane in 50 ml. of ether. The reaction mixture was worked up in the usual manner after another hour and twenty-four minutes of stirring. The residue was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave 0.76 g. (10.5%) of bromotriphenylsilylacetylene, m.p. 111-112.5° after recrystallization from ethanol. The infrared spectrum showed a sharp absorption band at 5.70 μ such as is characteristic of a triple bond.

Anal. Calcd. for $C_{20}H_{15}SiBr$: Si, 7.73. Found: Si, 7.69, 7.61. Elution with carbon tetrachloride gave 0.35 g. (3.2%) of bis(triphenylsilyl)acetylene, which was identified by a mixed melting point determination with an authentic sample.

(2) Run 2 (in a mixture of ether and THF at -60° ~ room temperature) An ethereal solution of phenyllithium (0.09 mole) was added dropwise to 12.75 g. (0.03 mole) of pentabromoethane in 70 ml. of THF at -60°. After the addition was completed, the reaction mixture was allowed to warm to room temperature. Within 20 minutes the reaction mixture turned from clear to black. The stirring was continued for 2.5 hours. Chlorotriphenylsilane (9.0 g., 0.03 mole) in 30 ml. of THF was

then added. The reaction mixture was hydrolyzed with dilute acid after another 1.5 hours of stirring. A black solid was separated by filtration. When dry, it was a powdery material and appeared to be carbon. The yield was 1.10 g. The organic layer was worked up by the same procedure as in Run 1 to give a trace amount of bromotriphenylsilylacetylene.

(3) <u>Run 3 (in a mixture of ether and THF at -60°)</u> An ethereal solution of phenyllithium (0.06 mole) was added dropwise over a period of half an hour to 8.50 g. (0.02 mole) of pentabromoethane in 80 ml. of THF at -60°. Color Test 1 was negative shortly after the completion of this addition. The stirring was continued for 30 minutes at -60° before 6.0 g. (0.02 mole) of chlorotriphenylsilane in 30 ml. of THF was added. The reaction mixture was stirred at -60° for a while and then it was allowed to warm to room temperature. It turned dark, but only a trace amount of black material was obtained. After 3 hours of stirring the reaction mixture was worked up by the same procedure as in Run 1 to give 1.95 g. (26.8%) of pure bromotriphenylsilylacetylene, m.p. 111.5-113.5°. Bis(triphenylsilyl)acetylene was not isolated.

b. <u>From tetrabromoethane</u>

(1) <u>Run 1 (in ether)</u> An ethereal solution of phenyllithium (0.06 mole) was added dropwise over a period of one-half hour to 6.92 g. (0.02 mole) of tetrabromoethane in 100 ml. of ether at -60°. The reaction mixture was allowed to warm to room temperature. Its color was an opaque light yellow and Color Test 1 was negative. After a stirring of 3 hours there was added 6.0 g. (0.02 mole) of chlorotriphenylsilane

in 50 ml. of THF. The reaction mixture was worked up in the usual manner after another 18 hours of stirring. The residue was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave 0.35 g. (6.2%) of triphenylsilylacetylene, which was identified by its infrared spectrum. Elution with carbon tetrachloride gave 4.20 g. (38.8%) of bis(triphenylsilyl)acetylene, m.p. 155-156° (mixed m.p.).

(2) Run 2 (in a mixture of ether and THF) An ethereal solution of phenyllithium (0.09 mole) was added dropwise over a period of half an hour to 10.4 g. (0.03 mole) of tetrabromoethane in 100 ml. of THF at -60°. The reaction mixture was allowed to warm to room temperature. After a stirring of 3.5 hours there was added 9.0 g. (0.03 mole) of chlorotriphenylsilane in 30 ml. of THF. The appearance of the reaction mixture changed from cloudy to clear upon the addition of chlorotriphenylsilane. After being stirred for another 1.5 hours, the reaction mixture was worked up by the same procedure as in Run 1 to give 3.85 g. (35.4%) of bromotriphenylsilylacetylene, m.p. 109.5-110.5° (mixed m.p.); 0.75 g. (8.8%) of triphenylsilylacetylene; and 0.90 g. (5.5%) of bis(triphenylsilyl)acetylene, m.p. 154-156° (mixed m.p.).

6. Reaction of triphenylsilyllithium with chlorotriphenylsilylacetylene

A solution of triphenylsilyllithium (0.02 mole) was added dropwise over a period of one hour to 5.55 g. (0.0174 mole) of chlorotriphenylsilylacetylene in 60 ml. of ether. The reaction mixture became slightly warm at this rate of addition, and an orange color developed. Color Test I was weakly positive. After a stirring of 3.5 hours the reaction mixture was hydrolyzed with dilute acid. Hexaphenyldisilane, 2.05 g. (22.7%), was separated by filtration. The organic layer was dried with sodium sulfate. The solvent was removed and the residue was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave in the first fraction 0.85 g. of a mixture of triphenylsilane and chlorotriphenylsilylacetylene, as shown by the infrared spectrum. Recrystallization of this partially solidified mixture from ethanol gave 0.30 g. (6.0%) of the pure starting material, chlorotriphenylsilylacetylene, m.p. 100-102° (mixed m.p.). Further elution with the same solvent gave 0.80 g. (15.8%) of triphenylsilylacetylene, which was identified by its infrared spectrum.

Elution with carbon tetrachloride gave a solid material which was crystallized from petroleum ether (b.p. 60-70°) to give 4.58 g. (48.5%) of bis(triphenylsilyl)acetylene, which was identified by a mixed melting point determination with a sample prepared from dilithium acetylide and chlorotriphenylsilane, and by a comparison of infrared spectra.

7. Reaction of triphenylsilyllithium with bromotriphenylsilylacetylene

A solution of triphenylsilyllithium (0.015 mole) was added dropwise over a period of half an hour to 4.95 g. (0.0136 mole) of bromotriphenylsilylacetylene in 60 ml. of ether at room temperature. After one hour's stirring the reaction mixture was worked up by the same procedure as in the reaction with chlorotriphenylsilylacetylene above. The following compounds were isolated: hexaphenyldisilane, 1.30 g. (18.4%); triphenylsilane, 0.05 g. (1.3%); the starting material, 0.45 g. (9.1%);

triphenylsilylacetylene, 0.95 g. (24.6%); and bis(triphenylsilyl)-acetylene, 3.90 g. (52.9%).

8. Reaction of triphenylsilyllithium with bis(triphenylsilyl)acetylene

A solution of triphenylsilyllithium (0.02 mole) was added dropwise over a period of 15 minutes to 10.85 g. (0.02 mole) of bis(triphenylsilyl)acetylene in 80 ml. of THF. During this addition the formation of a precipitate was observed. The reaction mixture was stirred at room temperature for 5 hours, at which time Color Test I was faintly positive. The mixture was worked up by the same procedure as in the reaction with chlorotriphenylsilylacetylene. The following compounds were isolated: hexaphenyldisilane, 9.65 g. (93.1%); triphenylsilane, 0.15 g. (2.9%); and triphenylsilylacetylene, 4.95 g. (87.1%).

9. Reaction of phenyllithium with chlorotriphenylsilylacetylene

An ethereal solution of phenyllithium (0.015 mole) was added dropwise over a period of 15 minutes to 4.10 g. (0.013 mole) of chlorotriphenylsilylacetylene in 50 ml. of THF. After being stirred for 3.5 hours, the reaction mixture was hydrolyzed with dilute acid. The insoluble material was filtered off and washed with ether several times. It was identified as tetraphenylsilane, m.p. 233-235° (mixed m.p.); the yield was 0.65 g. The organic layer was worked up in the usual manner and the residue was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave 0.57 g. more of tetraphenylsilane. Further elution with carbon tetrachloride gave 0.36 g. of the same compound. The combined yield of tetraphenylsilane was 1.58 g. (36.1%). The oily residue remaining after the separation of tetraphenylsilane failed to yield any further compounds.

10. Reaction of phenyllithium with bis(triphenylsilyl)acetylene

An ethereal solution of phenyllithium (0.01 mole) was added dropwise to 5.30 g. (0.0098 mole) of bis(triphenylsilyl)acetylene in 50 ml. of THF. Almost immediately after the addition of all the phenyllithium there appeared a white precipitate and some slight heat was evolved. After being stirred for 2 hours, the reaction mixture was worked up by the same procedure as in the reaction with chlorotriphenylsilylacetylene. The following compounds were isolated: tetraphenylsilane, 3.30 g. (98%); triphenylsilylacetylene, 2.10 g. (75.5%); and the starting material, 0.20 g. (3.8%).

11. Reaction of methyllithium with chlorotriphenylsilylacetylene

An ethereal solution of methyllithium (0.02 mole) was added dropwise over a period of 45 minutes to 5.75 g. (0.018 mole) of chlorotriphenylsilylacetylene in 70 ml. of THF. Color Test I was positive. After being stirred for 4 hours, the reaction mixture was worked up in the usual manner and the residue was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave in the first fraction 2.90 g. (54.0%) of 1-triphenylsilylpropyne, which was identified by a mixed melting point determination with an authentic sample. Further elution with the same solvent gave in the second fraction 1.00 g. (19.6%) of triphenylsilylacetylene, which was identified by its infrared spectrum. Elution with carbon tetrachloride gave 0.28 g. (5.7%) of bis(triphenylsilyl)acetylene, m.p. 154-156° (mixed m.p.).

12. Reaction of phenylmagnesium bromide with chlorotriphenylsilylacetylene

An ethereal solution of phenylmagnesium bromide (0.02 mole) was added dropwise over a period of 10 minutes to 6.00 g. (0.0188 mole) of chlorotriphenylsilylacetylene in 50 ml. of THF. The reaction mixture was stirred for 18 hours before it was worked up in the usual manner. The residue was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave in the first fraction a mixture of biphenyl and chlorotriphenylsilyl acetylene. Crystallization from ethanol gave 2.30 g. (38.3%) of the starting material, m.p. 100-102° (mixed m.p.). From the mother liquor there were obtained 0.15 g. of biphenyl, m.p. 69-71.5°, and 0.75 g. of the mixture of two compounds above, m.p. 50-90°. Further elution with the same solvent gave in the second fraction 2.10 g. (39.4%) of triphenylsilylacetylene. No other product was isolated.

13. Reaction of phenylmagnesium bromide with bis(triphenylsilyl)acetylene

An ethereal solution of phenylmagnesium bromide (0.02 mole) was added dropwise to 10.00 g. (0.0184 mole) of bis(triphenylsilyl)acetylene in 70 ml. of THF. The reaction mixture was stirred for 18 hours. It was worked up by the same procedure as in the reaction with chlorotriphenylsilylacetylene above. The starting material, bis(triphenylsilyl)acetylene, was recovered in a yield of 8.78 g. (87.8%).

14. Reaction of methylmagnesium iodide with chlorotriphenylsilylacetylene

An ethereal solution of methylmagnesium iodide (0.04 mole) was added dropwise over a period of one-half hour to 10.0 g. (0.0314 mole) of chlorotriphenylsilylacetylene in 50 ml. of THF. The reaction mixture became white from the formation of some precipitate and was slightly warm. Color Test I was positive at the end of the addition. It remained positive after 5 hours. The reaction mixture was worked up in the usual manner, followed by chromatography on alumina. Elution with petroleum ether (b.p. 60-70°) gave in the first fraction 5.35 g. (53.5% recovery) of chlorotriphenylsilylacetylene. Further elution with the same solvent gave in the second fraction 0.17 g. (1.8%) of 1-triphenylsilylpropyne, which was identified by a mixed melting point determination with an authentic sample. Elution was continued with petroleum ether (b.p. 60-70°) and then with carbon tetrachloride. Triphenylsilylacetylene, 3.03 g. (34.0%), was the final product obtained.

15. Preparation of triphenylsilylethynyllithium

An ethereal solution of phenyllithium (0.02 mole) was added to 5.55 g. (0.0195 mole) of triphenylsilylacetylene in 50 ml. of THF. The rate of addition was such that room temperature was maintained. The solution was an opaque pale yellow. It was stirred at room temperature for 3 hours before use.

Derivatization with chlorotriphenylsilane: A solution of triphenylsilylethynyllithium (0.0049 mole) prepared as above was added to 1.50 g. (0.005 mole) of chlorotriphenylsilane in 30 ml. of THF. The reaction mixture was stirred for one hour before it was worked up. The solid residue obtained was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave only a trace of material. Further elution with carbon tetrachloride gave 2.20 g. (83%) of crude product, bis(triphenylsilyl)acetylene. Recrystallization from petroleum ether (b.p. 60-70°) gave 1.85 g. (69.6%) of pure product. It was identified by a mixed melting point determination with an authentic sample.

16. Reaction of triphenylsilylethynyllithium with triphenylsilylacetylene

A solution of triphenylsilylethynyllithium (0.0063 mole) was added dropwise to 1.60 g. (0.0056 mole) of triphenylsilylacetylene in 30 ml. of THF. The reaction mixture was stirred for 19 hours. It remained as a colorless, clear solution throughout. A work-up by the usual procedure gave a solid residue which was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave 1.85 g. (54.7% based on the total obtainable amount) of triphenylsilylacetylene, which was identified by its infrared spectrum. Further elution with carbon tetrachloride gave 1.0 g. (33.0% based on triphenylsilylacetylene) of crude bis(triphenylsilyl)acetylene, which was recrystallized from an ethyl acetate-methanol mixture to give 0.67 g. (22.0%) of pure compound, m.p. 155-157° (mixed m.p.).

17. Reaction of triphenylsilylethynyllithium with chlorotriphenylsilylacetylene

A solution of triphenylsilyethynyllithium (0.015 mole) was added dropwise to 4.80 g. (0.015 mole) of chlorotriphenylsilylacetylene in

50 ml. of THF. The reaction mixture was stirred at room temperature for 17.5 hours, at which time it became black. It was hydrolyzed with dilute acid. A small amount of black solid was removed by filtration. The organic layer was worked up by the same procedure as in the reaction with triphenylsilylacetylene above. The following compounds were isolated: chlorotriphenylsilylacetylene, 1.18 g. (24.6% recovery); triphenylsilylacetylene, 1.10 g. (25.8%); and bis(triphenylsilyl)-acetylene, 4.43 g. (54.5%).

18. Reaction of triphenylsilylethynyllithium with bromotriphenylsilylacetylene

A solution of triphenylsilylethynyllithium (0.0095 mole) was added dropwise to 3.30 g. (0.0091 mole) of bromotriphenylsilylacetylene in 30 ml. of THF. The color of the reaction mixture gradually changed from light yellow to a dark reddish-brown over the 18 hour period of stirring. The reaction mixture was worked up by the same procedure as in the reaction with triphenylsilylacetylene. The following compounds were obtained: bromotriphenylsilylacetylene, 0.70 g. (21.2% recovery); triphenylsilylacetylene, 0.60 g. (22.2%); and bis(triphenylsilyl)-acetylene, 3.52 g. (71.4%).

19. Reaction of triphenylsilylethynyllithium with methyl iodide

A solution of triphenylsilylethynyllithium (0.01 mole) was added dropwise over a period of half an hour to 2.84 g. (0.02 mole) of methyl iodide in 30 ml. of THF. Color Test I was negative after one hour of stirring. Work-up by the general procedure gave a solid which was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave 2.32 g. (77.9%) of 1-triphenylsilylpropyne, m.p. 115-117°, after recrystallization from methanol. This compound was identified by a mixed melting point determination with an authentic sample. Further elution with carbon tetrachloride gave 0.20 g. (7.4%) of bis(triphenylsilyl)acetylene.

20. Reaction of lithium acetylide with triphenylsilane

A stream of acetylene was passed into 130 ml. of THF for 10 minutes. An ethereal solution of phenyllithium (0.10 mole) was then added, acetylene being passed through the solution continuously. After an hour's stirring there was added 26.0 g. (0.10 mole) of triphenylsilane in 100 ml. of THF. There was no observable reaction. The reaction mixture was worked up by the general procedure after a stirring of 2.5 hours. The oily residue was chromatographed on alumina. Triphenylsilane, 23.45 g. (90.3% recovery), was eluted with petroleum ether (b.p. 60-70°). No other product was isolated from the reaction mixture.

21. Reaction of propynyllithium with triphenylsilane

A solution of 4.65 g. (0.04 mole) of 1,2-dichloropropene in 100 ml. of THF was added dropwise to 2.4 g. (0.34 mole) of finely cut lithium wire. The reaction mixture was cooled in a water bath. After one hour's stirring the milky solution (Color Test I being faintly positive) was transferred to another flask after a filtration through glass wool. Triphenylsilane, 12.80 g. (0.04 mole), in 100 ml. of ether was added. Color Test I appeared to be negative. After a stirring of 4.5 hours the solution was divided into equal parts. One-half was hydrolyzed with dilute acid. A work-up gave 5.0 g. of triphenylsilane and 0.16 g. (2.7%) of 1-triphenylsilylpropyne, m.p. 115-116.5°. To the other half there was added 3.0 g. (0.01 mole) of chlorotriphenylsilane in ether and the reaction mixture was worked up after 1.5 hours of stirring. Triphenylsilane was recovered in a yield of 5.10 g. and 1-triphenylsilylpropyne was isolated in a yield of 1.40 g. (23.6%).

22. Preparation of anhydrous inorganic salts

Inorganic salt was heated at 100-150° in an atmosphere of dry hydrogen chloride gas until a constant weight had been attained. Hydrogen chloride was replaced by nitrogen and the system was evacuated for at least half an hour in the presence of potassium hydroxide and concentrated sulfuric acid.

Commercially available cobaltous chloride hexahydrate and anhydrous cupric chloride were dried in this manner before use. It took several hours for a gram of salt to become completely dehydrated.

23. Preparation of triphenylsilylethynylmagnesium chloride from chlorotriphenylsilylacetylene and magnesium in THF

Six grams (0.0188 mole) of chlorotriphenylsilylacetylene was dissolved in 25 ml. of THF. Five milliliters of this solution was added to 0.60 g. (0.025 mole) of magnesium turnings with a pinch of iodine. The mixture was stirred and heated to around 40°. Within a few minutes the reaction started, as evidenced by the disappearance of the iodine color. The rest of the solution was added dropwise and the stirring was continued about one hour. The solution was diluted by adding an equivolume of ether. Acid titration showed the yield to be 96.8%, while acid hydrolysis gave 88.0% of triphenylsilylacetylene.

24. Coupling reaction of triphenylsilylethynylmagnesium chloride in the presence of anhydrous cobaltous chloride and bromobenzene

A solution of triphenylsilylethynylmagnesium chloride (0.019 mole) was added to 3.1 g. (0.02 mole) of bromobenzene and 0.65 g. (0.005 mole) of anhydrous cobaltous chloride in 20 ml. of ether. The reaction mixture was refluxed for 2 hours. The resulting black solution was worked up by the usual procedure, followed by chromatography on alumina. Elution with petroleum ether (b.p. 60-70°) gave 0.35 g. (6.5%) of triphenylsilylacetylene, which was identified by its infrared spectrum. Elution with carbon tetrachloride gave a large amount of a dark reddish oil from which 0.29 g. (5.5%) of crude bis(triphenylsilyl)butadiyne was isolated. This compound was also identified by its infrared spectrum.

25. Coupling reaction of triphenylsilylethynylmagnesium chloride in the presence of anhydrous cobaltous chloride and ethyl bromide

A solution of triphenylsilylethynylmagnesium chloride (0.014 mole) was added to 0.85 g. (0.0045 mole) of anhydrous cobaltous chloride and 2.1 g. (0.019 mole) of ethyl bromide in 20 ml. of ether. The mixture was refluxed for 5.5 hours. The reaction mixture was treated with benzene (300 ml.) and water (20 ml.). The water layer was extracted twice with benzene. Work-up of the organic layer in the usual manner gave an oily black residue which was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave 1.85 g. (42.4%) of

1-triphenylsilyl-1-butyne, which was identified by a mixed melting point determination with an authentic sample. Further elution with carbon tetrachloride yielded 0.22 g. (5.5%) of crude bis(triphenylsilyl)-butadiyne, which was identified by its infrared spectrum.

26. Coupling reaction of triphenylsilylethynylmagnesium chloride in the presence of anhydrous cupric chloride

A solution of triphenylsilylethynylmagnesium chloride (0.017 mole) was added to 2.30 g. (0.017 mole) of anhydrous cupric chloride. The reaction mixture was refluxed for 10 hours before it was hydrolyzed. Work-up in the usual manner gave a solid residue, which was chromatographed on alumina. Nothing was eluted with petroleum ether (b.p. 60-70°). Elution with carbon tetrachloride, however, gave 0.83 g. (17.8%) of triphenylsilylacetylene and 2.18 g. (45.3%) of bis(triphenylsilyl)butadiyne, m.p. 294.5-296.5°, after two recrystallizations from ethyl acetate. The infrared spectrum showed a sharp band at 4.84 μ (see Table 6).

Anal. Calcd. for $C_{40}H_{30}Si_2$: Si, 9.91. Found: Si, 9.83, 9.73.

27. Coupling reaction of triphenylsilylethynylmagnesium bromide in the presence of anhydrous cupric chloride

Triphenylsilylethynylmagnesium bromide was prepared from bromotriphenylsilylacetylene and magnesium in THF essentially in the same manner as in the preparation of triphenylsilylethynylmagnesium chloride. Heating was not necessary to initiate the reaction. The solution was stirred for one hour at 40-50°. Acid titration indicated the yield of the Grignard reagent to be 95.3%.

