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Organosilylmetallic compounds and derivatives

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ORGANOSILYLMETALLIC COMPOUNDS AND DERIVATIVES

by

Glen Dale Lichtenwalter

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
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DOCTOR OF PHILOSOPHY

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INTRODUCTION

Research in the field of organosilylmetallic compounds and derivatives, after lying relatively dormant for a period of several years, received impetus through the use of tetrahydrofuran as a solvent. The remarkable influence which tetrahydrofuran as a solvent exerted over certain organometallic reactions^{1,2} prompted this investigation into its possible use as a solvent for organosilylmetallic compounds. Initial successes in this direction^{3,4} added further stimulus to the study. Whereas organosilylmetallic compounds previously had been restricted to the triaryl types, notably triphenylsilylpotassium suspensions in diethyl ether^{5,6} and unstable triphenylsilylmetallic solutions in ethylene glycol dimethyl ether,⁷ the use of tetrahydrofuran as a solvent made possible the preparation of organosilylmetallic compounds containing aliphatic as well as aromatic groups. These tetra-

¹H. Gilman and B. Gaj, J. Org. Chem., 22, 447 (1957).

²H. Gilman and T. S. Soddy, ibid., 22, 1121 (1957).

³H. Gilman and G. D. Lichtenwalter, J. Am. Chem. Soc., 80, 607 (1958).

⁴H. Gilman and G. D. Lichtenwalter, ibid., 80, 608 (1958).

⁵R. A. Benkeser and R. G. Severson, ibid., 73, 1424 (1951).

⁶H. Gilman and T. C. Wu, ibid., 73, 4031 (1951).

⁷A. G. Brook and H. Gilman, ibid., 76, 278 (1954).

hydrofuran solutions were, in addition, fairly stable over extended periods of time, a distinct advantage over the use of ethylene glycol dimethyl ether as a solvent.

The interactions of reactive silicon-metal bonds with a variety of functional groups is potentially the source of new silicon types. These need not be restricted to silicon-carbon bonds. It may be possible to form bonds between silicon and almost any element.

Recent interest in the use of silicon-containing compounds as high temperature lubricants and antioxidants provides for synthetic applications of organosilylmetallic compounds. In particular, it should be possible through the use of organosilylmetallic compounds to synthesize molecules possessing the high degree of dissymmetry necessary for low melting lubricants. In addition, compounds containing silicon bonded to elements less commonly found in organosilicon compounds may show promise as synthetic lubricants.

This investigation has shown that organosilylmetallic compounds react with ketones to give α -silylcarbinols; with aliphatic amines to give silylamines; with aza-aromatic heterocycles to give addition products; with sulfur to give new silicon-sulfur bonds; with metal chlorides to give unstable silicon-metal intermediates; and with disilanes to give cleavage products.

In the Discussion section, an attempt has been made to

draw comparisons between organosilylmetallic and organometallic compounds.

In conclusion it should be pointed out that many promising synthetic applications of organosilylmetallic compounds still remain.

HISTORICAL

In 1849 Frankland⁸ reported the preparation of diethylzinc from the reaction of ethyl iodide with metallic zinc. This early discovery marked the beginning of organometallic chemistry, the synthetic applications of which have since expanded tremendously. Only recently, however, have organosilylmetallic compounds appeared in the literature.

Preparation of Organosilylmetallic Compounds

The work of Kraus

Kraus and Nelson⁹ in 1924 reported the preparation of triethylsilyllithium and triphenylgermyllithium via the cleavage of triethylsilyltriphenylgermane with lithium in ethylamine. Subsequent addition of ammonium bromide gave triethylsilane and triphenylgermane, respectively, identified by their boiling points. From the reaction of triphenylsilane with sodium in liquid ammonia, followed by addition of ammonium bromide, bis(triphenylsilyl)amine was isolated.¹⁰ In this instance, triphenylsilylsodium was indicated as the inter-

⁸E. Frankland, Ann., 71, 213 (1849).

⁹G. A. Kraus and W. K. Nelson, J. Am. Chem. Soc., 56, 195 (1924).