A solution of triphenylsilylethynylmagnesium bromide (0.0109 mole) was added to 1.25 g. (0.0093 mole) of anhydrous cupric chloride in 10 ml. of ether. The reaction mixture was refluxed for 6 hours. It was then treated with benzene (150 ml.) and water (20 ml.). The water layer was extracted twice with benzene. The combined organic layer was dried with sodium sulfate. The solid residue after removal of the solvent was crystallized from ethyl acetate to give 1.15 g. (37.2%) of bis(triphenylsilyl)butadiyne, m.p. 292.5-294.5° (mixed m.p.). The oil, obtained from the mother liquor after removal of the solvent, was chromatographed on alumina to yield a trace amount of the starting material, bromotriphenylsilylacetylene, and 1.10 g. (36.8%) of triphenylsilylacetylene, both of which compounds were identified by infrared spectra.

F. Reactions of Triphenylsilyllithium with Epihalohydrins and Related Reactions

1. Reaction of triphenylsilyllithium with epichlorohydrin

a. Normal addition

(1) Run 1 (1:1, room temperature) A solution of triphenylsilyllithium (0.05 mole) was added dropwise over a period of one-half hour to 4.62 g. (0.05 mole) of epichlorohydrin. The reaction was exothermic and Color Test I was negative immediately after the addition. The reaction mixture was worked up by the general procedure and the residue was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave 1.20 g. (8%) of allyltriphenylsilane, m.p. 85-88°,

identified by a mixed melting point determination with an authentic sample and by a comparison of infrared spectra. Elution with carbon tetrachloride gave 2.95 g. (19%) of a compound, possibly 2,5-bis(triphenylsilylmethyl)-1,4-dioxane, m.p. 144-145.5°, after recrystallization from petroleum ether (b.p. 60-70°).

<u>Anal</u>. Calcd. for $C_{42}H_{40}O_2Si_2$: Si, 8.88; mol. wt., 633.0. Found: Si, 8.71, 8.68; mol. wt., 623.5 (Rast).

The compound was unaffected by lithium aluminum hydride in THF at room temperature. After one hour of refluxing in the same solvent with a large excess of lithium aluminum hydride 50% of the starting material was recovered unchanged. No 1-(triphenylsilyl)propan-2-ol was detected.

Further elution with acetone and methanol gave 1.10 g. (8%) of triphenylsilanol, m.p. 148-150° (mixed m.p.).

(2) <u>Run 2 (1:1, -60°)</u> A solution of triphenylsilyllithium (0.08 mole) was added dropwise to 7.4 g. (0.08 mole) of epichlorohydrin at -60°. Color Test I was negative immediately after the addition. The reaction mixture was worked up by the same procedure as in Run 1 to give 17.10 g. (60.5%) of 1-triphenylsilyl-3-chloropropan-2-ol, m.p. 94-95°, after recrystallization from petroleum ether (b.p. 60-70°).

<u>Anal</u>. Calcd. for $C_{21}H_{21}OSiCl$: Si, 7.96. Found: Si, 7.95, 7.90.

The infrared spectrum supports the proposed structure.

(3) <u>Run 3 (2:1, -60° ∼ room temperature)</u> A solution of triphenylsilyllithium (0.08 mole) was added dropwise to 3.7 g. (0.04 mole) of epichlorohydrin at -60°. Color Test I was negative when 0.04 mole of triphenylsilyllithium had been added. It became strongly

positive, however, when 0.06 mole had been added. The reaction mixture was allowed to warm to room temperature and stirred for 20 minutes, at which time Color Test I became only faintly positive. Addition of the remaining 0.02 mole caused evolution of some heat and the color test was negative. The work-up by the same procedure as in Run 1 gave 10.0 g. (43.3%) of 1,3-bis(triphenylsilyl)propan-2-ol, m.p. 142.5-143.5°, after recrystallization from a benzene-petroleum ether (b.p. 60-70°) mixture. A mixed melting point with the compound obtained in Run 1, possibly 2,5-bis(triphenylsilylmethyl)-1,4-dioxane, was depressed. The infrared spectrum showed the characteristic band for an hydroxy group at 2.79μ. The dehydration product with phosphorus pentoxide, 1,3-bis(triphenylsilyl)propene, was identical with the product obtained from the reaction of triphenylsilyllithium with 1,3-dichloropropene in a 2:1 ratio. Analysis for silicon, however, gave considerably lower values than the calculated value for the proposed structure.

Anal. Calcd. for $C_{39}H_{36}OSi_2$: Si, 9.74. Found: Si, 9.07, 9.01, 8.99.

(4) Run 4 (8:5, room temperature) A solution of triphenylsilyllithium (0.08 mole) was added dropwise to 4.62 g. (0.05 mole) of epichlorohydrin at room temperature. Color Test I was negative immediately after the addition. The reaction mixture was worked up by the same procedure as in Run 1, leaving an oil which was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave 1.20 g. (7.6%) of a compound, m.p. 97-100°. A mixed melting point with 1-triphenylsilyl-3-chloropropan-2-ol, which was obtained in Run 2, was depressed and the

two infrared spectra were different. The compound may possibly have been 1,2-epoxy-3-triphenylsilylpropane. Elution with carbon tetrachloride and benzene gave 10.80 g. (46.7%) of 1,3-bis(triphenylsilyl)propan-2-ol, m.p. 143-144° (mixed m.p.).

b. Reverse addition A solution of epichlorohydrin in 30 ml. of THF was added dropwise to 0.05 mole of triphenylsilyllithium at room temperature. Color Test I was negative when 0.025 mole of epichlorohydrin had been added. The work-up of the reaction mixture by the same procedure as in Run 1 gave 4.60 g. (31.8%) of 1,3-bis(triphenylsilyl)-propan-2-ol, m.p. 139.5-140.5° (mixed m.p.).

2. Reaction of triphenylsilyllithium with epibromohydrin

a. Normal addition

(1) Run 1 (1:1) A solution of triphenylsilyllithium (0.10 mole) was added over a period of 15 minutes to 13.7 g. (0.10 mole) of epibromohydrin which was cooled in a Dry Ice-acetone bath. Immediately a white precipitate formed. After a stirring of 10 minutes the reaction mixture was hydrolyzed with dilute acid. Hexaphenyldisilane, 17.76 g. (68.6%), was separated by filtration. A work-up of the organic layer left a solid residue which was treated with petroleum ether (b.p. 60-70°). Triphenylsilanol, 1.2 g. (4.4%), was obtained, m.p. 147-150° (mixed m.p.).

(2) Run 2 (2:1) A solution of triphenylsilyllithium (0.08 mole) was added dropwise to 5.5 g. (0.04 mole) of epibromohydrin at -60°. The color of the reaction mixture was a pale green and Color Test

I was faintly positive. The mixture was allowed to warm to room temperature. Its color changed to white. Subsequent to hydrolysis, hexaphenyldisilane, 16.4 g. (79.0%), was separated by filtration. The work-up of the organic layer in the usual manner gave an oily residue which was chromatographed on alumina. An oily material eluted with carbon tetrachloride gave 1.0 g. of a solid, m.p. 253-256°, after standing for 3 months. The structure of this compound has not been determined.

b. <u>Reverse addition</u> To 0.05 mole of triphenylsilyllithium was added dropwise over a period of 10 minutes 6.85 g. (0.05 mole) of epibromohydrin. An addition of one drop caused refluxing of the solvent. After cooling to room temperature the reaction mixture was hydrolyzed. Hexaphenyldisilane, 9.42 g. (72.6%), was separated by filtration. The work-up of the organic layer followed by chromatography on alumina gave 0.13 g. (1%) of allyltriphenylsilane, which was identified by a mixed melting point determination with an authentic sample, m.p. 88-91° (mixed m.p.) and by a comparison of their infrared spectra.

3. Reaction of triphenylsilyllithium with 1,2-epoxy-3-(2-chloroethoxy)propane

a. Normal addition

(1) <u>Run 1 (1:1)</u> A solution of triphenylsilyllithium (0.04 mole) was added slowly to 5.4 g. (0.04 mole) of 1,2-epoxy-3-(2-chloroethoxy)propane at room temperature. Color Test I was negative immediately after the addition. The reaction mixture was worked up by the general procedure, followed by chromatography on alumina. Elution with petroleum ether (b.p. 60-70°) gave in the first fraction 0.50 g.

(4.0%) of 1-triphenylsilyl-3-(2-triphenylsilylethoxy)propan-2-ol, m.p. 141.5-142.5°, after recrystallization from ethanol. The infrared spectrum of this compound shows a characteristic absorption band for an hydroxy group at 2.80μ.

Anal. Calcd. for $C_{41}H_{40}O_2Si_2$: Si, 9.05. Found: Si, 8.88, 8.85.

Further elution with the same solvent gave 1.65 g. of an oil. Further elutions with carbon tetrachloride and benzene gave still more oil, which was then distilled under reduced pressure to give 5.00 g. of an oil, b.p. 213-215°/0.03 mm, n_D^{20} 1.5999. Silicon analysis of this oil agrees with a structure of 1-triphenylsilyl-3-(2-chloroethoxy)propan-2-ol. The infrared spectrum shows the characteristic bands of an hydroxy group at 2.77 and 2.88μ. The combined yield was 6.65 g. (41.9%).

Anal. Calcd. for $C_{23}H_{25}O_2SiCl$: Si, 7.08. Found: Si, 7.19, 6.98.

(2) Run 2 (2:1) A solution of triphenylsilyllithium (0.04 mole) was added slowly to 2.7 g. (0.02 mole) of 1,2-epoxy-3-(2-chloroethoxy)propane. The reaction was exothermic and Color Test I was negative immediately after addition. Subsequent to hydrolysis hexaphenyldisilane, 0.45 g. (4.3%), was separated by filtration. The organic layer was worked up by the same procedure as in Run 1 to give 5.60 g. (45.0%) of 1-triphenylsilyl-3-(2-triphenylsilylethoxy)propan-2-ol, m.p. 143.5-145°, after recrystallization from ethyl acetate. A mixed melting point with the sample obtained in Run 1 was not depressed.

b. Reverse addition A solution of 1,2-epoxy-3-(2-chloroethoxy)propane in THF was added dropwise to 0.03 mole of triphenylsilyllithium at room temperature. When 0.015 mole of the compound had been added Color Test I became negative. Subsequent to hydrolysis, hexaphenyldisilane, 0.85 g. (10.9%), was separated by filtration. The organic layer was worked up in the same manner as in Run 1 of the above section to yield 2.25 g. (24.2%) of 1-triphenylsilyl-3-(2-triphenylsilylethoxy)propan-2-ol, m.p. 142-143° (mixed m.p.).

4. Reaction of triphenylsilyllithium with 1-allyloxy-2,3-epoxypropane

a. 1:1 ratio   A solution of triphenylsilyllithium (0.03 mole) was added dropwise to 3.5 g. (0.03 mole) of 1-allyloxy-2,3-epoxypropane at room temperature. The reaction was exothermic and Color Test I was negative immediately after the addition. The reaction mixture was worked up by the general procedure leaving an oily residue which was distilled under reduced pressure. 1-allyloxy-3-triphenylsilylpropan-2-ol was obtained in a yield of 6.25 g. (56.0%), b.p. 190-195°/0.01 mm, n_D^{20} 1.5940.

Anal. Calcd. for $C_{24}H_{26}O_2Si$: Si, 7.50. Found: Si, 7.81, 7.61. The distillation residue was chromatographed on alumina, but no product was isolated.

b. 2:1 ratio   A solution of triphenylsilyllithium (0.04 mole) was added dropwise to 2.3 g. (0.02 mole) of 1-allyloxy-2,3-epoxypropane at room temperature. Color Test I was negative when the addition was completed. The reaction mixture was worked up in the usual manner leaving a solid residue which was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave 0.90 g. (15%) of allyltriphenylsilane, m.p. 90-92°, after recrystallization from ethanol. A mixed melting point with an authentic sample was not depressed and the infrared spectra were identical. Elution with acetone gave 2.60 g. (39%) of 1,2-dihydroxy-3-triphenylsilylpropane, m.p. 135-136°, after recrystallization from a benzene-petroleum ether (b.p. 60-70°) mixture. The infrared spectrum showed a broad band in the region of 2.8-3.2μ with peaks at 2.8μ and 3.15μ. Silicon analysis agrees with the proposed structure.

Anal. Calcd. for $C_{21}H_{22}O_2Si$: Si, 8.40. Found: Si, 8.26, 8.26.

5. Dehydration of 1,3-bis(triphenylsilyl)propan-2-ol with phosphorus pentoxide

Two grams of 1,3-bis(triphenylsilyl)propan-2-ol was refluxed for 45 minutes with 2 g. of phosphorus pentoxide in 50 ml. of benzene. The reaction mixture was hydrolyzed with saturated ammonium chloride solution. The organic layer was dried with sodium sulfate. The solvent was removed and the residue was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave 0.30 g. (29%) of allyltriphenylsilane, m.p. 89-91° (mixed m.p.).

Further elution with carbon tetrachloride gave 0.60 g. (31%) of 1,3-bis(triphenylsilyl)propene, m.p. 157-160°. A mixed melting point with the product obtained from the reaction of triphenylsilyllithium with 1,3-dichloropropene in a 2:1 ratio was not depressed.

IV. DISCUSSION

A. Reactions of Triphenylsilyllithium with Alkyl Halides

1. Reactions with primary halides

The reactions of triphenylsilyllithium with n-butyl chloride and n-butyl bromide were found to be strikingly different. With n-butyl chloride there was obtained n-butyltriphenylsilane in a yield of 75%. With n-butyl bromide, hexaphenyldisilane (58%) and n-butyltriphenylsilane (27.5%) were the products. The formation of hexaphenyldisilane is explained by an initial halogen-metal interconversion with a subsequent coupling of bromotriphenylsilane and triphenylsilyllithium.[9]

(1) $n\text{-BuBr} + Ph_3SiLi \longrightarrow n\text{-BuLi} + Ph_3SiBr$

(2) $Ph_3SiBr + Ph_3SiLi \longrightarrow Ph_3SiSiPh_3 + LiBr$

The coupling of organosilyllithium compounds with organohalosilanes was noted to be an extremely fast reaction.[1, 5] Triphenylsilyllithium reacted almost instantaneously with chlorotriphenylsilane even at -60° to form hexaphenyldisilane.[5] Therefore, the halogen-metal interconversion reactions between triphenylsilyllithium and alkyl halides end up as irreversible reactions, even though equation 1 may be reversible.[85]

In the case of n-butyl chloride, halogen-metal interconversion becomes less likely because of the increased electronegative character

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[85] H. Gilman and R. G. Jones, J. Am. Chem. Soc., 63, 1443 (1941).

of the chlorine atom. The reaction may be a simple displacement of the SN_2 type.

Studies have been made[86, 87] to compare the ratio of the coupling reaction to the halogen-metal interconversion reaction in a series of ethyl halides and n-octyl halides. The results are summarized in Table 1.

The coupling products obtained with bromides and iodides may have arisen at least in part from the reaction of alkyllithium compounds and halotriphenylsilane, both of which are formed as a result of halogen-metal interconversion.[88]

The reaction with isobutyl chloride gave a small amount (3.25%) of hexaphenyldisilane and isobutyltriphenylsilane (62%).[89] Neopentyl chloride, however, gave a 64% yield of hexaphenyldisilane and a 9.3% yield of neopentyltriphenylsilane.[89] Steric hindrance might be responsible for the increased halogen-metal interconversion reaction.

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[86] G. Dappen, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Information concerning the reactions of triphenylsilyllithium with n-octyl halides. Private communication. 1961.

[87] H. Gilman and L. Tushaus, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Information concerning the reactions of triphenylsilyllithium with ethyl halides. Private communication. 1961.

[88] For the coupling reactions of organolithium compounds with organohalosilanes, see C. Eaborn. Organosilicon Compounds. London, Butterworths Scientific Publications. 1960. pp. 19-25.

[89] G. Dappen, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Information concerning the reactions of triphenylsilyllithium with isobutyl chloride and neopentyl chloride. Private communication. 1961.

Table 1. Reactions of Ph_3SiLi with primary halides

Compound	Coupling product	Hexaphenyldisilane
ethyl chloride	80	0
ethyl bromide	45-54	25-29
ethyl iodide	28-30	37-40
n-octyl fluoride	86.6	0
n-octyl chloride	73.7	0
n-octyl bromide	34.3	44.4
n-octyl iodide	23.0	52.3

Another anomaly is noted in the reaction of β-chloroethyltriphenylsilane.[90] Hexaphenyldisilane was obtained in 37% yield, in addition to 1,2-bis(triphenylsilyl)ethane (29.2%). A large part of the hexaphenyldisilane in this case may have arisen as a result of a β-elimination reaction.[91]

2. Reactions with secondary halides

Triphenylsilyllithium reacted with secondary chlorides to yield

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[90] E. A. Zuech. Cyclic organosilicon and related compounds. Unpublished Ph.D. Thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1960.

[91] C. Eaborn. Organosilicon Compounds. London, Butterworths Scientific Publications. 1960. pp. 133-137.

largely coupling products, but the reaction was accompanied by the production of a small amount of hexaphenyldisilane as well. Isopropylbromide reacted predominantly by halogen-metal interconversion. Only a small amount (5.8%) of isopropyltriphenylsilane was isolated.[92] The results are summarized in Table 2.

Table 2. Reactions of Ph_3SiLi with secondary halides

Compound	Coupling product	Hexaphenyldisilane
isopropyl chloride[92]	71.2	6.7
<u>sec</u>-butyl chloride[92]	24.8	13.3
cyclopentyl chloride	40.0	9.3
isopropyl bromide[92]	5.8	73.5

3. Reactions with tertiary halides

Dappen[92] studied the reactions of triphenylsilyllithium with <u>tert</u>-butyl chloride and bromide. The bromide reacted in the expected way, yielding hexaphenyldisilane (52%) and <u>tert</u>-butyltriphenylsilane (2%). The chloride, however, reacted with triphenylsilyllithium in much

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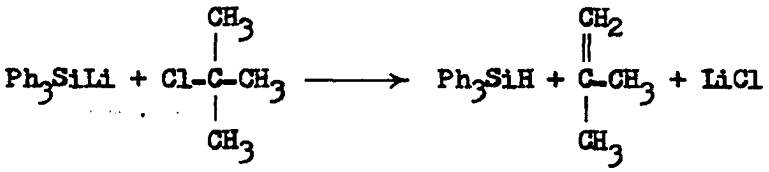
[92] G. Dappen, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Information concerning the reactions of triphenylsilyllithium with secondary and tertiary halides. Private communication. 1961.

the same way as it does with bases[93] and organolithium compounds.[41] Triphenylsilane was obtained in a 56.7% yield, whereas the yield of hexaphenyldisilane was 3.5%. The reaction may be of the E2 type, as in the case of the reactions with organolithium compounds. The latter reactions were shown to be first order in the organolithium compound and in the alkyl halide.



$$Ph_3SiLi + Cl\text{-}\underset{CH_3}{\overset{CH_3}{C}}\text{-}CH_3 \longrightarrow Ph_3SiH + \underset{CH_3}{\overset{CH_2}{\overset{\|}{C}}}\text{-}CH_3 + LiCl$$

4. Reactions with methylene chloride

Unlike the reactions of organolithium compounds with methylene chloride, where metalation rather than halogen-metal interconversion occurs,[60] the reaction of triphenylsilyllithium with methylene chloride proceeds _via_ halogen-metal interconversion, as evidenced by the formation of hexaphenyldisilane (35-56%) and by the absence of triphenylsilane, which would be formed if metalation took place. Three other products, methyltriphenylsilane (15.5-34.2%), chloromethyltriphenylsilane (0-11.7%), and bis(triphenylsilyl)methane (5.4-17.4%), were isolated. The yields of all four compounds varied with reaction conditions such as temperature, mode of addition, molar ratio of the reactants, and,

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[93] For the reactions of tertiary halides with bases, see, for example, J. Hine. Physical Organic Chemistry. New York, N.Y., McGraw-Hill Book Company, Inc. 1956. p. 174.

probably, rate of addition and stirring.

Chloromethyltriphenylsilane was not isolated when reverse addition was employed, nor when excess triphenylsilyllithium was added to methylene chloride in a normal addition. This fact suggests that bis(triphenylsilyl)methane was formed by a coupling reaction between the silyllithium compound and chloromethyltriphenylsilane. Independently, triphenylsilyllithium and chloromethyltriphenylsilane were allowed to react under similar conditions. It was noted that extensive halogen-metal interconversion (36.8% of hexaphenyldisilane) accompanied the coupling reaction (32.4% of bis(triphenylsilyl)methane). This result may be compared with those from the reactions of triphenylsilyllithium with chloromethyltrimethylsilane and with chloromethyldimethylvinylsilane, where only coupling products were obtained, triphenylsilylmethyltrimethylsilane (82%) and triphenylsilylmethyldimethylvinylsilane (65%), respectively. The reason for this difference may very well be steric hindrance. Neopentyl chloride gave a large amount of hexaphenyldisilane, whereas chloromethyltrimethylsilane gave none. The larger silicon atom may be responsible for making the latter system less hindered.

It is somewhat surprising that a relatively lower yield (35.2%) of hexaphenyldisilane was obtained when reverse addition was employed. This result may be explained by the fact that two competing reactions exist in the system, namely the reactions of triphenylsilyllithium with chlorotriphenylsilane and with carbene, both reactions being generated by halogen-metal interconversion:

$$\begin{tikzcd}
Ph_3SiLi + CH_2Cl_2 \arrow[r] & CH_2ClLi + Ph_3SiCl \arrow[d, "-LiCl"] \\
Ph_3Si\text{-}CH_2Li & {[:CH_2]} \arrow[l, "Ph_3SiLi"']
\end{tikzcd}$$

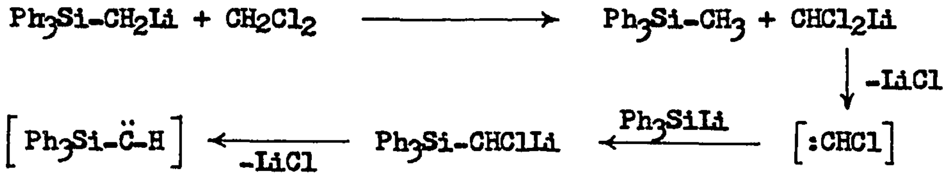
Electrophilic attack by carbene on triphenylsilyllithium results in triphenylsilylmethyllithium, which in turn can compete with triphenylsilyllithium to react with chlorotriphenylsilane:

$$Ph_3SiLi + Ph_3SiCl \longrightarrow Ph_3SiSiPh_3 + LiCl$$

$$Ph_3Si\text{-}CH_2Li + Ph_3SiCl \longrightarrow Ph_3Si\text{-}CH_2\text{-}SiPh_3 + LiCl$$

An attempt was made to prepare triphenylsilylmethyllithium from bromomethyltriphenylsilane and lithium in THF. The conditions employed were not the best ones possible, however, and hydrolysis of the reaction mixture, which gave a positive Color Test I, yielded 1,2-bis(triphenylsilyl)ethane (38.8%) and methyltriphenylsilane (9.7%). Undoubtedly, the triphenylsilylmethyllithium formed coupled immediately with bromomethyltriphenylsilane to give 1,2-bis(triphenylsilyl)ethane under the conditions employed.

The formation of methyltriphenylsilane and chloromethyltriphenylsilane has not been clearly established. It is quite possible, however, that triphenylsilylmethyllithium is an intermediate. Being a true organolithium compound, this latter compound can abstract hydrogen from methylene chloride to yield methyltriphenylsilane and chlorocarbene,[60] which can further react with triphenylsilyllithium to form triphenylsilylcarbene. The fate of the triphenylsilylcarbene may be the



formation of bis(triphenylsilyl)methyllithium, which either before or after hydrolysis becomes bis(triphenylsilyl)methane.

Triphenylsilylmethyllithium can also abstract hydrogen from the solvent (THF), yielding methyltriphenylsilane. The metalated tetrahydrofuran may then disproportionate.[94]

The triphenylsilyl group might exert some influence on the character of triphenylsilylmethyllithium. Triphenylsilylmethyllithium may also undergo halogen-metal interconversion with methylene chloride, forming chloromethyltriphenylsilane. Chloromethyltriphenylsilane may, however, be a product of a simple coupling reaction between triphenylsilyllithium and methylene chloride.

5. Reactions with methylene bromide

The reaction of triphenylsilyllithium with methylene bromide yielded hexaphenyldisilane (42.5-59.4%), methyltriphenylsilane (trace-40.0%), and bromomethyltriphenylsilane (0-9.6%). Again, the reaction conditions

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[94] For cleavage reactions of ethers by organometallic compounds, see, for example, K. Ziegler and H. G. Gellert, Ann., 567, 185 (1950). R. L. Letsinger and D. F. Pollart, J. Am. Chem. Soc., 78, 6079 (1956).

employed had a great influence on the yields of the products. Bis(triphenylsilyl)methane was not isolated in any case.

The metalation reaction of triphenylsilylmethyllithium with methylene bromide seems to be unlikely in view of the fact that the reaction of methyllithium with methylene bromide in the presence of cyclohexene was shown to give only norcarane,[53] and also in view of the fact that bromocarbene, which would result from the metalation reaction, would eventually give rise to bis(triphenylsilyl)methane (cf. the reaction of triphenylsilylmethyllithium with methylene chloride (p. 123) and the reaction of triphenylsilyllithium with dichloromethyltriphenylsilane (p. 127).

There are three main competing paths for triphenylsilylmethyllithium to take: abstraction of hydrogen from the solvent, the halogen-metal interconversion reaction with methylene bromide, and the coupling reaction with bromotriphenylsilane. Apparently the first reaction is the preferred one, as evidenced by the relatively large yield of methyltriphenylsilane (32.4 and 40.0%) and the smaller yields of other possible products.

A relatively small yield of hexaphenyldisilane (42.5% compared to 57 and 59% for the other cases) and a relatively larger yield of methyltriphenylsilane (40.0% compared to a trace amount and 32.4% for the other cases) were obtained when cyclohexene was used as a part of the solvent in the hope of capturing the carbene intermediate. The reason for this discrepancy is not known.

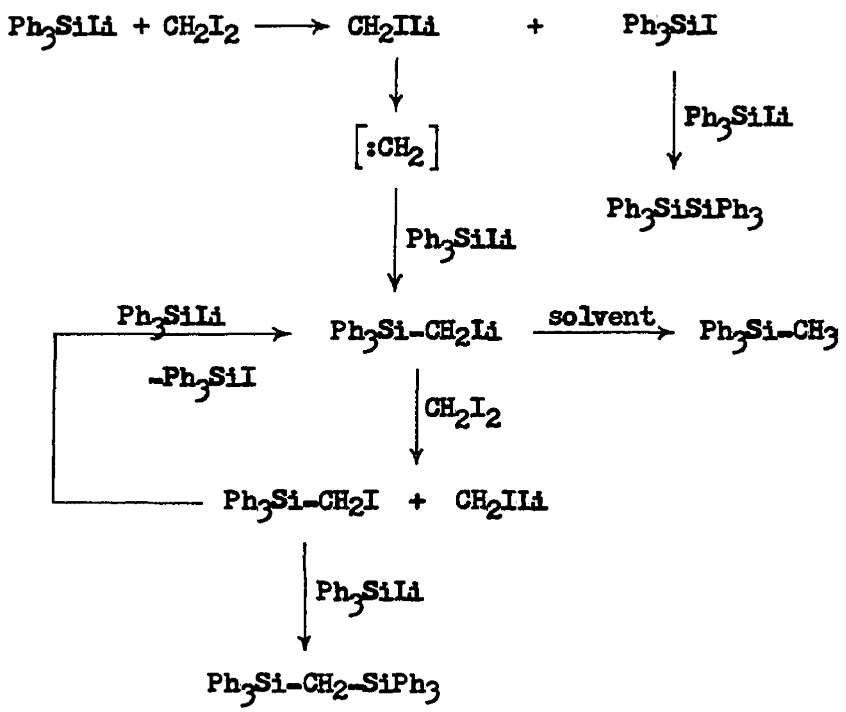
6. Reactions with methylene iodide

In the reaction of methylene iodide with triphenylsilyllithium, hexaphenyldisilane was obtained in yields of 50 to 65%, the highest yield being obtained when the reaction was carried out at room temperature. This finding is in accord with the tendency of methylene iodide to undergo halogen-metal interconversion.

When the reaction was carried out at -60°, methyltriphenylsilane and iodomethyltriphenylsilane were obtained in yields of 16.4-28.3% and 6.3-23.0%, respectively. In one case, bis(triphenylsilyl)methane (5.6%) was isolated.

The apparent similarity of the results of the methylene iodide reaction to those of the methylene chloride reaction, in contrast to those of the methylene bromide reactions, suggests that the mechanisms of the reactions of methylene iodide and methylene chloride may differ from each other at certain stages of the reaction.

It was suggested that chloromethyltriphenylsilane may be formed from a halogen-metal interconversion reaction between triphenylsilylmethyllithium and methylene chloride (p. 123). While such a reaction is rather improbable for methylene chloride in view of its metalation reaction with organolithium compounds, such a reaction course is quite possible for methylene iodide, since iodides in general undergo the halogen-metal interconversion reaction much more readily than chlorides or bromides.



7. Reactions with chloroform

Triphenylsilyllithium reacted with chloroform predominantly by halogen-metal interconversion, yielding hexaphenyldisilane (51.6-60.5%). Appreciable amounts of metalation also occurred, however, forming triphenylsilane (5.3-13.0%).

Three other products were isolated: chloromethyltriphenylsilane (3.2-6.5%), dichloromethyltriphenylsilane (0-11.7%), and bis(triphenylsilyl)methane (1.7-10.3%).

A possible sequence of reactions is as follows:

First step:

$$\begin{tikzcd} & Ph_3SiH + CCl_3Li \arrow[r, "-LiCl"'] & {[:CCl_2]} \\ CHCl_3 + Ph_3SiLi \arrow[ur] \arrow[dr] & & \\ & Ph_3SiCl + CHCl_2Li \arrow[r, "-LiCl"'] & {[:CHCl]} \end{tikzcd}$$

Second step:

$$[:CCl_2] + Ph_3SiLi \longrightarrow Ph_3Si\text{-}CCl_2Li \xrightarrow[-LiCl]{} [Ph_3Si\text{-}\ddot{C}\text{-}Cl]$$

$$[:CHCl] + Ph_3SiLi \longrightarrow Ph_3Si\text{-}CHClLi \xrightarrow[-LiCl]{} [Ph_3Si\text{-}\ddot{C}\text{-}H]$$

Third step:

$$[Ph_3Si\text{-}\ddot{C}\text{-}Cl] + CHCl_3 \longrightarrow Ph_3Si\text{-}CHCl_2 + [:CCl_2]$$

$$[Ph_3Si\text{-}\ddot{C}\text{-}H] + CHCl_3 \longrightarrow Ph_3Si\text{-}CH_2Cl + [:CCl_2]$$

Fourth step:

$$\begin{tikzcd} & Ph_3Si\text{-}CH_2\text{-}SiPh_3 + LiCl \\ Ph_3Si\text{-}CH_2Cl + Ph_3SiLi \arrow[ur] \arrow[dr] & \\ & Ph_3Si\text{-}CH_2Li + Ph_3SiCl \end{tikzcd}$$

$$\begin{tikzcd} & Ph_3Si\text{-}CHCl_2 + Ph_3SiLi \arrow[r] & Ph_3Si\text{-}CHClLi + Ph_3SiCl \arrow[d, "-\ LiCl"] \\ & & {[Ph_3Si\text{-}\ddot{C}\text{-}H]} \arrow[d, "Ph_3SiLi"] \\ Ph_3Si\text{-}CH_2\text{-}SiPh_3 & & Ph_3Si\text{-}\overset{Li}{\overset{|}{C}}H\text{-}SiPh_3 \arrow[ll, "H^+"'] \end{tikzcd}$$

In the first step dichlorocarbene and chlorocarbene are formed as a result of metalation and halogen-metal interconversion, respectively. In the second step the carbenes then react with triphenylsilyllithium yielding new carbenes: chlorotriphenylsilylcarbene and triphenylsilylcarbene. The third step may be a questionable one; in the literature no analogous reaction has been found.[95]

Electrophilic carbenes may very well attack the negatively polarized end of chloroform, thereby initiating α-dehydrohalogenation. The formation of dichlorocarbene in this step also accounts for the relatively high yield of dichloromethyltriphenylsilane, comparable to the yield of triphenylsilane and of chloromethyltriphenylsilane, since the other source of dichlorocarbene, which is undoubtedly an intermediate in the formation of dichloromethyltriphenylsilane, is the metalation step, which occurs only to the extent of one-fifth of the halogen-metal interconversion. One might argue, however, that dichlorocarbene is more stable than chlorocarbene and that not much of it may be lost before it has a chance to react with triphenylsilyllithium, hence the relatively higher yield of dichloromethyltriphenylsilane.

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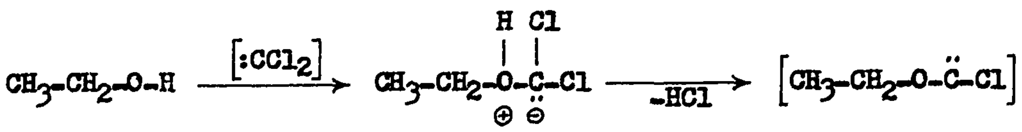
[95] Hine *et al.*, however, postulated an electrophilic attack by dichlorocarbene on the oxygen atom of alcohol:



$$CH_3\text{-}CH_2\text{-}O\text{-}H \xrightarrow{[:CCl_2]} CH_3\text{-}CH_2\text{-}\underset{\oplus}{\overset{H}{O}}\text{-}\underset{\ominus}{\underset{\cdot\cdot}{\overset{Cl}{C}}}\text{-}Cl \xrightarrow[-HCl]{} [CH_3\text{-}CH_2\text{-}O\text{-}\ddot{C}\text{-}Cl]$$

See J. Hine, E. L. Pollitzer, and H. Wagner, *J. Am. Chem. Soc.*, *75*, 5607 (1953).

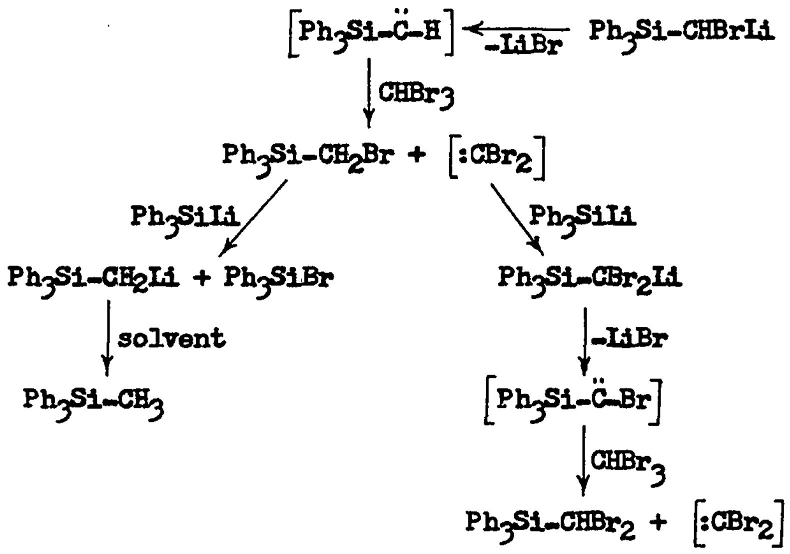
The reaction of chloromethyltriphenylsilane and triphenylsilyllithium has been described in connection with the reaction of methylene chloride. The second half of the fourth step, the reaction between dichloromethyltriphenylsilane and triphenylsilyllithium, was investigated separately. The products isolated from this reaction were hexaphenyldisilane (46.4%) and bis(triphenylsilyl)methane (34.3%).

8. Reactions with bromoform

It is not surprising to find that only a trace amount (less than 2%) of triphenylsilane was isolated in two cases (one of which showed a slightly positive Color Test I before work-up, so that it is even doubtful that the triphenylsilane came from the reaction) because the hydrogen of bromoform is less acidic than that of chloroform and because the bromides are in general more susceptible to the halogen-metal interconversion reaction than the chlorides. The yields of hexaphenyldisilane varied from 48.7 to 62.5%. Methyltriphenylsilane (0.9-10.3%) and bromomethyltriphenylsilane (20.5-34.0%) were isolated in every case. Dibromomethyltriphenylsilane was isolated from the two runs in yields of 4.0 and 13.9%. Bis(triphenylsilyl)methane was not isolated; in this respect the reaction was analogous to the methylene bromide reaction.

Possible reaction paths are as follows:

$$\begin{tikzcd}
\mathrm{CHBr_3 + Ph_3SiLi} \arrow[r] & \mathrm{Ph_3SiBr + CHBr_2Li} \arrow[r, "-\mathrm{LiBr}"'] & {[:\mathrm{CHBr}]} \arrow[d, "\mathrm{Ph_3SiLi}"] \\
 & & {}
\end{tikzcd}$$



The reaction of triphenylsilylcarbene with bromoform would give bromomethyltriphenylsilane and dibromocarbene. The formation of dibromomethyltriphenylsilane renders some support to the above reaction mechanism, since no other reaction path would give dibromocarbene. It is very unlikely that dibromomethyltriphenylsilane was formed as a result of direct displacement of the bromide ion from bromoform by triphenylsilyllithium. Methyltriphenylsilane is formed by the initial halogen-metal interconversion reaction between bromomethyltriphenylsilane and triphenylsilyllithium, followed by hydrogen abstraction from the solvent on the part of the resulting triphenylsilylmethyllithium.

9. Reactions with iodoform

When triphenylsilyllithium was added to iodoform at room temperature until the solution gave a positive Color Test I, three products were obtained: hexaphenyldisilane (60.5%), methyltriphenylsilane

(23.7%), and bis(triphenylsilyl)methane (19.7%). The ratio of the reactants was approximately 3 (triphenylsilyllithium) to 1 (iodoform). When the ratio was 2 to 1, methyltriphenylsilane and bis(triphenylsilyl)methane were not isolated, but iodomethyltriphenylsilane (15.6%) and diiodomethyltriphenylsilane (14.5%) were obtained in addition to a 60% yield of hexaphenyldisilane.

In the first case sufficient triphenylsilyllithium was added to react with the intermediates, mono- and diiodomethyltriphenylsilane, to form methyltriphenylsilane and bis(triphenylsilyl)methane by the same mechanisms as those illustrated for the reactions of bromomethyltriphenylsilane and dichloromethyltriphenylsilane.

When reverse addition was employed until all of the triphenylsilyllithium was used up, as indicated by a negative Color Test I, the yield of hexaphenyldisilane was 64.7%. The other products were methyltriphenylsilane (11.0%), bis(triphenylsilyl)methane (3.1%), and 1,2-bis(triphenylsilyl)ethane (2.4%).

1,2-bis(triphenylsilyl)ethane might be expected in all reactions which involve triphenylsilylmethyllithium as an intermediate:

$$Ph_3Si\text{-}CH_2Li + Ph_3Si\text{-}CH_2X \longrightarrow Ph_3Si\text{-}CH_2\text{-}CH_2\text{-}SiPh_3$$

This, however, is the only case in which this compound was actually isolated.

10. Reactions with carbon tetrachloride

A 250% excess of triphenylsilyllithium was required to react completely with a given amount of carbon tetrachloride at -60°. The compounds obtained were hexaphenyldisilane (57.2%) and dichloromethyltriphenylsilane (42.2% based on carbon tetrachloride, 16.2% based on triphenylsilyllithium). When a 2:1 ratio of triphenylsilyllithium to carbon tetrachloride was used, the yield of dichloromethyltriphenylsilane was only 13.0% (based on carbon tetrachloride), while the yield of hexaphenyldisilane remained the same. When, however, carbon tetrachloride was added to the solution of triphenylsilyllithium, a 73.6% yield of hexaphenyldisilane and a 11.2% yield of dichloromethyltriphenylsilane were obtained.

The formation of dichloromethyltriphenylsilane is not clearly understood. The reaction of triphenylsilyllithium with dichlorocarbene, generated as a result of an initial halogen-metal interconversion, would give chlorotriphenylsilylcarbene. It is very unlikely that chlorotriphenylsilylcarbene would abstract chloride ions from symmetrical carbon tetrachloride to form dichlorotriphenylsilylcarbanion and trichlorocarbonium ion. Even if such ions are formed, they might collapse to give pentachlorotriphenylsilylethane.

The structure of chlorotriphenylsilylcarbene might prove to be quite an interesting one, since an unfilled orbital of the carbon atom, as well as *d*-orbitals of the silicon atom, are present in the system. In short, chlorotriphenylsilylcarbene might behave as a diradical rather than as a mere electron deficient species. In such a case, it could abstract a chlorine atom from carbon tetrachloride, forming a dichlorotriphenylsilylmethyl radical, which would then abstract a hydrogen atom from the solvent. The trichloromethyl radical is stabilized by resonance, and carbon tetrachloride is known to undergo free-radical reactions of this type.[96]

11. Reactions with carbon tetrabromide

The reaction of carbon tetrabromide with triphenylsilyllithium was found to be quite different from the reaction of carbon tetrachloride with triphenylsilyllithium. The yields of hexaphenyldisilane are comparable for both normal and reverse additions. In the reaction with carbon tetrachloride, however, the secondary product was dichloromethyltriphenylsilane, while in the case of carbon tetrabromide four compounds were obtained in trace amounts: bromomethyltriphenylsilane (2.8%), dibromomethyltriphenylsilane (1.4%), bromotriphenylsilylacetylene (2.0%), and bis(triphenylsilyl)acetylene (4.3%).

This surprising difference may well be due to the different nature of the supposed intermediates, bromotriphenylsilylcarbene as opposed to chlorotriphenylsilylcarbene. One might argue that, because of the greater size and polarizability of the bromine atom as compared to the chlorine atom, it would be easier for the electron cloud of the bromine atom to drift toward the unoccupied orbital of the carbon atom. Thus, in contrast to chlorotriphenylsilylcarbene, bromotriphenylsilylcarbene would be more an electron deficient species than a diradical. If this were so, then one might expect that bromotriphenylsilylcarbene would

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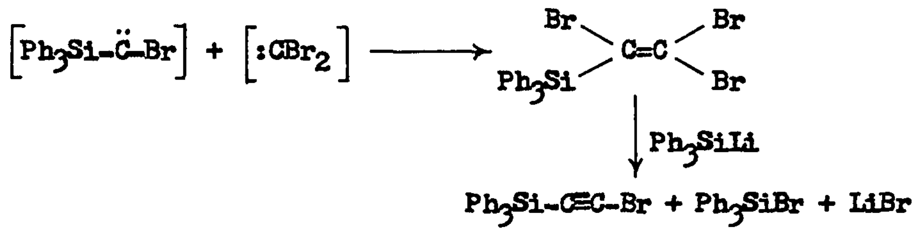
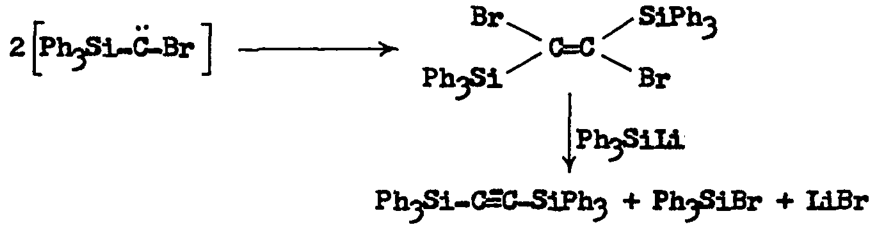
[96] For a general discussion of free-radical reactions of polyhalomethanes, see, for example, E. S. Gould. Mechanism and Structure in Organic Chemistry. New York, N.Y., Henry Holt and Co. 1959. pp. 743-748.

combine with other carbenes present in the system rather than attack carbon tetrabromide.