¹⁰H. R. Reynolds, L. A. Bigelow and G. A. Kraus, ibid., 51, 3067 (1929).

mediate. By treatment of bromotriphenylsilane with lithium in ethylamine, a low-boiling compound was isolated¹¹ by distillation. This was described as a solvated free radical, "triphenylsilyl ethylamine". In refluxing ether solution, this free radical supposedly coupled to give hexaphenyldisilane. Treatment of the radical with lithium in ethylamine gave a red solution which was described as containing triphenylsilyllithium.

It has since been shown that organosilylmetallic compounds are instantly ammonolyzed by ammonia,¹² primary amines¹² and secondary amines.^{12,13} Benkeser and co-workers¹³ in an attempt to repeat the work of Kraus,¹¹ found the solvated free radical "triphenylsilyl ethylamine" to be N-ethyl-1,1,1-triphenyl-silylamine. In refluxing ether, this compound did not give hexaphenyldisilane as reported. A red solution did form on treatment of the silylamine with lithium in ethylamine, but this color was attributed to the reduction of the aromatic ring system rather than to the presence of triphenylsilyllithium.

¹¹C. A. Kraus and H. Eatough, *ibid.*, 55, 5008 (1933).

¹²T. C. Wu. "Comparisons of some organic compounds containing group IV-B elements." Unpublished Ph.D. Thesis. Ames, Iowa, Iowa State College Library. 1952.

¹³R. A. Benkeser, R. E. Robinson and H. Landesman, *J. Am. Chem. Soc.*, 74, 5699 (1952).

Triarylsilylmetallic compounds

The first preparation of an authentic triarylsilylmetallic compound was by way of the cleavage of phenylisopropyltriphenylsilane by sodium-potassium alloy in diethyl ether.⁵ Triphenylsilylpotassium, obtained as a suspension, was shown to react with hydrochloric acid to give triphenylsilane, with carbon dioxide to give triphenylsilanecarboxylic acid, with chlorotrimethylsilane to give 1,1,1-trimethyl-2,2,2-triphenyldisilane, and with bromobenzene to give tetraphenylsilane. Triphenylsilanecarboxylic acid was found to decompose at the melting point to give carbon monoxide and triphenylsilanol.

A somewhat superior method for the preparation of triphenylsilylpotassium involves the cleavage of hexaphenyldisilane by sodium-potassium alloy in diethyl ether.⁶ Suspensions of triphenylsilylpotassium prepared in this manner are free from side-products. The somewhat troublesome use of sodium-potassium alloy was partially overcome through the use of mercury to amalgamate the excess alloy, thus rendering it unreactive.¹⁴ Cleavage of hexaphenyldisilane by rubidium and cesium in diethyl ether¹⁴ and by sodium-potassium alloy in di-n-butyl ether⁶ were successful, but attempted cleavage by

¹⁴H. Gilman and T. C. Wu, J. Org. Chem., 18, 753 (1953).

sodium dispersion in either xylene or dioxane⁶ failed. Direct preparation of triphenylsilylpotassium by the reactions of chlorotriphenylsilane,^{6,14} ethoxytriphenylsilane,¹⁴ tetraphenylsilane,¹⁴ or 1,1,1-trimethyl-2,2,2-triphenyldisilane¹⁴ with sodium-potassium alloy in diethyl ether was successful.

It was found possible to eliminate the use of sodium-potassium alloy by employing ethylene glycol dimethyl ether as a solvent for cleavages of hexaphenyldisilane with lithium, sodium or potassium.⁷ Solutions of triphenylsilylmetallic compounds were obtained in this manner, an advantage over the suspensions obtained in diethyl ether. These solutions were, however, unstable with time.

Both the advantages of stability and solubility for triarylsilylmetallic compounds were realized through the use of tetrahydrofuran as a solvent.³ Solutions of triphenylsilyllithium prepared by cleavage of hexaphenyldisilane with lithium in this solvent were found to be fairly stable with time, a distinct advantage over the use of ethylene glycol dimethyl ether as a solvent.