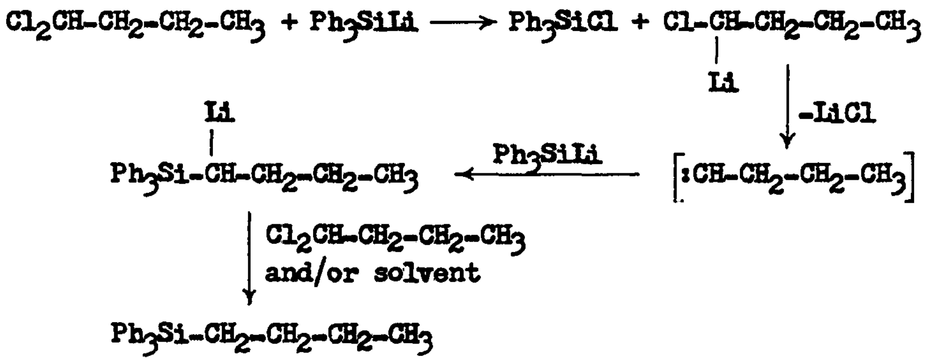




12. Reactions with 1,1-dichlorobutane

When triphenylsilyllithium was added to 1,1-dichlorobutane, hexaphenyldisilane and *n*-butyltriphenylsilane were obtained in yields of 58.0% and 39.0%, respectively. When the addition was reversed, 10% more of hexaphenyldisilane and 12% less of *n*-butyltriphenylsilane were isolated.

These results are rather simple in comparison to those of the methylene chloride reactions. The coupling reaction, which might have existed between methylene chloride and triphenylsilyllithium to form chloromethyltriphenylsilane, may be disfavored in the case of 1,1-dichlorobutane by steric considerations. A possible sequence of reactions is as follows:



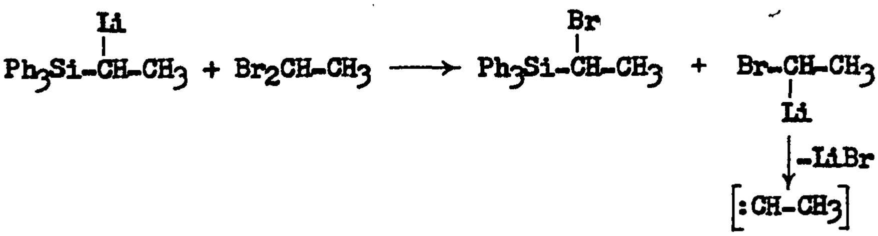
$$Cl_2CH\text{-}CH_2\text{-}CH_2\text{-}CH_3 + Ph_3SiLi \longrightarrow Ph_3SiCl + Cl\text{-}\underset{\substack{|\\ Li}}{CH}\text{-}CH_2\text{-}CH_2\text{-}CH_3 \xrightarrow{-LiCl} [:CH\text{-}CH_2\text{-}CH_2\text{-}CH_3]$$

$$[:CH\text{-}CH_2\text{-}CH_2\text{-}CH_3] \xrightarrow{Ph_3SiLi} Ph_3Si\text{-}\overset{\substack{Li\\ |}}{CH}\text{-}CH_2\text{-}CH_2\text{-}CH_3 \xrightarrow[\text{and/or solvent}]{Cl_2CH\text{-}CH_2\text{-}CH_2\text{-}CH_3} Ph_3Si\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$$

13. Reactions with 1,1-dibromoethane

In the reaction of 1,1-dibromoethane and triphenylsilyllithium, 1-bromo-1-triphenylsilylethane was formed in a 4.6% yield, in addition to the expected ethyltriphenylsilane (33.2%) and hexaphenyldisilane (59.4%).

As in the case of the methylene bromide reaction, it is unlikely that 1-bromo-1-triphenylsilylethane was formed by a coupling reaction between 1,1-dibromoethane and triphenylsilyllithium in view of the fact that the corresponding 1-chloro-1-triphenylsilylbutane was not formed in the reaction of 1,1-dichlorobutane and in view of the fact that chlorides undergo the coupling reaction more readily than bromides. It is more likely that 1-bromo-1-triphenylsilylethane was formed by halogen-metal interconversion between 1-triphenylsilylethyllithium and 1,1-dibromoethane.



$$Ph_3Si\text{-}\overset{\substack{Li\\ |}}{CH}\text{-}CH_3 + Br_2CH\text{-}CH_3 \longrightarrow Ph_3Si\text{-}\overset{\substack{Br\\ |}}{CH}\text{-}CH_3 + Br\text{-}\underset{\substack{|\\ Li}}{CH}\text{-}CH_3 \xrightarrow{-LiBr} [:CH\text{-}CH_3]$$

B. Reactions of Triphenylsilyllithium with Alkenyl Halides

1. Reactions with 1-chloropropene

The reaction of triphenylsilyllithium with 1-chloropropene did not proceed very rapidly at -60°. These two compounds did, however, react smoothly from 0° to room temperature. The halogen-metal interconversion reaction occurred to an extent of 13-15%. The products were 1,2-bis(triphenylsilyl)propane (45.5%) and hexaphenyldisilane.

One might expect that 1-triphenylsilylpropene would be an intermediate:

$$Ph_3SiLi + Cl\text{-}CH{=}CH\text{-}CH_3 \longrightarrow Ph_3Si\text{-}CH{=}CH\text{-}CH_3 + LiCl$$

With this in mind, 1-triphenylsilylpropene was prepared from the reaction of chlorotriphenylsilane and propenyllithium.[97] The addition reaction of triphenylsilyllithium to 1-triphenylsilylpropene was found, however, to be slower than the reaction of 1-chloropropene with triphenylsilyllithium. The mixture was stirred at room temperature for 22 hours and subsequently refluxed for 2 hours to give 38.4% of 1,2-bis(triphenylsilyl)propane.

The increased rate of reaction and the higher yield of product for the reaction with 1-chloropropene, coupled with the fact that 1-triphenylsilylpropene was not isolated, would necessitate the proposal of a different mechanism for this reaction.

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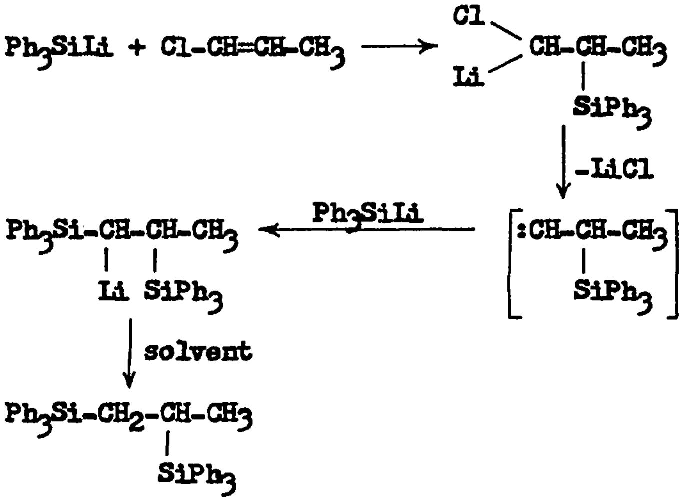
[97] E. A. Braude and J. A. Coles, J. Chem. Soc., 1951, 2078.



The reaction of triphenylsilyllithium and the carbene intermediate is expected to be a reasonably fast reaction even at -60°.[60] Therefore, the addition of triphenylsilyllithium to 1-chloropropene[98] must be the slow step, since the reaction proceeds very slowly at a temperature below 0°. 1,2-bis(triphenylsilyl)propyllithium appears to be very unstable, as are other α-triphenylsilylorganolithium compounds, such as

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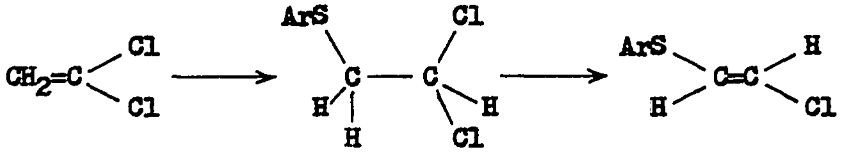
[98] The highly nucleophilic arylthiolate ion was shown to undergo an addition-elimination reaction with vinylidene chloride and related compounds.



I II

Both compounds I and II were isolated. See, for example, W. E. Truce and M. M. Boudakian, *J. Am. Chem. Soc.*, **78**, 2748 (1956).

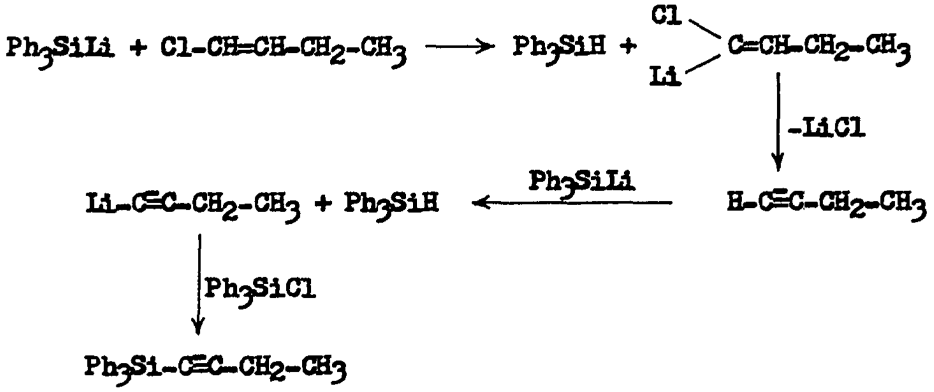
triphenylsilylmethyllithium, 1-triphenylsilylethyllithium, and 1-triphenylsilylbutyllithium.

2. Reactions with 1-chloro-1-butene

Triphenylsilyllithium reacted with 1-chloro-1-butene much more slowly than it did with 1-chloropropene. When the equimolar mixture had been stirred for 28 hours at room temperature, Color Test I was still positive. The major product was 1,2-bis(triphenylsilyl)butane (22.2%). Hexaphenyldisilane was not isolated. When the mixture was refluxed for 2 hours, 1,2-bis(triphenylsilyl)butane was obtained in a 26.0% yield. Again, hexaphenyldisilane was not isolated.

In a third run the reaction mixture was treated with chlorotriphenylsilane after 16 hours of stirring. Hexaphenyldisilane was obtained in a yield of 15.1%, which was the measure of unreacted triphenylsilyllithium. Triphenylsilane (13.0%) and 1-triphenylsilyl-1-butyne (7.4%) were isolated in addition to 1,2-bis(triphenylsilyl)butane (29.6%).

Reactions which would lead to the formation of triphenylsilane and 1-triphenylsilyl-1-butyne might be as follows:



$$\begin{tikzcd}
\mathrm{Ph_3SiLi + Cl\text{-}CH{=}CH\text{-}CH_2\text{-}CH_3} \arrow[r] & \mathrm{Ph_3SiH} + \overset{\mathrm{Cl}}{\underset{\mathrm{Li}}{>}}\mathrm{C{=}CH\text{-}CH_2\text{-}CH_3} \arrow[d, "-\mathrm{LiCl}"] \\
\mathrm{Li\text{-}C{\equiv}C\text{-}CH_2\text{-}CH_3 + Ph_3SiH} \arrow[d, "\mathrm{Ph_3SiCl}"] & \mathrm{H\text{-}C{\equiv}C\text{-}CH_2\text{-}CH_3} \arrow[l, "\mathrm{Ph_3SiLi}"'] \\
\mathrm{Ph_3Si\text{-}C{\equiv}C\text{-}CH_2\text{-}CH_3} &
\end{tikzcd}$$

3. Reactions with 1-bromopropene

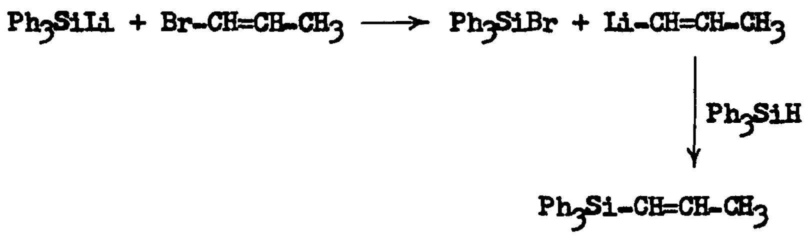
Of all the reactions presented in this thesis, that of triphenylsilyllithium and 1-bromopropene was the most complicated. The yield of hexaphenyldisilane in most cases was around 70%. Other products and their yields were as follows:

	No Ph_3SiCl added	Ph_3SiCl added
Triphenylsilane	?	13.5
1,2-bis(triphenylsilyl)propane	6.8	7.7
1-triphenylsilylpropene	11.0	6.7
1,3-bis(triphenylsilyl)propene	-	2.2
1-triphenylsilylpropyne	7.1	15.3
1,3-bis(triphenylsilyl)propyne	7.2	4.3
Tris(triphenylsilyl)propadiene	0.2	6.4

These values represent the largest yields obtained for each compound. Since the separation of the products was difficult and since even a slight change in reaction conditions seemed to affect product ratios, not all the compounds were obtained in every run.

1,2-bis(triphenylsilyl)propane seems to have been formed by the same mechanism as in the case of the 1-chloropropene reaction.

The formation of 1-triphenylsilylpropene is probably the result of the reaction of triphenylsilane and the propenyllithium which would be formed from the halogen-metal interconversion reaction.

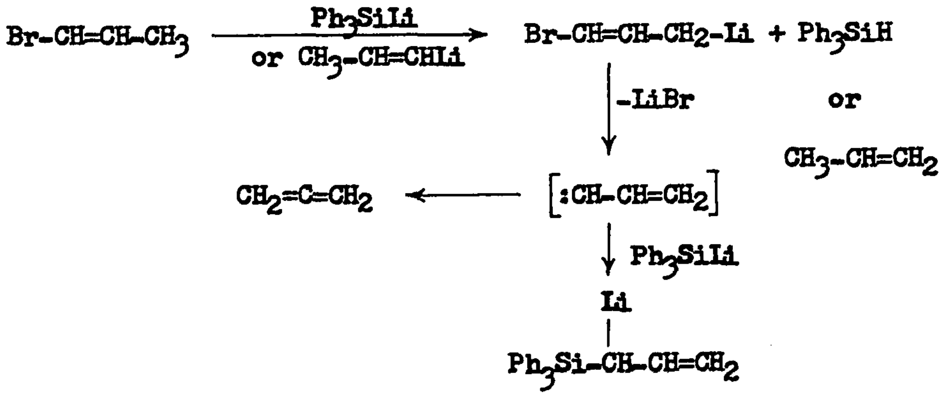


$$\begin{tikzcd} Ph_3SiLi + Br\text{-}CH{=}CH\text{-}CH_3 \arrow[r] & Ph_3SiBr + Li\text{-}CH{=}CH\text{-}CH_3 \arrow[d, "Ph_3SiH"] \\ & Ph_3Si\text{-}CH{=}CH\text{-}CH_3 \end{tikzcd}$$

The reaction of triphenylsilane and propenyllithium was investigated and it was found that they react smoothly at room temperature to give a 91.5% yield of 1-triphenylsilylpropene after 4.5 hours of stirring.

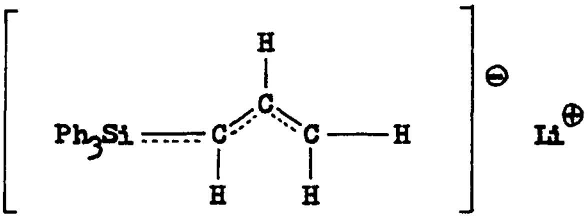
Propenyllithium seemed, however, to be unstable under the reaction conditions, as evidenced by the fact that the yield of 1-triphenylsilylpropene did not increase with the addition of chlorotriphenylsilane.

All the other products seem to have a common ancestral intermediate. Propenyllithium, as well as triphenylsilyllithium, may participate in the formation of this intermediate. The abstraction of a γ-hydrogen from 1-bromopropene by triphenylsilyllithium (or by propenyllithium) and the subsequent elimination of lithium bromide would give a vinylcarbene, which may either rearrange to an allene or react with triphenylsilyllithium to form a metalated allyltriphenylsilane:

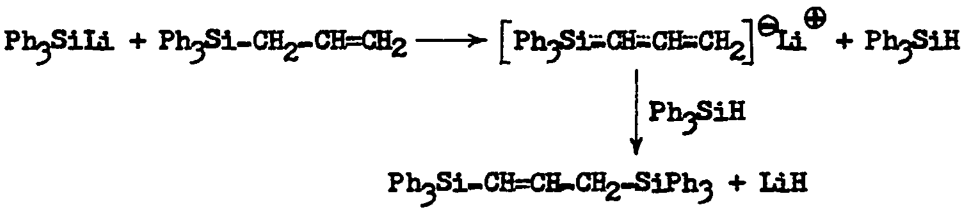


$$\begin{tikzcd} Br\text{-}CH{=}CH\text{-}CH_3 \arrow[r, "Ph_3SiLi", "\text{or } CH_3\text{-}CH{=}CHLi"'] & Br\text{-}CH{=}CH\text{-}CH_2\text{-}Li \arrow[d, "-LiBr"] & + \; Ph_3SiH \; \text{or} \; CH_3\text{-}CH{=}CH_2 \\ CH_2{=}C{=}CH_2 & {[:CH\text{-}CH{=}CH_2]} \arrow[l] \arrow[d, "Ph_3SiLi"] & \\ & Ph_3Si\text{-}\overset{\displaystyle Li}{\overset{|}{C}H}\text{-}CH{=}CH_2 & \end{tikzcd}$$

The metalated allyltriphenylsilane actually exists as a resonance hybrid of the structure as shown below.[99, 100]



When a mixture of triphenylsilyllithium and allyltriphenylsilane was stirred at room temperature for 22 hours, 1,3-bis(triphenylsilyl)propene was obtained in a 40% yield.



$$Ph_3SiLi + Ph_3Si{-}CH_2{-}CH{=}CH_2 \longrightarrow \left[Ph_3Si{=}CH{=}CH{=}CH_2\right]^{\ominus}Li^{\oplus} + Ph_3SiH$$

$$\Big\downarrow Ph_3SiH$$

$$Ph_3Si{-}CH{=}CH{-}CH_2{-}SiPh_3 + LiH$$

Probably vinylcarbene rearranges to an allene within a short period of time so that there may be little chance for triphenylsilyllithium to react with it to form the metalated allyltriphenylsilane, hence a very low yield of 1,3-bis(triphenylsilyl)propene and no yield of allyltriphenylsilane at all. Vinylcarbene may also form cyclopropene, although no derivative of cyclopropene was isolated.[62]

The allene may then be metalated by triphenylsilyllithium:

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[99] E. J. Lanpher, *ibid.*, *79*, 5578 (1957).

[100] H. F. Herbrandson and D. S. Mooney, *ibid.*, *79*, 5809 (1957).

$$CH_2{=}C{=}CH_2 + Ph_3SiLi \longrightarrow Li{-}CH{=}C{=}CH_2 + Ph_3SiH$$

The resulting anion can exist as a resonance hybrid:

$$\left[\overset{\ominus}{C}H{=}C{=}CH_2 \longleftrightarrow H{-}C{\equiv}C{-}\overset{\ominus}{C}H_2\right]$$

Since this is a vinyllithium-type compound, it might be expected to couple with triphenylsilane to give triphenylsilylpropadiene, which in turn might rearrange to form the more stable 1-triphenylsilylpropyne either before or after hydrolysis. Both triphenylsilylpropadiene and 1-triphenylsilylpropyne undergo further metalation and coupling reactions which give 1,3-bis(triphenylsilyl)propyne and tris(triphenylsilyl)-propadiene. These reactions will be discussed in separate sections later.

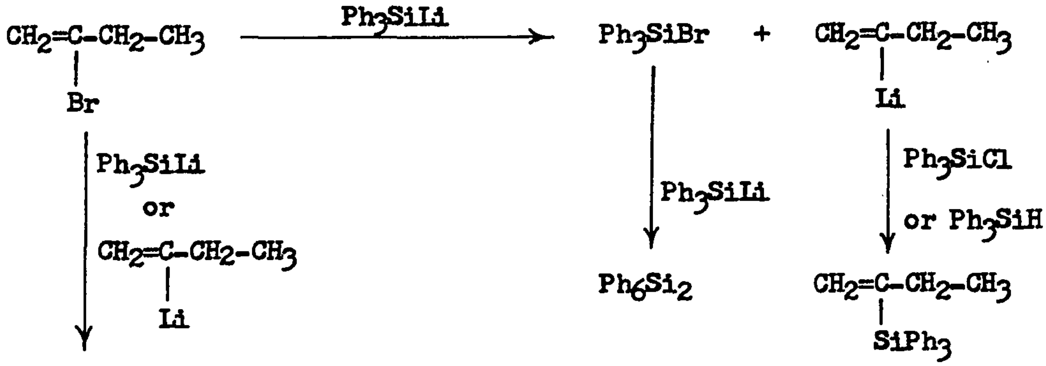
4. Reactions with 1-bromo-1-butene

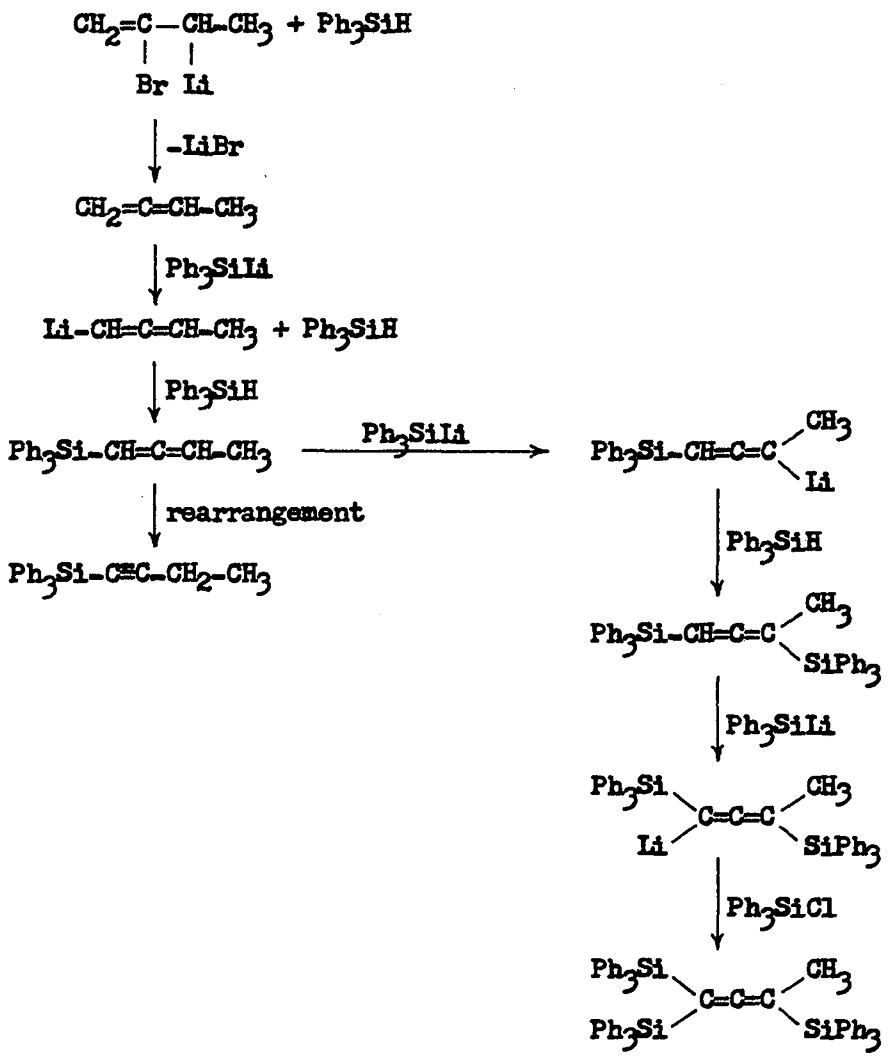
The reaction of 1-bromo-1-butene with triphenylsilyllithium took quite a different course from the 1-bromopropene reaction. A solution of triphenylsilyllithium (0.08 mole) was added to 1-bromo-1-butene (0.025 mole) in 100 ml. of ether at room temperature and the mixture was stirred for 2.5 hours. Triphenylsilyllithium was in excess, as evidenced by a positive Color Test I and a large yield (53.4%) of triphenylsilane. The halogen-metal interconversion occurred to the extent of 33.6%, as shown by the yield of hexaphenyldisilane. Two compounds were isolated, one melting at 223.5-225°, the other at 198-202°. Both compounds are unidentified. It will be shown later that 1-triphenylsilyl-1-butyne behaves differently from 1-triphenylsilylpropyne toward triphenylsilyllithium.

5. Reactions with 2-bromo-1-butene

It is interesting that with triphenylsilyllithium 2-bromo-1-butene gave results similar to those of 1-bromopropene, while 1-bromo-1-butene reacted in a completely different manner. A slight excess (0.047 mole) of triphenylsilyllithium was added to 2-bromo-1-butene (0.04 mole) in 100 ml. of ether and the mixture was stirred for 2 hours at room temperature. Color Test I was positive. Chlorotriphenylsilane was added to derivatize any organometallic compounds present in the reaction mixture. The yield of hexaphenyldisilane was 7.25 g., representing a yield of 59.6% if the entire amount resulted from the halogen-metal interconversion reaction, but it is not at all unlikely that at least a part of the yield came from the reaction of unreacted triphenylsilyllithium with chlorotriphenylsilane. The other products were triphenylsilane (1.7%), 2-triphenylsilyl-1-butene (11.5%), 1-triphenylsilyl-1-butyne (8.8%), and 1,1,3-tris(triphenylsilyl)-1,2-butadiene.

The following reaction sequence may be suggested:



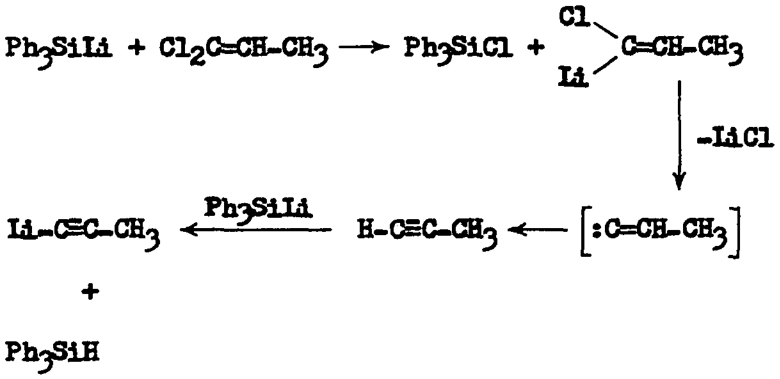


6. Reactions with 1,1-dichloropropene

The reaction of 1,1-dichloropropene and triphenylsilyllithium gave hexaphenyldisilane in yields ranging from 52.5 to 77.6%. The other products were triphenylsilane (in a higher yield when excess of triphenylsilyllithium was used), 1-triphenylsilylpropyne (0-26.2% depending on reaction conditions and on the ratio of the reactants), 1-triphenylsilylpropene (a trace amount), 2-chloro-3-triphenylsilylpropene (4.2% and 1.6% in two runs), 1,2-bis(triphenylsilyl)propene (5.4%), and tris(triphenylsilyl)propadiene (5.9%).

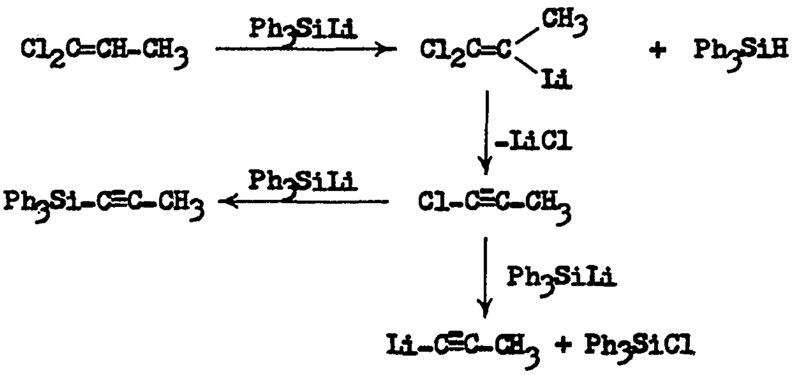
When the reaction was carried out at -60°, the yield of hexaphenyldisilane was somewhat higher on the average than when it was carried out at room temperature. Triphenylsilane and 1-triphenylsilylpropyne were obtained in significantly higher yields in the latter case than in the former.

The main question here is how 1-triphenylsilylpropyne was formed. The halogen-metal interconversion reaction would give propynyllithium after several steps:



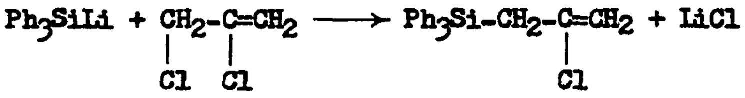
$$\begin{tikzcd}
Ph_3SiLi + Cl_2C{=}CH{-}CH_3 \arrow[r] & Ph_3SiCl + \begin{matrix}Cl \\ Li\end{matrix}\!\!>C{=}CH{-}CH_3 \arrow[d, "-LiCl"] \\
Li{-}C{\equiv}C{-}CH_3 + Ph_3SiH & H{-}C{\equiv}C{-}CH_3 \arrow[l, "Ph_3SiLi"'] & \left[:C{=}CH{-}CH_3\right] \arrow[l]
\end{tikzcd}$$

The reactions of propynyllithium with triphenylsilane and chlorotriphenylsilane were investigated and it was found that triphenylsilane reacted with propynyllithium only to the extent of 1-2% under comparable conditions. It is unlikely, therefore, that the coupling of triphenylsilane and propynyllithium would give as high as 26% of 1-triphenylsilylpropyne. In the case of chlorotriphenylsilane, it is doubtful that propynyllithium can compete with triphenylsilyllithium in the coupling reaction (see page 167). At least a part of the 1-triphenylsilylpropyne may, however, have resulted from a coupling between propynyllithium and chlorotriphenylsilane. There is a possibility that 1-chloropropyne might be an intermediate. The reaction of 1-chloropropyne with triphenylsilyllithium is discussed in connection with the reactions of halotriphenylsilylacetylenes. The yield of 1-triphenylsilylpropyne (11.7%) from this reaction, however, does not satisfactorily account for the total yield of 1-triphenylsilylpropyne.



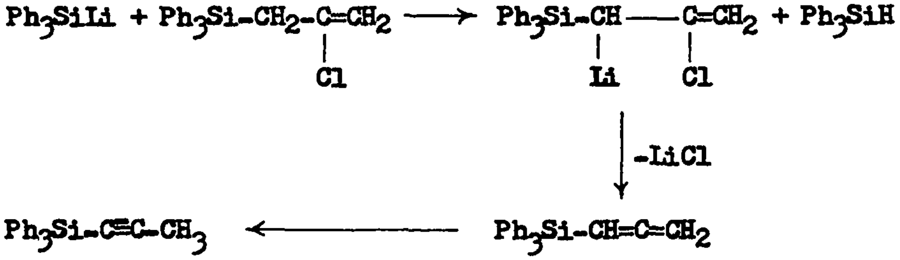
An intermediate compound, then, which would give 1-triphenylsilylpropyne was sought. When triphenylsilyllithium was added to a two-fold excess of 1,1-dichloropropene, such a compound was isolated in a yield of 4.2%. The compound was found to be identical with the compound obtained from the reaction of 2,3-dichloropropene with triphenylsilyllithium, as determined by a mixed melting point determination, as well as by infrared and n.m.r. spectra. Largely from the study of the n.m.r. spectrum a structure of 2-chloro-3-triphenylsilylpropene was assigned to the compound (see page 153). The formation of this compound from

2,3-dichloropropene may easily be justified by supposing a straightforward coupling of triphenylsilyllithium at the saturated carbon:



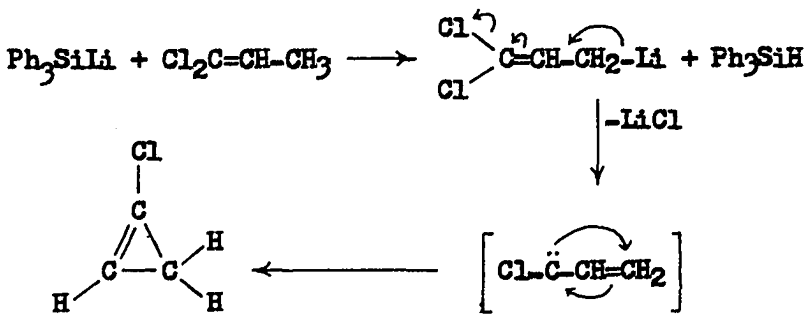
$$Ph_3SiLi + \underset{Cl}{CH_2}\text{-}\underset{Cl}{C}{=}CH_2 \longrightarrow Ph_3Si\text{-}CH_2\text{-}\underset{Cl}{C}{=}CH_2 + LiCl$$

The reaction of 2-chloro-3-triphenylsilylpropene and triphenylsilyllithium in a 1:1 ratio gave 64.1% of triphenylsilane and 62.9% of 1-triphenylsilylpropyne as expected:

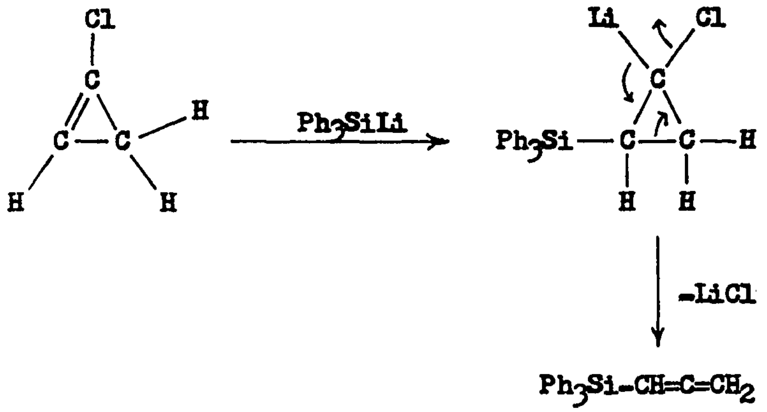


$$\begin{tikzcd}[column sep=small]
Ph_3SiLi + Ph_3Si\text{-}CH_2\text{-}\underset{Cl}{C}{=}CH_2 \arrow[r] & Ph_3Si\text{-}\underset{Li}{CH}\text{—}\underset{Cl}{C}{=}CH_2 + Ph_3SiH \arrow[d, "-LiCl"] \\
Ph_3Si\text{-}C{\equiv}C\text{-}CH_3 & Ph_3Si\text{-}CH{=}C{=}CH_2 \arrow[l]
\end{tikzcd}$$

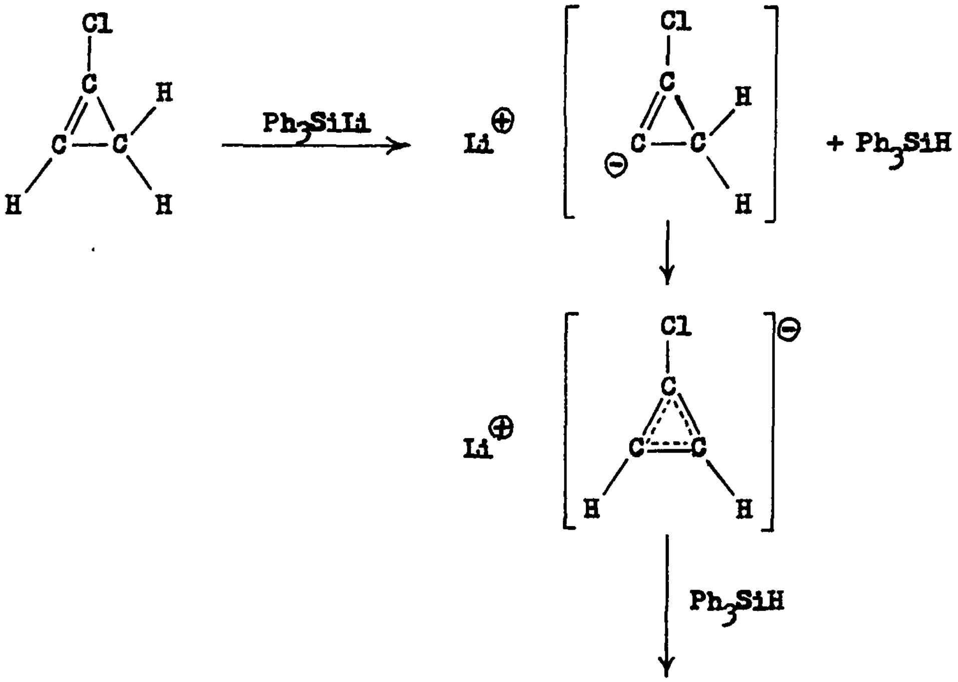
The question of how 2-chloro-3-triphenylsilylpropene is formed from the 1,1-dichloropropene reaction is unanswered. Perhaps 1-chlorocyclopropene might be an intermediate:[62]

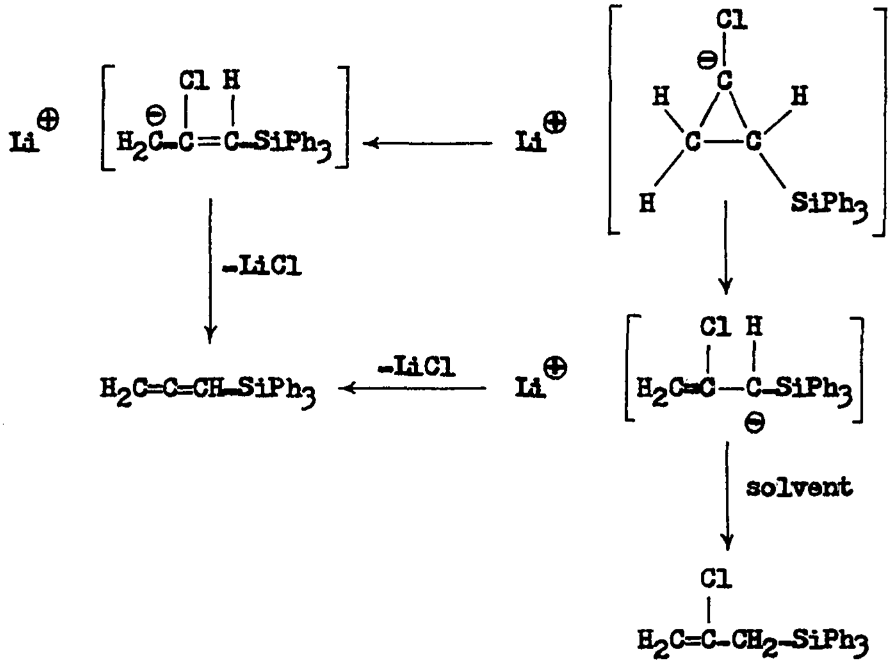


Triphenylsilyllithium may add to the double bond, followed by a subsequent elimination and rearrangement[58] to give triphenylsilylpropadiene:



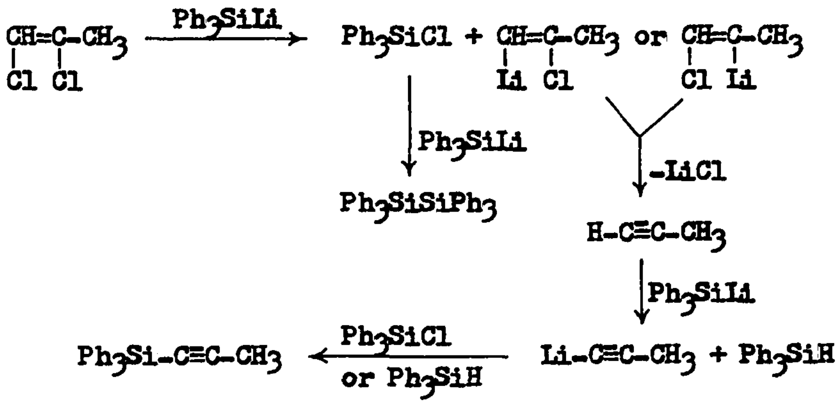
1-chlorocyclopropene may, however, undergo a series of metalation, rearrangement, and addition reactions:





7. Reactions with 1,2-dichloropropene

The reaction of 1,2-dichloropropene with two equivalents of triphenylsilyllithium gave 61.8% of hexaphenyldisilane and 2% of 1-triphenylsilylpropyne. When 3 equivalents of triphenylsilyllithium were used, hexaphenyldisilane (92%) and triphenylsilane (36.5%) were isolated.



8. Reactions with 1,3-dichloropropene

According to Bert,[19] 1,3-dichloropropene reacts with phenylmagnesium bromide to give an almost quantitative yield of 1-chloro-3-phenylpropene. Triphenylsilyllithium, however, reacted with 1,3-dichloropropene in a somewhat more complicated manner. The halogen-metal interconversion reaction occurred to the extent of about 10%. When an equivalent amount of triphenylsilyllithium was added to 1,3-dichloropropene in THF at room temperature, a mixture of 1-triphenylsilyl-3-chloropropene (I), m.p. 105-107.5°, and 1-chloro-3-triphenylsilylpropene (II), m.p. 112.5-115.5°, was obtained in a 75% yield in addition to 9.7% of hexaphenyldisilane.

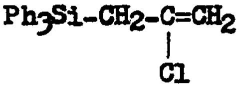
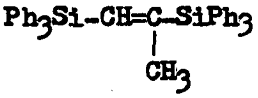
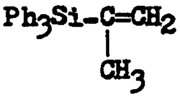
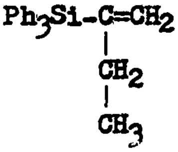
$$
\begin{array}{ll}
\mathrm{Ph_3SiLi + Cl\text{-}CH{=}CH\text{-}CH_2\text{-}Cl} \longrightarrow & \left.\begin{array}{ll}\mathrm{Ph_3Si\text{-}CH{=}CH\text{-}CH_2\text{-}Cl} & \text{(I)}\\ \mathrm{+\ Ph_3Si\text{-}CH_2\text{-}CH{=}CH\text{-}Cl} & \text{(II)}\end{array}\right\} 75\% \\
 & \mathrm{+\ Ph_3SiSiPh_3} \qquad\qquad 9.7\%
\end{array}
$$

The ratio of compounds (I) and (II) was approximately 5 to 4 judging from the n.m.r. spectrum of a typical mixture. The separation of these two compounds was very difficult and only small amounts of each were obtained in pure form after working up the mixture by a combination of chromatography and fractional recrystallizations from <u>n</u>-propanol.

The n.m.r. and infrared spectra data are given in Tables 3 and 4, respectively, together with those of compounds with similar structures.