Organosilylmetallic compounds containing alkyl and aryl groups

Through the use of tetrahydrofuran as a solvent,³ it was found possible to obtain methyldiphenylsilyllithium and dimethylphenylsilyllithium by lithium cleavages of the corre-

sponding symmetrical disilanes. Previously, methyldiphenylsilylpotassium was prepared by cleavage of 1,2-dimethyl-1,1,2,2-tetraphenyldisilane with sodium-potassium alloy in diethyl ether.¹⁵ Addition of bromobenzene gave methyltriphenylsilane in only four percent yield. In contrast, dimethylphenylsilylpotassium was not prepared successfully by cleavage of 1,1,2,2-tetramethyl-1,2-dipenyldisilane with sodium-potassium alloy.¹⁶

Trialkylsilylmetallic compounds

Numerous attempts have been made to synthesize trialkylsilylmetallic compounds. Success has been limited since no stable solutions of trialkylsilylmetallic compounds useful for synthetic purposes have been prepared.

Reactions of triethylsilane with alkylolithium compounds gave coupling products^{17,18} rather than the desired triethylsilyllithium. Attempted cleavages of hexaethyldisilane by sodium-potassium alloy in diethyl ether¹⁵ or lithium in tetra-

¹⁵H. Gilman, R. K. Ingham and A. G. Smith, ibid., 18, 1743 (1953).

¹⁶A. G. Smith. "Some cleavage reactions of alkyl and aryl silanes." Unpublished M.S. Thesis. Ames, Iowa, Iowa State College Library. 1953.

¹⁷H. Gilman and S. P. Massie, J. Am. Chem. Soc., 68, 1128 (1946).

¹⁸R. N. Meals, ibid., 68, 1880 (1946).

hydrofuran¹⁹ were unsuccessful. A low yield of trimethylphenylsilane was isolated from the cleavage of 1,1,1-trimethyl-2,2,2-triphenyldisilane by sodium-potassium alloy in diethyl ether,¹⁵ followed by addition of bromobenzene.

Cleavage of 1,1,1-triethyl-2,2,2-triphenyldisilane by lithium in tetrahydrofuran, followed by acid hydrolysis, gave rise to triethylsilane (11 percent), hexaethyldisilane (14 percent),²⁰ and triphenylsilane (92 percent), clear evidence for the formation of triethylsilyllithium. Formation of hexaethyldisilane in this reaction is through the cleavage of 1,1,1-triethyl-2,2,2-triphenyldisilane by triethylsilyllithium, with the accompanying formation of triphenylsilyllithium.

Kraus and Nelson⁹ observed no reaction between triethylphenylsilane and sodium in liquid ammonia. Benkeser and Severson⁵ reported no reaction between phenylisopropyltrimethylsilane and sodium-potassium alloy in diethyl ether.

Organosilylmetallic compounds containing more than one silicon atom

An early attempt to synthesize pentaphenyldisilanyl-

¹⁹M. B. Hughes. "Some correlations between organosilicon and organogermanium compounds." Unpublished Ph.D. Thesis. Ames, Iowa, Iowa State College Library. 1958.

²⁰D. Wittenberg, Chemistry Dept., Iowa State College, Ames, Iowa. Private communication concerning the cleavage of 1,1,1-triethyl-2,2,2-triphenyldisilane by lithium in tetrahydrofuran. 1958.

lithium from chloropentaphenyldisilane and lithium in refluxing ether or di-n-butyl ether gave no apparent reaction.¹²

Cleavage of octaphenyltrisilane by lithium in tetrahydrofuran²¹ produces pentaphenyldisilanyl lithium and triphenylsilyllithium, identified, after acid hydrolysis, as pentaphenyldisilane and triphenylsilane, respectively. These two compounds, in addition to heptaphenyltrisilanyl lithium, were formed by the cleavage of decaphenyltetrasilane with lithium in tetrahydrofuran. It is noteworthy that apparently no diphenylsilyldilithium was formed in these cleavages since diphenylsilane was not isolated after acid hydrolysis.

Reactions of Organosilylmetallic Compounds

With ketones

Shortly following the synthesis of triphenylsilylpotassium from the cleavage of hexaphenyldisilane with sodium-potassium alloy in diethyl ether,⁶ the addition of this silylmetallic compound to benzophenone was investigated.²² Addition occurred, but following hydrolysis the product isolated was benzhydryloxytriphenylsilane rather than triphenyl-

²¹D. Wittenberg and M. V. George, Chemistry Dept., Iowa State College, Ames, Iowa. Private communication concerning the cleavage of polysilanes by lithium in tetrahydrofuran. 1958.

²²H. Gilman and T. C. Wu, J. Am. Chem. Soc., 75, 2935 (1953).

silyldiphenylcarbinol. Since it did not seem likely that inverse addition had taken place, it was postulated that normal addition had occurred, followed by a rearrangement. Triphenylsilyllithium, methylphenylsilyllithium, and dimethylphenylsilyllithium in tetrahydrofuran³ solution were found to react with benzophenone to give the corresponding alkoxysilanes instead of carbinols.⁴

Support for the rearrangement theory²² for the formation of alkoxysilanes from the reactions of silylmetallic compounds with benzophenone was obtained by Brook,²³ who succeeded in preparing triphenylsilyldiphenylcarbinol and showed that under the mildest basic conditions this compound rearranges to benzhydryloxytriphenylsilane.

From the reactions of triphenylsilylpotassium with aliphatic ketones, no pure products were isolated.¹² However, triphenylsilyllithium in tetrahydrofuran was shown to undergo addition to aliphatic ketones to give alpha-silylcarbinols.²⁴ Thus, triphenylsilyllithium added normally to acetone, cyclohexanone, 2-nonadecanone, 3-octadecanone, 9-nonadecanone, 8-pentadecanone and 12-tricosanone. These alpha-silylcarbinols derived from aliphatic ketones failed to undergo rearrangement

²³A. G. Brook, *ibid.*, 80, 1886 (1958).

²⁴H. Gilman and G. D. Lichtenwalter, *ibid.*, 80, 2680 (1958).

to the isomeric alkoxy silanes, even under strongly basic conditions.

With aldehydes

From the reaction of triphenylsilylpotassium with formaldehyde, triphenylsilylmethanol was obtained²⁵ in a low yield.

In connection with a proof of structure, it was shown²⁶ that triphenylsilyllithium³ in tetrahydrofuran solution adds normally to acetaldehyde to give 1-(triphenylsilyl)-ethanol.

In a rather complex series of reactions, it was shown²⁷ that triphenylsilyllithium undergoes normal addition to benzaldehyde, followed by rearrangement. Following hydrolysis, the products isolated were benzoxytriphenylsilane, hexaphenyldisilane and 1,2-dihydroxy-1,2-diphenylethane.

With acid chlorides

Recently, Brook²⁸ reported the preparation of triphenylsilylphenyl ketone from the reaction of triphenylsilylpotas-

²⁵H. Gilman and T. C. Wu, ibid., 76, 2502 (1954).

²⁶D. Wittenberg and H. Gilman, ibid., in press (ca. 1958).

²⁷D. Wittenberg and H. Gilman, ibid., in press (ca. 1958).

²⁸A. G. Brook, ibid., 79, 4373 (1957).

sium with benzoyl chloride. This alpha-silyl ketone was found to be extremely sensitive to hydrolysis with aqueous base to give triphenylsilanol and benzaldehyde.

From the reaction of triphenylsilyllithium with acetyl chloride,²⁶ a rather complex transformation occurred, from which the products isolated were acetyltriphenylsilane and 1,1-bis(triphenylsilyl)-ethanol. The latter compound was found to undergo rearrangement in the presence of base to triphenyl-1-(triphenylsiloxyethyl)-silane in a manner similar to the rearrangement of triphenylsilyldiphenylcarbinol to benzhydryloxytriphenylsilane.²³

With carbon dioxide (carbonation)

The first paper describing the preparation of triphenylsilylpotassium⁵ contains an account of its reaction with carbon dioxide. The acid obtained was a slightly impure sample of triphenylsilanecarboxylic acid, which, unlike the analogous triphenylacetic acid, decomposes at the melting point to give carbon monoxide and triphenylsilanol.