It can be seen from Table 3 that the n.m.r. spectra of compounds (I) and (II) are very similar to each other and also to that of

Table 3. Nuclear magnetic resonance data (τ-values)[a]

Compounds		Olefinic hydrogens			$-CH_2-$	$-CH_3$
$Ph_3Si-CH=CH-CH_2-Cl$	(I)	4.15(m)[b]			7.48(m)	
$Ph_3Si-CH_2-CH=CH-Cl$	(II)	4.22(m)			7.70(d)	
 $Ph_3Si-CH_2-\underset{\underset{\displaystyle Cl}{\mid}}{C}=CH_2$	(III)		5.04(d)	5.16(q)	7.23(d)	
$Ph_3Si-CH_2-CH=CH_2$		4.16(m)	5.00(m)	5.25(d)	7.64(d)[c]	
$Ph_3Si-CH_2-CH=CH-SiPh_3$		3.84(m)			7.33(d)	
$(Ph_3Si)_2CH-CH=CH-SiPh_3$		4.00(m)			6.50(q)	
 $Ph_3Si-CH=\underset{\underset{\displaystyle CH_3}{\mid}}{C}-SiPh_3$		2.77(q)				8.17(d)
 $Ph_3Si-\underset{\underset{\displaystyle CH_3}{\mid}}{C}=CH_2$		4.06(m)	4.56(m)			8.05(t)
 $Ph_3Si-\underset{\underset{\underset{\underset{\displaystyle CH_3}{\mid}}{CH_2}}{\mid}}{C}=CH_2$		4.03(m)	4.49(m)		7.76(q)[c]	9.01(t)
$(Ph_3Si)_2C=C=CH-SiPh_3$				5.75(s)		

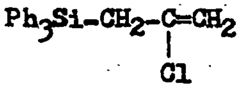
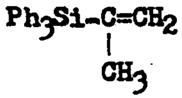
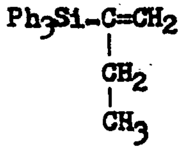
---

[a] Run at 60 Mc. in $CDCl_3$ using tetramethylsilane as the internal standard.

[b] s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet.

[c] Each peak is further divided into triplets.

Table 4. Infrared absorption spectra of triphenylsilyl substituted propenes and butenes

Compounds	Characteristic absorption bands							
$Ph_3Si-CH=CH-CH_2-Cl$ (I)	6.17(m)[a]	7.56(s)	8.87(m)	10.05(s)	-	-	12.51(m)	13.21(m)
$Ph_3Si-CH_2-CH=CH-Cl$ (II)	6.19(w)	-	8.02(m)	-	10.70(m)	12.00(s)	-	12.70(m)
 $Ph_3Si-CH_2-C(Cl)=CH_2$ (III)	6.18(s)	-	8.35(m)	-	10.72(m)	11.64(s)	-	12.95(s)
$Ph_3Si-CH=CH-CH_3$	6.20(s)	-	8.11(w)	10.19(s)	-	-	-	13.10(s)
$Ph_3Si-CH=CH-CH_2-CH_3$	6.25(s)	-	-	10.15(m)	-	-	12.34(w)	12.75(w)
 $Ph_3Si-C(CH_3)=CH_2$	-	-	-	-	10.75(s)	-	-	-
 $Ph_3Si-C(CH_2CH_3)=CH_2$	6.22(vw)	-	-	-	10.75(s)	11.53(w)	-	-

---

[a] Letters in parentheses indicate the relative intensities of absorption bands: s=strong; m=medium; w=weak; vw=very weak.

-1,3-bis(triphenylsilyl)propene, all showing a structure of $\left[-CH_2-CH=CH-\right]$. Olefinic hydrogens of the type $\left[-CH=CH-\right]$ in compounds, (I), (II), allyltriphenylsilane, 1,3-bis(triphenylsilyl)propene, and 1,3,3-tris(triphenylsilyl)propene, show their proton resonance spectra as multiplets at approximately the same τ-values: 4.15, 4.22, 4.16, 3.84, and 4.00, respectively.

One other isomer, 2-chloro-3-triphenylsilylpropene (III), the formation of which was discussed under the 1,1-dichloropropene reaction, shows an entirely different n.m.r. spectrum. Comparing this spectrum with those of compounds having terminal vinyl hydrogens, particularly with that of allyltriphenylsilane, it can be seen that the signals appearing at 5.04 and 5.16τ for compound (III) are due to the terminal vinyl hydrogens. The absence of signals in the 4.00τ region suggests that no other olefinic hydrogen is present.

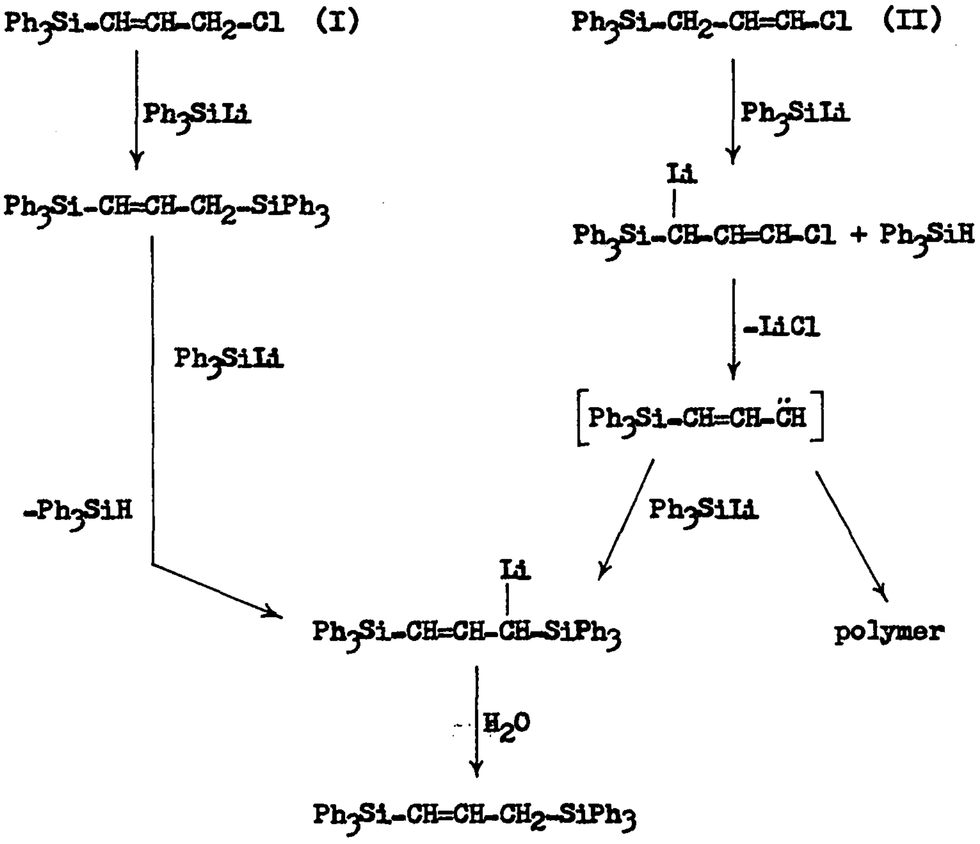
Looking now at Table 4, one finds striking similarities between the spectra of compounds (II) and (III). On the other hand, the spectrum of compound (I) is shown to be quite similar to that of 1-triphenylsilylpropene and 1-triphenylsilyl-1-butene. We suppose, therefore, that in compound (I) the double bond is located adjacent to the silicon atom. Thus, the structures of isomeric compounds (I), (II), and (III) have been determined.

The addition of two equivalents of triphenylsilyllithium to 1,3-dichloropropene gave 31.0% of 1,3-bis(triphenylsilyl)propene in addition to 12.5% of hexaphenyldisilane. When 3 equivalents of triphenylsilyllithium were used, 1,3-bis(triphenylsilyl)propene was isolated in a 50.5% yield, the other products being hexaphenyldisilane (6.7%) and triphenylsilane (77.0% based on the dichloride).

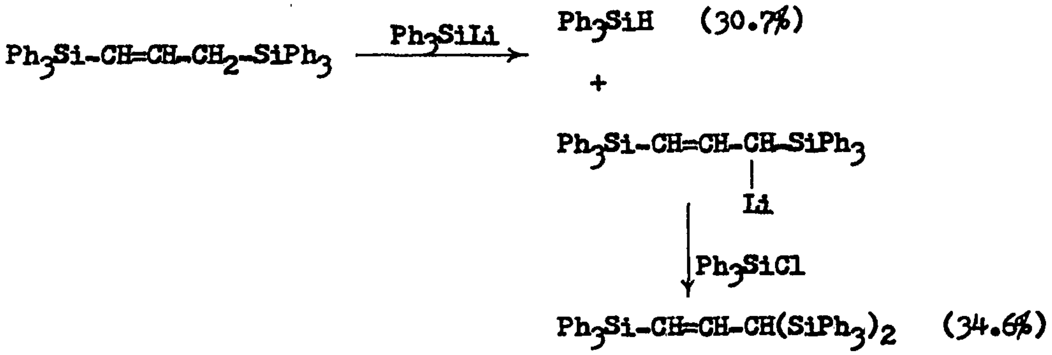
When a mixture of compounds (I) and (II) was treated with 2 equivalents of triphenylsilyllithium, triphenylsilane (96.2% based on the mixture) and 1,3-bis(triphenylsilyl)propene (57.7%) were obtained.

In all these reactions there were fair amounts of noncrystallizing, polymeric material.

These results suggest the following reaction paths:



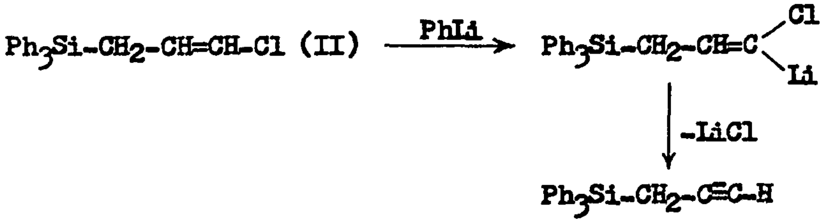
In order to see how readily 1,3-bis(triphenylsilyl)propene is metalated by triphenylsilyllithium, a two-fold excess of triphenylsilyllithium was added to the compound. Almost immediately a deep reddish color developed indicating the metalation reaction. After 24 hours of stirring chlorotriphenylsilane was added. It required 11 hours for chlorotriphenylsilane to react completely with the intermediate organolithium compound, as evidenced by the slow discharge of the color, probably because of the sterically hindered product.



$$Ph_3Si\text{-}CH{=}CH\text{-}CH_2\text{-}SiPh_3 \xrightarrow{Ph_3SiLi} Ph_3SiH\ (30.7\%) + Ph_3Si\text{-}CH{=}CH\text{-}\underset{Li}{CH}\text{-}SiPh_3 \xrightarrow{Ph_3SiCl} Ph_3Si\text{-}CH{=}CH\text{-}CH(SiPh_3)_2\ (34.6\%)$$

It is interesting that the treatment of the mixture of compounds (I) and (II) with phenyllithium gave a 10.7% yield of 3-triphenylsilylpropyne, together with a small amount of polymeric material and some starting material (27.6%).

The formation of 3-triphenylsilylpropyne may be brought about as follows:



$$Ph_3Si\text{-}CH_2\text{-}CH{=}CH\text{-}Cl\ (II) \xrightarrow{PhLi} Ph_3Si\text{-}CH_2\text{-}CH{=}C\begin{smallmatrix}Cl\\Li\end{smallmatrix} \xrightarrow{-LiCl} Ph_3Si\text{-}CH_2\text{-}C{\equiv}C\text{-}H$$

It appears that triphenylsilyllithium is not so strong a base as phenyllithium in abstracting an olefinic hydrogen from the compound (II).

9. Reactions with 2,3-dichloropropene

The formation of 2-chloro-3-triphenylsilylpropene from the reaction of 2,3-dichloropropene with triphenylsilyllithium was mentioned previously in connection with the 1,1-dichloropropene reaction. The structure determination was also discussed.

This compound was obtained in 19.4% yield when equimoles of the reactants were used. The other products were hexaphenyldisilane (28.3%), triphenylsilane (10.9%), and 1-triphenylsilylpropyne (7.8%).

The addition of a two-fold excess of triphenylsilyllithium, followed by derivatization with chlorotriphenylsilane, converted almost all of the 2-chloro-3-triphenylsilylpropene to 1-triphenylsilylpropyne.

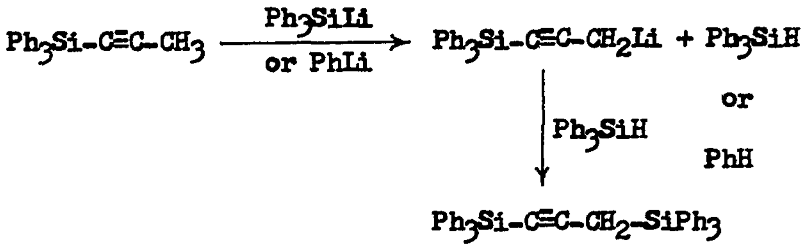
When the ratio of triphenylsilyllithium to 2,3-dichloropropene was 2.6 to 1 and chlorotriphenylsilane was added after 6 hours of stirring, most of the 1-triphenylsilylpropyne was converted to 1,2-bis(triphenylsilyl)propene (5.4%), 1,3-bis(triphenylsilyl)propyne (4.5%), and tris(triphenylsilyl)propadiene (18.0%).

C. Reactions of Triphenylsilyllithium with 1-triphenylsilylpropyne and Related Reactions

The reactions of triphenylsilyllithium with 1-bromopropene, 1,1-dichloropropene, and 2,3-dichloropropene have been shown to give 1-triphenylsilylpropyne, 1,3-bis(triphenylsilyl)propyne, and tris(triphenylsilyl)propadiene. The possibility that the latter two compounds resulted from 1-triphenylsilylpropyne (and/or triphenylsilylpropadiene) prompted the investigation of the reaction of 1-triphenylsilylpropyne with triphenylsilyllithium.

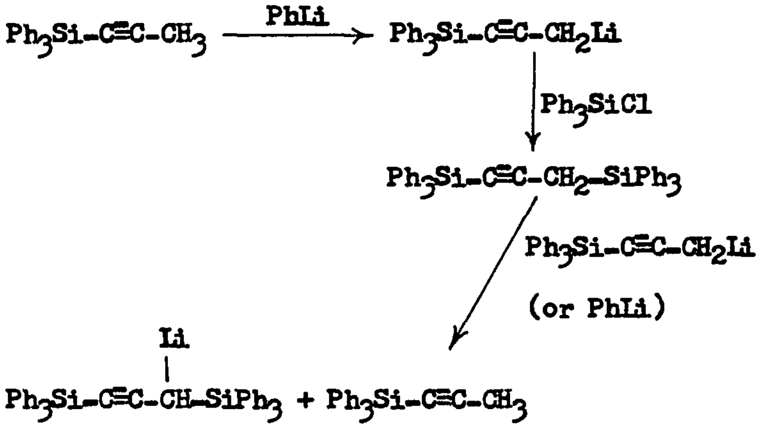
When an equimolar mixture of triphenylsilyllithium and 1-triphenylsilylpropyne was stirred at room temperature for 5 hours, there was obtained, after hydrolysis with dilute acid, triphenylsilane (51.3%), 1,2-bis(triphenylsilyl)propene (18.5%), 1,3-bis(triphenylsilyl)propyne (29.9%), and the starting material (18.4%).

In order to verify that 1,3-bis(triphenylsilyl)propyne is formed by the coupling reaction between triphenylsilane and the metalated 1-triphenylsilylpropyne, phenyllithium was allowed to react with 1-triphenylsilylpropyne under similar conditions and subsequently triphenylsilane was added. When the mixture was stirred for 5 hours, 1,3-bis(triphenylsilyl)propyne was obtained in a yield of 27.2%. The yield increased slightly to 31.7% when stirring was continued for 24 hours.



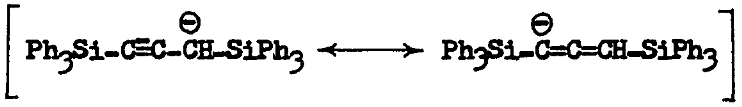
$$\begin{tikzcd}
Ph_3Si{-}C{\equiv}C{-}CH_3 \arrow[r, "Ph_3SiLi", "\text{or PhLi}"'] & Ph_3Si{-}C{\equiv}C{-}CH_2Li \arrow[d, "Ph_3SiH"] & + Ph_3SiH \text{ or } PhH \\
 & Ph_3Si{-}C{\equiv}C{-}CH_2{-}SiPh_3 &
\end{tikzcd}$$

When chlorotriphenylsilane was used as a derivatizing agent, tris(triphenylsilyl)propadiene (22.5%) and 1,3-bis(triphenylsilyl)propyne (12.6%) were isolated. The fact that the starting material, 1-triphenylsilylpropyne, was recovered in a larger yield from the reaction using chlorotriphenylsilane than in the case of triphenylsilane addition, 32.5% vs 17.2%, suggests that triphenylsilylethynylmethyllithium as well as unreacted phenyllithium metalates 1,3-bis(triphenylsilyl)propyne as soon as it is formed.



$$Ph_3Si\text{-}C{\equiv}C\text{-}CH_3 \xrightarrow{PhLi} Ph_3Si\text{-}C{\equiv}C\text{-}CH_2Li \xrightarrow{Ph_3SiCl} Ph_3Si\text{-}C{\equiv}C\text{-}CH_2\text{-}SiPh_3 \xrightarrow[\text{(or PhLi)}]{Ph_3Si\text{-}C{\equiv}C\text{-}CH_2Li} Ph_3Si\text{-}C{\equiv}C\text{-}\overset{Li}{\overset{|}{C}H}\text{-}SiPh_3 + Ph_3Si\text{-}C{\equiv}C\text{-}CH_3$$

The 1,3-bis(triphenylsilyl)propyne anion undoubtedly exists as a resonance hybrid:



$$\left[Ph_3Si\text{-}C{\equiv}C\text{-}\overset{\ominus}{C}H\text{-}SiPh_3 \longleftrightarrow Ph_3Si\text{-}\overset{\ominus}{C}{=}C{=}CH\text{-}SiPh_3\right]$$

It is with the allenic form that chlorotriphenylsilane couples because of the steric requirement of the product.

The metalation reaction of 1,3-bis(triphenylsilyl)propyne by triphenylsilyllithium was virtually complete as evidenced by the isolation of a small amount (2.9%) of hexaphenyldisilane when chlorotriphenylsilane was added. In the case of 1-triphenylsilylpropyne, hexaphenyldisilane was obtained in a 15.8% yield, which was a measure of unreacted triphenylsilyllithium.

$$\mathrm{Ph_3Si\text{-}C{\equiv}C\text{-}CH_2\text{-}SiPh_3}$$

$$\Big\downarrow \ \mathrm{Ph_3SiLi}\text{, 3.5 hours}$$

$$\Big\downarrow \ \mathrm{Ph_3SiCl}\text{, 3.0 hours}$$

$$\mathrm{Ph_3SiSiPh_3}\ (2.9\%) + \mathrm{Ph_3SiH}\ (88.5\%)$$

$$+ \mathrm{(Ph_3Si)_2C{=}C{=}CH\text{-}SiPh_3}\ (50.8\%) + \mathrm{(Ph_3Si)_2C{=}C{=}C(SiPh_3)_2}\ \text{(trace)}$$

Tris(triphenylsilyl)propadiene was identified by physical and chemical evidence. The elementary analysis and molecular weight determination were compatible with the formula. Its infrared spectrum showed a strong absorption band at 5.30μ. The usual allenic absorption bands appear at 5.0μ.[101] It is seen from Table 5 that an increase in the number of triphenylsilyl groups in a molecule shifts the position of the band to a longer wave length. This may be due to the increased number of participating d-orbitals of the silicon atoms for partial bond formation; thereby reducing allenic bond character.

The n.m.r. spectrum of tris(triphenylsilyl)propadiene showed a resonance peak at $5.75\ \tau$. The value is close to that given in the

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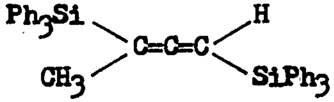
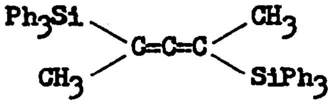
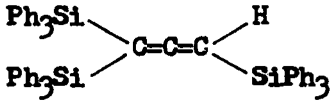
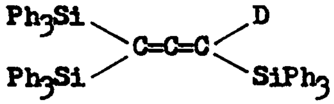
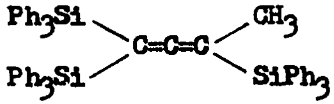
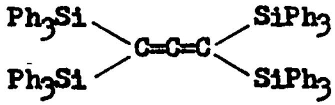
[101] L. J. Bellamy. The Infrared Spectra of Complex Molecules. London, Methuen and Co., Ltd. 1954. p. 61.

Table 5. Infrared absorption spectra of triphenylsilyl substituted allenes

Compounds	m.p.	C=C=C	Other characteristic bands			
	-	5.23(s)[a]	7.35(w)	10.64(w)	-	13.79(s)
	174-175	5.23(vs)	7.37(m)	10.10(m)	11.03(w)	-
	188-189.5	5.30(vs)	-	-	11.52(m)	13.73(s)
	188-189.5	5.30(vs)	-	-	11.52(m)	-
	196-197.5	5.34(vs)	7.36(m)	10.56(w)	11.57(s)	-
	448-452	5.49(vs)	-	-	12.00(s) 12.18(s)	-

[a] Letters in parentheses indicate the relative intensities of absorption bands: vs=very strong; s=strong; m=medium; w=weak.