In a subsequent paper,²⁹ experimental conditions were described for obtaining triphenylsilanecarboxylic acid in good yields, free of impurities. The technique requires rapid acidification of the aqueous basic extract since the potassium

²⁹A. G. Brook and H. Gilman, ibid., 77, 2322 (1955).

salt of triphenylsilanecarboxylic acid undergoes rapid decomposition in the presence of base. Indeed, it was found that the acid itself undergoes slow decomposition to carbon monoxide and triphenylsilanol over extended periods of time. Triphenylsilanecarboxylic acid is readily converted in good yields to methyl triphenylsilanecarboxylate through the use of diazomethane.²⁹ Brook and Mauris³⁰ reported the preparation of some silyl esters by this technique in connection with an investigation of their rearrangements.

With olefins

1-Triphenylsilyl-1,2-diphenylethane was isolated³¹ from the reaction of triphenylsilylpotassium with trans-stilbene. The same olefin gave 1,2-bis(triphenylsilyl)-1,2-diphenylethane and 1-triphenylsilyl-1,2,3,4-tetraphenylbutane by reaction with triphenylsilyllithium in ethylene glycol dimethyl ether.³²

From the reaction of either triphenylsilyllithium in tetrahydrofuran or triphenylsilylpotassium in diethyl ether with 1,1-diphenylethylene, 1-triphenylsilyl-2,2-diphenyl-

³⁰A. G. Brook and R. J. Mauris, ibid., 79, 971 (1957).

³¹H. Gilman and T. C. Wu, ibid., 75, 234 (1953).

³²A. G. Brook, K. M. Tai and H. Gilman, ibid., 77, 6219 (1955).

ethane³³ was obtained. Attempts to add triphenylsilylpotassium to some other olefins failed.

With compounds containing the
azo and azomethine linkages

From the reaction of azobenzene with triphenylsilylpotassium in diethyl ether or triphenylsilyllithium in tetrahydrofuran, addition to the azo linkage takes place to give, after hydrolysis, N,N'-diphenyl-N-(triphenylsilyl)-hydrazine,³⁴ the structure of which was assigned on the basis of an alternate synthesis. Addition of lithium to azobenzene gave N,N'-dilithio-N,N'-diphenylhydrazine, which, by coupling with chlorotriphenylsilane, gave a mixture of N,N'-diphenyl-N-(triphenylsilyl)-hydrazine and N,N'-diphenyl-N,N'-bis(triphenylsilyl)-hydrazine. Benzophenone anil³³ reacted with either triphenylsilyllithium in tetrahydrofuran³⁴ or triphenylsilylpotassium in diethyl ether³³ to give N-diphenylmethyl-N-phenyl-1,1,1-triphenylsilylamine. It was postulated that this silylamine may have formed as the result of a normal addition of the silylmetallic compounds to the azomethine linkage, followed by a rearrangement in a manner similar to

³³T. C. Wu, D. Wittenberg and H. Gilman, ibid., in press (ca. 1958).

³⁴D. Wittenberg, M. V. George, T. C. Wu, D. H. Miles and H. Gilman, ibid., in press (ca. 1958).

the rearrangement which occurred by addition of triphenylsilylpotassium²² or triphenylsilyllithium⁴ to benzophenone.

As part of a study concerned with the addition of silyl-metallic compounds to aza-aromatic heterocycles, the cleavage of hexaphenyldisilane by lithium in pyridine was carried out.³⁵ In situ attack of the triphenylsilyllithium at the 4-position on the pyridine nucleus occurred, in contrast to the usual attack of alkyl- and aryllithium compounds at the 2-position.³⁶ After hydrolysis, triphenyl-4-(1,4-dihydropyridyl)-silane was obtained in 63 percent yield. Oxidation with nitrobenzene gave triphenyl-4-pyridylsilane.

Since 4-bromopyridine was not available as a starting material, triphenyl-4-(1,4-dihydropyridyl)-silane was not prepared by reaction of 4-pyridyllithium and chlorotriphenylsilane. However, the product isolated from triphenylsilyllithium and pyridine, followed by oxidation, was shown to be different from triphenyl-2-pyridylsilane, prepared by reaction of 2-pyridyllithium and chlorotriphenylsilane.

Attempts to add triphenylsilylpotassium to a variety of aza-aromatic heterocycles gave no pure products.³⁷

³⁵D. Wittenberg and H. Gilman, Chemistry and Industry, 390 (1958).

³⁶K. Ziegler and H. Zieser, Ber., 63, 1847 (1930); Ann., 485, 174 (1931).