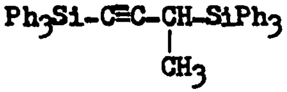
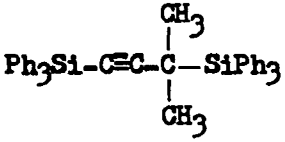
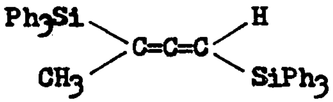
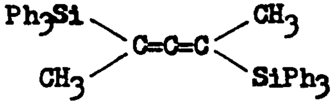
Table 6. Infrared absorption spectra of triphenylsilyl substituted acetylenes

Compounds	m.p.	$-C\equiv C-H$	$-C\equiv C-$	Other characteristic bands			
$Ph_3Si-C\equiv C-H$	146-149[a]	3.05(w)[b]	4.91(s)	-	-	-	-
$Ph_3Si-CH_2-C\equiv C-H$	89-91	3.02(w)	4.75(s)	-	-	10.50(w)	13.30(m)
$Ph_3Si-C\equiv C-Br$	111-112.5	-	4.70(s)	-	-	12.28(s)	-
$Ph_3Si-C\equiv C-Cl$	101.5-102.5	-	4.67(s)	-	-	11.08(s)	-
$Ph_3Si-C\equiv C-CH_2-SiPh_3$	127.5-128.5	-	4.65(s)	-	-	-	13.31(m)
$Ph_3Si-C\equiv C-\underset{CH_3}{\underset{\vert}{CH}}-SiPh_3$	135-136.5	-	4.65(s)	-	-	10.30(m) 10.99(m)	-
$Ph_3Si-C\equiv C-CH_3$	115-116	-	4.60(s)	-	9.71(s)	-	-
$Ph_3Si-C\equiv C-CH_2-CH_3$	90-91	-	4.62(s)	7.66(m)	9.35(s)	11.09(m)	-
$Ph_3Si-C\equiv C-\underset{CH_3}{\underset{\vert}{CH}}-CH_3$	79-81	-	4.60(s)	7.65(m)	-	10.38(m) 12.11(s)	-
$Ph_3Si-C\equiv C-SiPh_3$	156-157	-	-	-	-	12.82(s)	-
$Ph_3Si-C\equiv C-C\equiv C-SiPh_3$	294.5-296.5	-	4.84(s)	-	-	-	-

[a] Boiling point at 0.03mm. of pressure.

[b] Letters in parentheses indicate the relative intensities of absorption bands: s=strong; m=medium; w=weak.

Table 7. Infrared absorption spectra of some substituted propynes and allenes

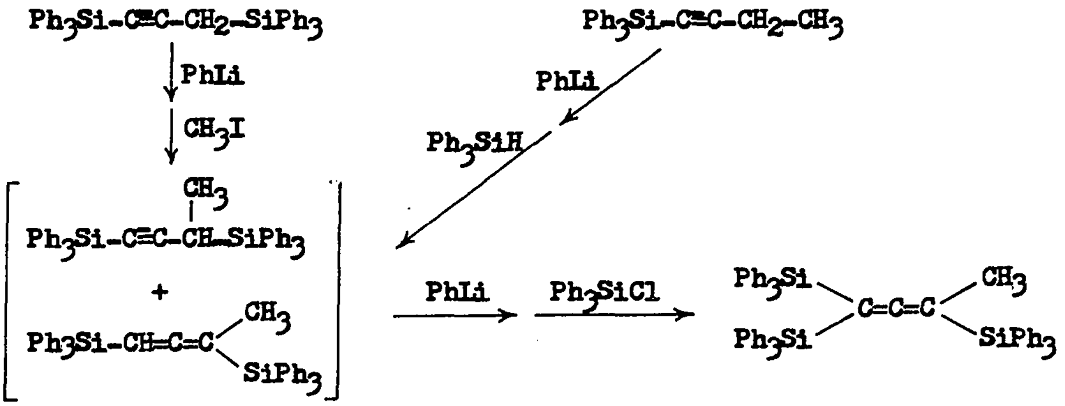
Compounds	m.p.	-C≡C-	C=C=C	-CH$_3$	Other characteristic bands			
$Ph_3Si-C{\equiv}C-CH_2-SiPh_3$	127.5-128.5	4.65	-	7.32(vw)[a]	-	-	13.31	13.77
 $Ph_3Si-C{\equiv}C-CH(CH_3)-SiPh_3$	135-136.5	4.64	-	7.30(w)	10.30	10.99	-	
 $Ph_3Si-C{\equiv}C-C(CH_3)_2-SiPh_3$	-	4.68	-	7.36(m)	-	11.84	-	
	-	-	5.23	7.35(w)	-	10.64	13.79	
	174-175	-	5.23	7.37(s)	10.10	11.03	-	
$Ph_3Si-C{\equiv}C-Cl$	101.5-102.5	4.67	-	7.32(vvw)	-	11.08	-	

[a] Intensities in this column are relative to neighboring peaks at 7.53, 7.70, and 7.95 μ.

literature.[102] The allenic hydrogen of tris(triphenylsilyl)propadiene was replaced by deuterium through metalation and hydrolysis with deuterium oxide. The n.m.r. spectrum of the deuterated compound showed no peak at 5.75 τ.

Tris(triphenylsilyl)propadiene was metalated by phenyllithium and subsequently treated with chlorotriphenylsilane. To introduce a fourth triphenylsilyl group into the molecule was found to be difficult and only 16.7% of pure tetrakis(triphenylsilyl)propadiene was obtained.[103] The n.m.r. spectrum showed only signals due to phenyl hydrogens.

When methyl iodide was used to derivatize the tris(triphenylsilyl)-propadienyllithium compound, the reaction proceeded smoothly and 1,1,3-tris(triphenylsilyl)-1,2-butadiene was obtained in a 67% yield. This compound was synthesized also by the following sequence of reactions:



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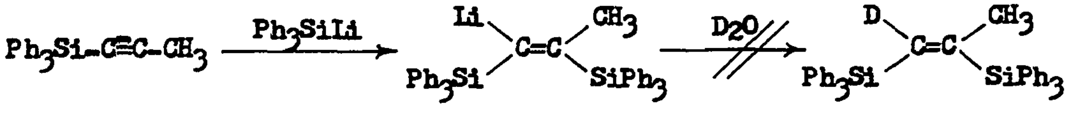
[102] L. M. Jackman. Applications of nuclear magnetic resonance spectroscopy in organic chemistry. In D. H. R. Barton and W. Doering, editors. International Series of Monographs on Organic Chemistry. Vol. 5. New York, N.Y., Pergamon Press, Inc. 1959.

[103] Tetrakis(trichlorosilyl)propadiene has been reported. See R. Müller and H. Beyer, Ber., 92, 1957 (1959).

During the course of the investigation it was noted that there is a definite correlation between stability of allenic compounds and the number of substituents. Apparently, as the number of bulky triphenylsilyl groups increases, the allenic structures provide better spacial arrangements of the substituent groups than the acetylenic structures. The results are summarized in Table 8.

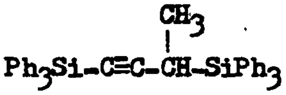
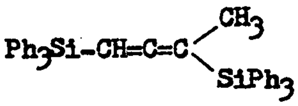
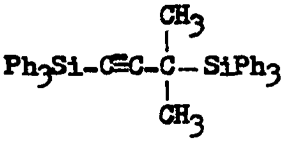
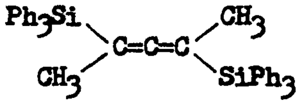
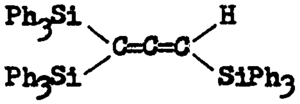
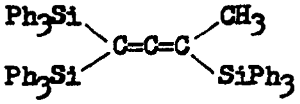
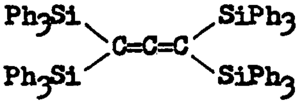
The reaction of 1-triphenylsilylpropyne and triphenylsilyllithium had an important side reaction. It is the addition of triphenylsilyllithium to the triple bond. 1,2-bis(triphenylsilyl)propene was obtained in a yield of 18.5%. Its n.m.r. spectrum was compatible with the structure (see Table 3), showing a doublet at 8.17τ and a quartet at 2.77τ. The reaction mixture was hydrolyzed with deuterium oxide in hope of isolating deuterated 1,2-bis(triphenylsilyl)propene. The attempt, however, failed.



This indicates that the intermediate 1,2-bis(triphenylsilyl)propenyllithium is unstable under the conditions employed and it must be protonated long before the hydrolysis step.

The reaction of triphenylsilyllithium and 1-triphenylsilyl-1-butyne, after 40 hours of stirring at room temperature, gave an oily residue from which several compounds were isolated in trace amounts: the unidentified compound obtained from the reaction of triphenylsilyllithium

Table 8. Isomer preference between some triphenylsilyl substituted acetylenes and allenes

Acetylenes	m.p.	Allenes	m.p.
$Ph_3Si{-}C{\equiv}C{-}CH_3$	115-116	——— [a]	———
$Ph_3Si{-}C{\equiv}C{-}CH_2{-}SiPh_3$	127.5-128.5	———	———
 $Ph_3Si{-}C{\equiv}C{-}\overset{CH_3}{\overset{\vert}{C}}H{-}SiPh_3$	135-136.5		----- [b]
 $Ph_3Si{-}C{\equiv}C{-}\overset{CH_3}{\underset{CH_3}{C}}{-}SiPh_3$	-----		174-175
———	———		188-189.5
———	———		196-197.5
———	———		448-452

[a] ——— Not isolated at all.

[b] ----- Not isolated as a pure product.

with 1-bromo-1-butene, tetraphenylsilane (4.4%), 1-triphenylsilyl-1-butyne (2.7%), 1,2-bis(triphenylsilyl)-1-butene (2%), and 1,3-bis(triphenylsilyl)-1-butyne (1.8%).

When the metalation was attempted by using phenyllithium and subsequently triphenylsilane was added, the major reaction was cleavage of the ethynyl group,[104] yielding 47% of tetraphenylsilane. Triphenylsilane was recovered in an 81.4% yield. The metalation-coupling products were obtained as a mixture of 1,3-bis(triphenylsilyl)-1-butyne and 1,3-bis(triphenylsilyl)-1,2-butadiene (11.7%), and as a pure 1,3-bis(triphenylsilyl)-1-butyne (3.2%).

In the case of the reaction of phenyllithium with 1-triphenylsilylpropyne, the cleavage occurred to the extent of 10%.

D. Reactions of Triphenylsilyllithium with Trichloroethylene and Related Reactions

1. Reactions of triphenylsilyllithium with trichloroethylene

When one equivalent of triphenylsilyllithium was added to a THF solution of trichloroethylene at room temperature, there was obtained hexaphenyldisilane (58.7%), triphenylsilane (6.2%), and chlorotriphenylsilylacetylene (5.0%). When two equivalents of triphenylsilyllithium were used, however, there was isolated hexaphenyldisilane (59.8%), triphenylsilane (10.0%), chlorotriphenylsilylacetylene (7.8%), and

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[104] H. Gilman and H. Hartzfeld, <u>J. Am. Chem. Soc.</u>, <u>73</u>, 5878 (1951).

bis(triphenylsilyl)acetylene (11.0%).

Since bis(triphenylsilyl)acetylene was formed when an excess of triphenylsilyllithium was used, it was reasonable to assume that chlorotriphenylsilylacetylene might have been an intermediate in the formation of bis(triphenylsilyl)acetylene. Therefore, chlorotriphenylsilylacetylene was synthesized and its reaction with triphenylsilyllithium was investigated.

The synthesis of chlorotriphenylsilylacetylene itself was a matter of interest. It will be discussed in detail, together with the preparation of bromotriphenylsilylacetylene and of bis(triphenylsilyl)acetylene.

Triphenylsilyllithium was allowed to react with chlorotriphenylsilylacetylene at room temperature; the products were hexaphenyldisilane (22.7%), triphenylsilylacetylene (15.8%), and bis(triphenylsilyl)acetylene (48.5%). The starting material was recovered in a 6% yield.

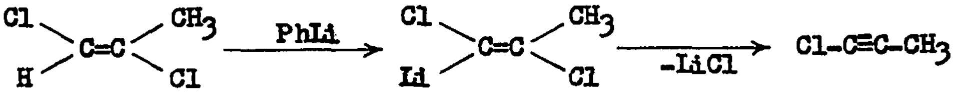
The surprisingly low yield of hexaphenyldisilane and the relatively high yield of bis(triphenylsilyl)acetylene should be noted. Since alkenyl chlorides give halogen-metal interconversion reactions to the extent of 10-30% (see reactions of 1-chloropropene, 1,3-dichloropropene, etc.), one might expect the halogen-metal interconversion reaction to increase in the case of the ethynyl chlorides and the resulting triphenylsilylethynyllithium to compete with triphenylsilyllithium in the coupling reaction with chlorotriphenylsilane:

$$Ph_3SiLi + Cl\text{-}C{\equiv}C\text{-}SiPh_3 \longrightarrow Ph_3SiCl + Li\text{-}C{\equiv}C\text{-}SiPh_3$$

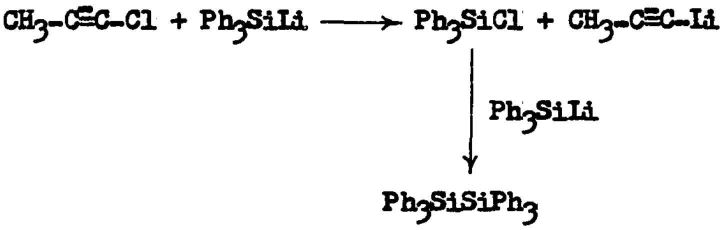
$$Ph_3SiLi + Ph_3SiCl \longrightarrow Ph_3SiSiPh_3$$

$$Ph_3Si-C\equiv C-Li + Ph_3SiCl \longrightarrow Ph_3Si-C\equiv C-SiPh_3$$

The reaction of phenyllithium with 1,2-dichloropropene would be expected to give 1-chloropropyne.[105]



Triphenylsilyllithium was added to a 1:1 mixture of phenyllithium and 1,2-dichloropropene. Color Test I was negative. The occurrence of an immediate reaction was evidenced by the discharge of the color of the triphenylsilyllithium solution. Color Test I became positive after the addition was completed. The products were hexaphenyldisilane (73.9%) and 1-triphenylsilylpropyne (11.7%).



$$CH_3-C\equiv C-Cl + Ph_3SiLi \longrightarrow Ph_3SiCl + CH_3-C\equiv C-Li$$

$$Ph_3SiCl \xrightarrow{Ph_3SiLi} Ph_3SiSiPh_3$$

Trichloroethylene was converted to dichloroacetylene[106] by treatment

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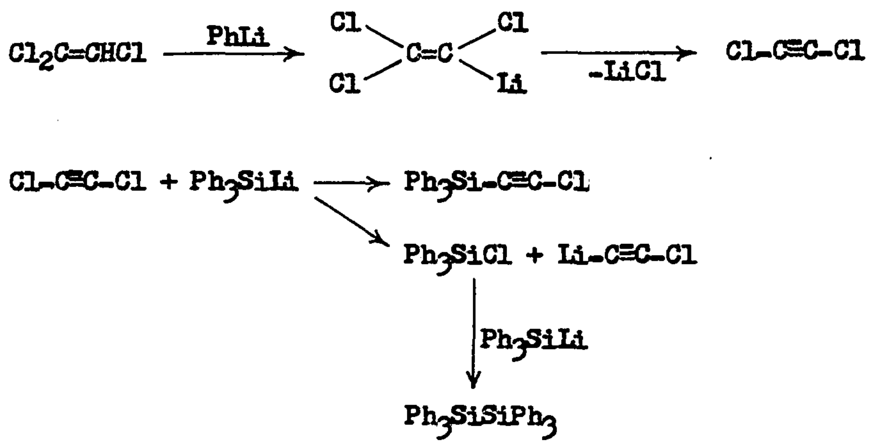
[105] The metalation reaction of organolithium compounds on polychloroethylenes having at least one hydrogen has been known. See, for example, G. H. Viehe, Ber., 92, 1950 (1959).

[106] For the nature of dichloroacetylene in ether, see J. H. Wotiz, F. Huba, and R. Vendley, J. Org. Chem., 26, 1626 (1961); E. Ott, Ber., 75, 1517 (1942).

with an equivalent amount of phenyllithium. The conversion was approximately 90% (see page 63) under the conditions employed. When chlorotriphenylsilane was added, chlorotriphenylsilylacetylene (9.4%) and bis(triphenylsilyl)acetylene (2.8%) were obtained. When triphenylsilyllithium was added, there was obtained hexaphenyldisilane (53.1%), chlorotriphenylsilylacetylene (17.0%), and bis(triphenylsilyl)acetylene (4.2%).



The comparison is by no means quantitative, but one can see the general trend of decreasing yields of hexaphenyldisilane and increasing yields of the coupling products in the series 1-chloropropyne, dichloroacetylene, and chlorotriphenylsilylacetylene (see Table 9).

The reactivities of the ethynyllithium compounds may differ only slightly within the series and would be expected to decrease in the order of $CH_3{-}C{\equiv}C{-}Li > Cl{-}C{\equiv}C{-}Li \sim Ph_3Si{-}C{\equiv}C{-}Li$, since the anion is stabilized by the inductive effect of the chlorine atom in the case of chloroethynyllithium and by the *d*-orbital participation of the silicon

Table 9. Reactions of Ph_3SiLi with ethynyl halides

Compound	$Ph_3SiSiPh_3$	Coupling product
$CH_3-C{\equiv}C-Cl$	73.9	11.7
$Cl-C{\equiv}C-Cl$	53.1	17.0
$Ph_3Si-C{\equiv}C-Cl$	22.7	48.5
$Ph_3Si-C{\equiv}C-Br$	18.4	52.9

atom in the case of triphenylsilylethynyllithium. This order is opposite to the order of the increasing yields of the coupling products. Therefore, it seems likely that the coupling reactions between the ethynyllithium compounds and chlorotriphenylsilane occurred only to a small extent, if at all.

Coupling reactions between organolithium compounds and the ethynyl halides appear to be uncommon. Gilman and Haubein[107] reported that the reactions between bromo- and chlorophenylacetylene and _n_-butyllithium underwent the halogen-metal interconversion reaction, yielding phenylpropiolic acid after carbonation (87 and 20%, respectively). Viehe[36] attempted without success the coupling between dichloroacetylene and propenyl- and phenyllithium.

Yet, the evidence indicates that triphenylsilyllithium couples with

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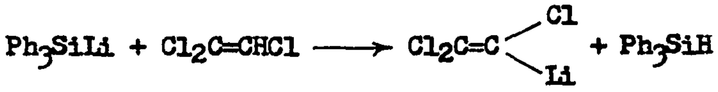
[107] H. Gilman and A. H. Haubein, _J. Am. Chem. Soc._, _67_, 1420 (1945).

the ethynyl halides. Probably the initial step is a nucleophilic addition of triphenylsilyllithium to a triple bond and then subsequently lithium chloride is eliminated. The reaction may, however, be a concerted one.

It was observed that in general the bromides undergo the halogen-metal interconversion reaction far more readily than the chlorides, giving higher yields of hexaphenyldisilane. In view of this generalization, it was surprising that the reaction of bromotriphenylsilylacetylene with triphenylsilyllithium gave only 18.4% of hexaphenyldisilane (see Table 9). The coupling product, bis(triphenylsilyl)acetylene, was obtained in a 52.9% yield.

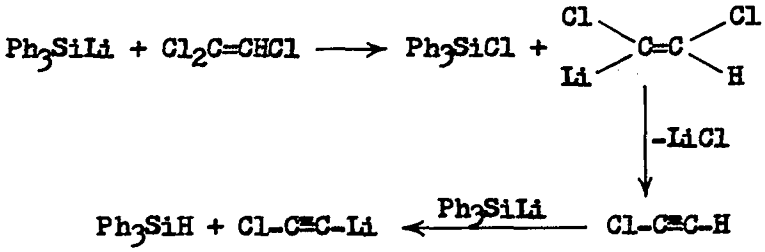
Returning to the original reaction of trichloroethylene with triphenylsilyllithium, the relatively small yield of triphenylsilane may be noted. Triphenylsilane could be formed by two possible reactions:

(1)



$$Ph_3SiLi + Cl_2C{=}CHCl \longrightarrow Cl_2C{=}C(Cl)Li + Ph_3SiH$$

(2)



$$Ph_3SiLi + Cl_2C{=}CHCl \longrightarrow Ph_3SiCl + (Cl)(Li)C{=}C(Cl)(H)$$

$$(Cl)(Li)C{=}C(Cl)(H) \xrightarrow{-LiCl} Cl{-}C{\equiv}C{-}H$$

$$Ph_3SiH + Cl{-}C{\equiv}C{-}Li \xleftarrow{Ph_3SiLi} Cl{-}C{\equiv}C{-}H$$

Both reactions are reasonable and probably are occurring simultaneously, although the reaction (2) may be more favored than the reaction (1).

From reaction (1) dichloroacetylene would be formed. It was shown in the foregoing discussion that triphenylsilyllithium reacted with dichloroacetylene to give chlorotriphenylsilylacetylene, as well as hexaphenyldisilane and chloroethynyllithium. Being a true organolithium compound, chloroethynyllithium would be expected to abstract hydrogen from trichloroethylene, thereby forming dichloroacetylene. Thus, once dichloroacetylene is formed, its concentration can increase without increasing the yield of triphenylsilane.

A possible reaction sequence is summarized on the following page.

2. Preparation of triphenylsilylacetylenes

Bis(triphenylsilyl)acetylene was first prepared by Hartmann and Beermann[108] by the reaction of bromotriphenylsilane with monosodium acetylide in a yield of 58%. The preparation was carried out by the reaction of dilithium acetylide and chlorotriphenylsilane in an ether-THF mixture. In the literature there was found a lone reference which described the preparation of dilithium acetylide from the reaction of phenyllithium and acetylene in ether.[109] When the reaction was carried out in ether alone, the yield of bis(triphenylsilyl)acetylene was 27%, versus 34% reported for the disubstituted derivative. When an ether-THF mixture was used, the yield increased to 41.6%. Moreover, triphenylsilylacetylene was obtained as a by-product in a yield of 17.8%.

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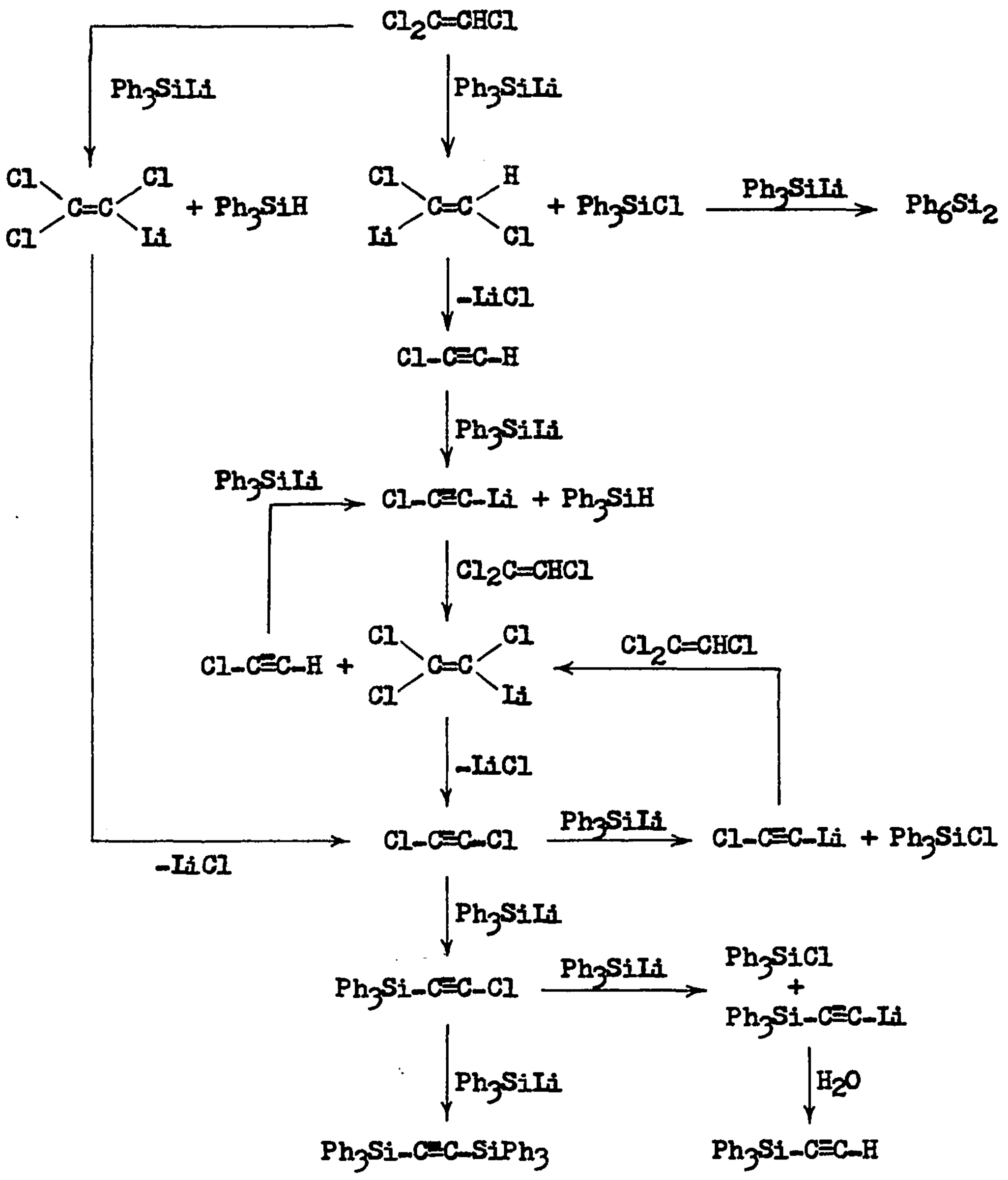
[108] H. Hartmann and C. Beermann, Z. anorg. u. allg. Chem., 276, 20 (1954).

[109] H. H. Inhoffen, H. Pommer, and E. G. Meth, Ann., 565, 45 (1949).

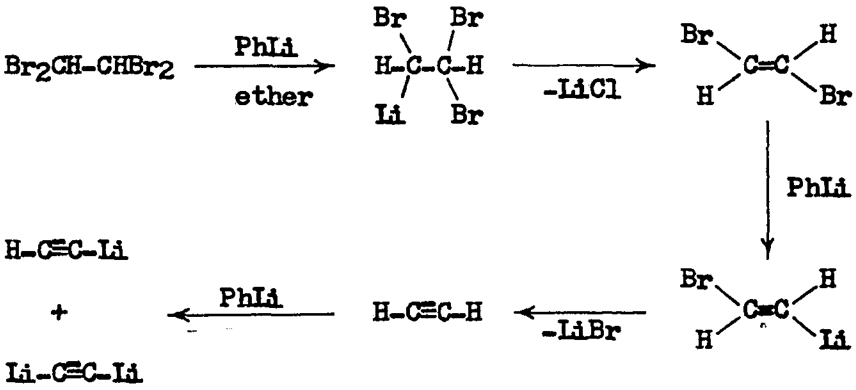

Cl2C=CHCl
Ph3SiLi
Ph3SiLi
Cl Cl C=C Cl Li + Ph3SiH
Cl H C=C Li Cl + Ph3SiCl
Ph3SiLi
Ph6Si2
-LiCl
Cl-C≡C-H
Ph3SiLi
Ph3SiLi
Cl-C≡C-Li + Ph3SiH
Cl2C=CHCl
Cl-C≡C-H +
Cl Cl C=C Cl Li
Cl2C=CHCl
-LiCl
Cl-C≡C-Cl
-LiCl
Ph3SiLi
Cl-C≡C-Li + Ph3SiCl
Ph3SiLi
Ph3Si-C≡C-Cl
Ph3SiLi
Ph3SiCl
+
Ph3Si-C≡C-Li
Ph3SiLi
H2O
Ph3Si-C≡C-SiPh3
Ph3Si-C≡C-H

Chlorotriphenylsilylacetylene was prepared from the reaction of chlorotriphenylsilane with chloroethynyllithium, which was formed from 1,2-dichloroethylene or trichloroethylene and two equivalents of phenyllithium.[105] Higher yields (80-92%) were obtained from 1,2-dichloroethylene than from trichloroethylene (55-71%).

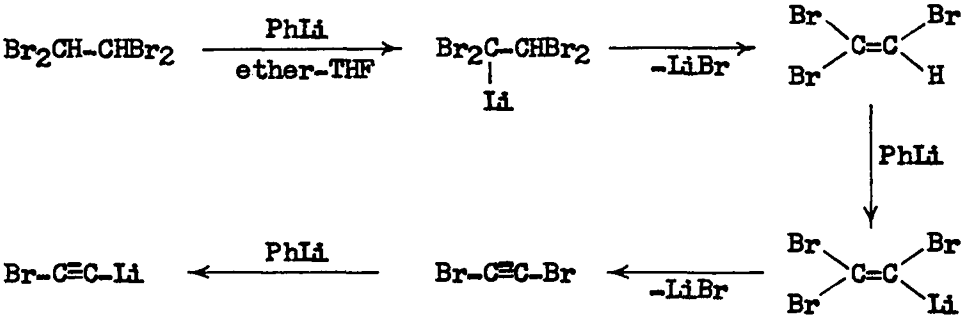
The preparation of bromotriphenylsilylacetylene was quite interesting. Three equivalents of phenyllithium were added to an ether solution of pentabromoethane at -60°. The reaction mixture was allowed to warm to room temperature before chlorotriphenylsilane was added. The yield of bromotriphenylsilylacetylene was 10.5%. When phenyllithium was added to a THF solution of pentabromoethane at -60° and the mixture was allowed to warm up, the solution soon turned black. The product was a black powdery material. Viehe reported that the reaction of trichloroethylene with sodium in liquid ammonia gave a black material.[105] When the mixture was kept at -60° and chlorotriphenylsilane was added at that temperature, bromotriphenylsilylacetylene was obtained in a 26.8% yield.

The solvent effect was striking when tetrabromoethane was used. In ether alone the products were triphenylsilylacetylene (6.2%) and bis(triphenylsilyl)acetylene (38.8%). In an ether-THF mixture, however, bromotriphenylsilylacetylene was obtained in a yield of 35.4%. Small amounts of triphenylsilylacetylene (8.8%) and bis(triphenylsilyl)-acetylene (5.5%) were also isolated.

In ether the halogen-metal interconversion reaction was favored:



In an ether-THF mixture, however, the metalation reaction was facilitated:



3. Cleavage reactions of triphenylsilylacetylenes by organometallic compounds

During the course of the investigation of the halotriphenylsilylacetylene reactions with triphenylsilyllithium, a question was raised as to whether triphenylsilyllithium would cleave the ethynyl group from a silicon atom. Halotriphenylsilylacetylenes are not suitable compounds with which to examine such a possibility because both the cleavage and halogen-metal interconversion reactions give hexaphenyldisilane. For the type of investigation mentioned above bis(triphenylsilyl)acetylene is an ideal compound.

When triphenylsilyllithium was added to an ethereal solution of bis(triphenylsilyl)acetylene at room temperature, an almost immediate precipitation of hexaphenyldisilane occurred. The yields of the cleavage products, hexaphenyldisilane and triphenylsilylacetylene, were 93.1 and 87.1%, respectively.

$$Ph_3Si{-}C{\equiv}C{-}SiPh_3 \xrightarrow{Ph_3SiLi} \xrightarrow{H_2O} Ph_3SiSiPh_3 + Ph_3Si{-}C{\equiv}C{-}H$$

When phenyllithium was added to bis(triphenylsilyl)acetylene, the cleavage reaction occurred and some heat was evolved. Tetraphenylsilane and triphenylsilylacetylene were obtained in yields of 98 and 75.5%, respectively.

The reaction of chlorotriphenylsilylacetylene and phenyllithium gave, however, only 36.1% of tetraphenylsilane. A large amount of polymeric oil was formed.

On the other hand, methyllithium reacted with chlorotriphenylsilylacetylene by a halogen-metal interconversion, yielding 1-triphenylsilylpropyne (54.0%), triphenylsilylacetylene (19.6%), and bis(triphenylsilyl)acetylene (5.7%). The absence of methyltriphenylsilane indicates that no cleavage occurred. 1-triphenylsilylpropyne was probably formed from the coupling reaction of triphenylsilylethynyllithium and methyl chloride, both of which were formed as a result of a halogen-metal interconversion reaction, rather than by the coupling of the original reactants.[36, 107] The ethynyllithium compounds are known to couple quite readily with primary halides.[110] When triphenylsilylethynyllithium was added to methyl iodide, 1-triphenylsilylpropyne was formed in a 77.9% yield. A by-product was bis(triphenylsilyl)acetylene (7.4%).

The formation of bis(triphenylsilyl)acetylene in the foregoing reactions immediately suggested the possibility of the cleavage of an ethynyl group by triphenylsilylethynyllithium. Triphenylsilylacetylene, chlorotriphenylsilylacetylene, and bromotriphenylsilylacetylene were allowed to react with triphenylsilylethynyllithium for 17.5-19 hours. Bis(triphenylsilyl)acetylene was obtained in yields of 33.0, 54.5, and 71.4%, respectively.

$$Ph_3Si\text{-}C{\equiv}C\text{-}X + Ph_3Si\text{-}C{\equiv}C\text{-}Li \longrightarrow Ph_3Si\text{-}C{\equiv}C\text{-}SiPh_3 + X\text{-}C{\equiv}C\text{-}Li$$

$$(X = H,\ Cl,\ Br)$$

Grignard reagents did not cleave triphenylsilylacetylenes under similar conditions. When phenylmagnesium bromide was allowed to react with bis(triphenylsilyl)acetylene for 18 hours, the starting material was recovered in an 87.8% yield. The functional exchange reaction occurred to the extent of almost 40% when chlorotriphenylsilylacetylene was treated with phenylmagnesium bromide under similar conditions. Some biphenyl was also formed; the exact yield, however, could not be determined because of the difficulties of separation.

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[110] For such a coupling reaction, see, for example, M. H. Durand and L. Piaux, Compt. rend., 248, 2763 (1959).

The reaction of methylmagnesium iodide with chlorotriphenylsilylacetylene gave after 5 hours 34.0% of triphenylsilylacetylene, 1.8% of 1-triphenylsilylpropyne, and 53.5% of the starting material.

4. Synthesis of bis(triphenylsilyl)butadiyne

The reaction of triphenylsilyllithium with 1,2-dichloroethylene gave a negative Color Test I even when a 3:1 ratio was used. The products were hexaphenyldisilane (46.4%), triphenylsilane (34.2%), and a compound with a melting range of 182-194°. The infrared spectrum of the latter compound was identical with that of a compound obtained from the reaction of carbon tetrabromide with triphenylsilyllithium. It was long suspected that this compound might be bis(triphenylsilyl)butadiyne. As many of the reaction intermediates were identified and their reactions with organometallic compounds studied, however, such a possibility became remote.

The synthesis of bis(triphenylsilyl)butadiyne was of interest. A reasonable attempt for its synthesis was a coupling reaction of triphenylsilylethynyl Grignard reagent in the presence of some inorganic halides.

The preparation of triphenylsilylethynylmagnesium halide was first investigated. The usual method of replacement of an acetylenic hydrogen by a readily available Grignard reagent was feasible. The synthesis of triphenylsilylacetylene was not, however, as convenient as that of chlorotriphenylsilylacetylene, although a successful preparation of the monomagnesium bromide of acetylene from ethylmagnesium bromide and acetylene in THF has been reported.[111]

On the other hand, high yields of pure chlorotriphenylsilylacetylene can easily be obtained. Thus, the direct preparation of acetylenic Grignard reagents from ethynyl halides, the method which was developed by Normant and Cuvigny,[112] was employed.

A fairly concentrated THF solution of chlorotriphenylsilylacetylene was stirred with magnesium turnings at a temperature around 40-50°. The reaction took place within a short period of time. In the case of bromotriphenylsilylacetylene, heating was not necessary to initiate the reaction. The yield in both cases was around 95% by acid titration.

The use of cobaltous chloride and bromobenzene or ethyl bromide as catalysts[31] failed to give bis(triphenylsilyl)butadiyne. When cupric chloride[34] was used as a catalyst, however, the desired coupling product was obtained in a yield of 45.3%.

E. Reactions of Triphenylsilyllithium with Epihalohydrins and Related Reactions

The reactions of epichlorohydrin with organometallic compounds have been shown to give chlorohydrins or 1,3-disubstituted propan-2-ols.[113, 114]

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[111] E. R. H. Jones, L. Scattebal, and M. C. Whiting, J. Chem. Soc., 1956, 4765.

[112] H. Normant and T. Cuvigny, Bull. soc. chim., 1957, 1447.

[113] H. Gilman, B. Hofferth, and J. B. Honeycutt, J. Am. Chem. Soc., 74, 1594 (1952).

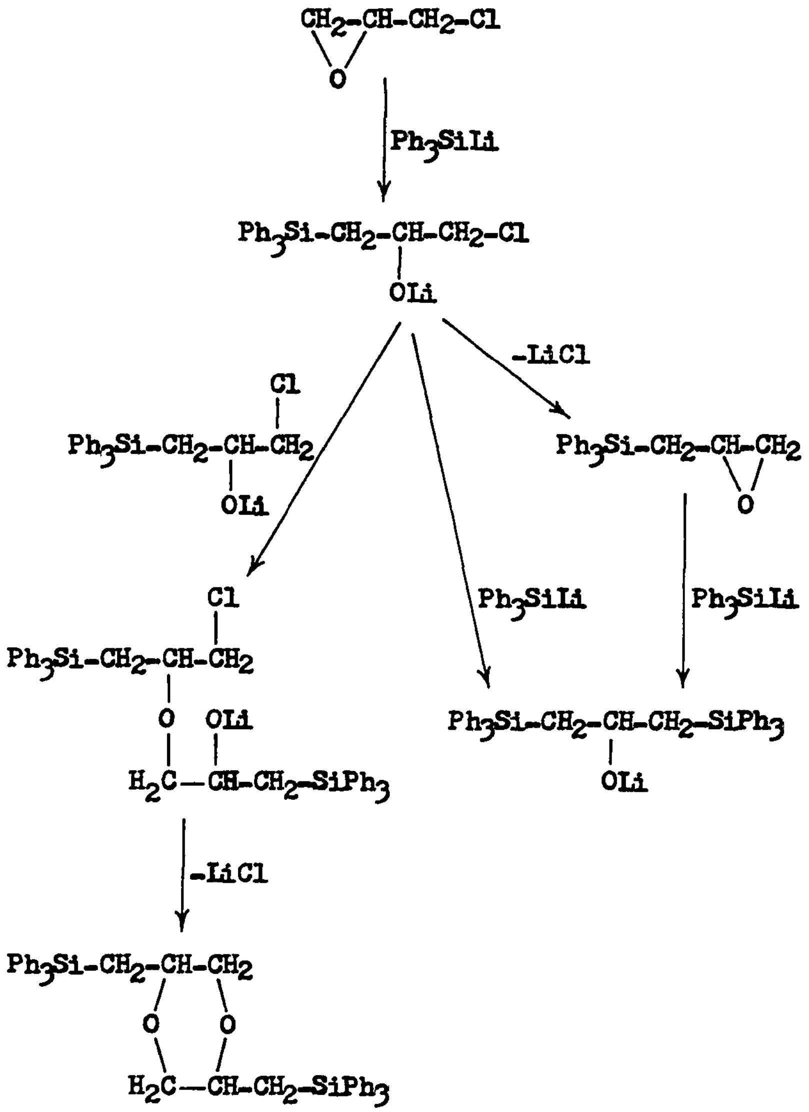
[114] K. Ivanov and G. Vasilev, Compt. rend. acad. bulgare sci., 9, No. 4, 61 (1956).

Triphenylsilyllithium reacted with epichlorohydrin not only in the normal manner, giving alcohol derivatives, but also in unexpected ways, depending on the reaction conditions.

When one equivalent of triphenylsilyllithium was added to epichlorohydrin at -60°, 1-triphenylsilyl-3-chloropropane-2-ol was isolated in a 60.5% yield. When two equivalents of triphenylsilyllithium were used, the product was 1,3-bis(triphenylsilyl)propan-2-ol (43.3%). The second half of the reaction did not occur at -60°, as evidenced by a positive Color Test I. Therefore, the reaction mixture was allowed to warm to room temperature before all of the triphenylsilyllithium solution was added. The second half of the reaction was found to be exothermic at room temperature.

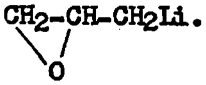
The reaction of an 8:5 ratio of triphenylsilyllithium to epichlorohydrin at room temperature gave 46.7% of 1,3-bis(triphenylsilyl)propan-2-ol and 7.6% of another compound, possibly 1,2-epoxy-3-triphenylsilylpropane. The latter compound, however, was not rigorously identified. Under similar conditions one equivalent of triphenylsilyllithium reacted with epichlorohydrin to give none of the products isolated in the above runs. The compounds obtained were allyltriphenylsilane (8%), triphenylsilanol (8%), and another compound, possibly 2,5-bis(triphenylsilylmethyl)-1,4-dioxane (19%).

Thus it appears that at -60° an epoxide ring can easily be opened by triphenylsilyllithium, but the primary chloride is not reactive enough at that low temperature to be displaced by the anions present. At room temperature, however, a chloride ion seems to be easily removed by an anion. At room temperature the following may be competing reactions:



The reactions of 1-triphenylsilyl-3-chloropropan-2-ol and triphenylsilyllithium at room temperature failed to give any isolable product.

Epibromohydrin reacted with triphenylsilyllithium by halogen-metal interconversion even at -60°. The yields of hexaphenyldisilane varied from 68.6 to 79.0%. No attempt was made to capture 2,3-epoxypropyllithium,



It is interesting that small amounts, 4.3 and 10.9%, of hexaphenyldisilane were obtained when a 2:1 ratio of triphenylsilyllithium to 1,2-epoxy-3-(2-chloroethoxy)propane were allowed to react. The question whether a neighboring ether linkage was responsible for the occurrence of the halogen-metal interconversion reaction was not investigated. The cleavage of the ether linkage occurred when two equivalents of triphenylsilyllithium were added to 1,2-epoxy-3-allyloxypropane, yielding allyltriphenylsilane (15%) and 1,2-dihydroxy-3-triphenylsilylpropane (39%).

V. SUMMARY

The reactions of triphenylsilyllithium with the various halides other than fluorides have been investigated. The reagent was found to undergo halogen-metal interconversion, coupling, metalation, and possibly addition-elimination reactions, depending on the nature of halides. In many cases more than one type of reactions occurred in the system. The halogen-metal interconversion reactions invariably led to the formation of hexaphenyldisilane as a result of the secondary coupling reaction of halotriphenylsilane and triphenylsilyllithium. This secondary reaction was so pronounced that the yield of hexaphenyldisilane could be used as a measure of the extent of halogen-metal interconversion reactions. Only simple primary chlorides did not undergo halogen-metal interconversion. These compounds coupled with triphenylsilyllithium to form tetra-substituted silanes.

The reactions with polyhalomethanes and related compounds seemed to involve carbene intermediates. Many of the products from these reactions could be explained by the reactions of these carbenes and triphenylsilyllithium, forming new organometallic compounds or new triphenylsilyl substituted carbenes.

Alkenyl mono- and polyhalides exhibited even more complex reactions with triphenylsilyllithium. The intermediate compounds, many of which appeared to involve carbenes, underwent further reaction with triphenylsilyllithium. Some of these intermediate compounds were isolated. α-hydrogens on a triphenylsilyl group, as well as on other functional groups such as multiple bonds, were greatly activated and easily metalated by triphenylsilyllithium or by organolithium compounds. In some cases the resulting triphenylsilane coupled with these metalated species.

Haloacetylenes and halotriphenylsilylacetylenes seemed to undergo addition-elimination reactions, resulting in the apparent coupling products, as well as halogen-metal interconversion. An ethynyl group could be cleaved from a silicon atom by organosilyllithium compounds.

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