³⁷J. B. Honeycutt. "Preparation of some nitrogen-containing organosilicon compounds." Unpublished M.S. Thesis. Ames, Iowa, Iowa State College Library. 1953.

With ethers

While it was demonstrated⁷ that triphenylsilylalkali metal compounds decompose rapidly in ethylene glycol dimethyl ether, no attempt was made to identify any of the products. Neither was an attempt made to identify the products from the decomposition of triphenylsilyllithium in refluxing tetrahydrofuran.³

Later, Gorsich³⁸ obtained 4-(triphenylsilyl)-butanol in 18 percent yield by refluxing a solution of triphenylsilyllithium in tetrahydrofuran for a period of 2.7 days. By heating a solution of triphenylsilyllithium in tetrahydrofuran in a sealed tube for three hours at 125°, 4-(triphenylsilyl)-butanol was obtained³⁹ in 71 percent yield.

A rather extensive study of the cleavage of ethers by silylmetallic compounds⁴⁰ has been carried out recently. Using the sealed tube technique,³⁹ 4-(methyldiphenylsilyl)-butanol was obtained from the cleavage of tetrahydrofuran by methyldiphenylsilyllithium. Triphenylsilyllithium in tetrahydrofuran solution reacted instantly with trimethylene oxide

³⁸R. D. Gorsich, Chemistry Dept., Iowa State College, Ames, Iowa. Private communication. 1957.

³⁹D. Wittenberg and H. Gilman, J. Am. Chem. Soc., **80**, 2677 (1958).

⁴⁰D. Wittenberg, D. Aoki and H. Gilman, ibid., in press (ca. 1958).

to give, after hydrolysis, 3-(triphenylsilyl)-propanol in 77 percent yield. A solution of triphenylsilyllithium in tetrahydrofuran, prepared by way of the cleavage of hexaphenyldisilane with lithium in this solvent, was heated in a sealed tube for 10 hours at 125°. Since the triphenylsilyllithium was not used up, as evidenced by a positive Color Test I,⁴¹ the solution was heated for another 40 hours at 200-220°. Only high melting, insoluble, resinous material was isolated. Cleavage of hexaphenyldisilane by lithium in dioxane gave, after hydrolysis, ethylene-bis(triphenylsilane) (10 percent), ethyltriphenylsilane (1 percent) and tetraphenylsilane (4 percent). When the solvent was removed from a solution of triphenylsilyllithium in tetrahydrofuran and replaced by dioxane and heated, the products isolated were ethylene-bis(triphenylsilane) (14 percent), 4-(triphenylsilyl)-butanol (5 percent), and tetraphenylsilane (4 percent). A solution of triphenylsilyllithium in ethylene glycol dimethyl ether was allowed to decompose to give methyltriphenylsilane (34 percent). From the cleavage of methyl benzyl ether by triphenylsilyllithium, the products isolated were tetraphenylsilane, 1-phenylethanol, triphenylsilane, benzyltriphenylsilane and 4-(triphenylsilyl)-butanol. With 1,4-dihydronaphthalene-1,4-endoxide, triphenylsilyllithium gave naphthalene (41 percent),

⁴¹H. Gilman and F. Schulze, *ibid.*, 47, 2002 (1925).

2-naphthyltriphenylsilane (10 percent) and triphenylsilanol (18 percent). Triphenylsilyllithium metalated diphenyl ether without cleavage (refer to the section on Metalation reactions).

With epoxides

Although Grignard reagents react with epoxides to give, in general, a mixture of isomers,⁴² organolithium react⁴³ more selectively to give beta-substituted carbinols.

Organosilylmetallic compounds have been shown recently to cleave epoxides to give beta-substituted carbinols⁴⁴ in a manner analogous to the above-mentioned organolithium compounds. From the interaction of triphenylsilyllithium in tetrahydrofuran solution with ethylene oxide and propylene oxide, the products isolated were 2-(triphenylsilyl)-ethanol (85 percent) and 1-(triphenylsilyl)-propane-2-ol (69 percent), respectively. With styrene oxide and triphenylsilyllithium, a 56 percent yield of 1-phenyl-2-(triphenylsilyl)-ethanol was obtained, which by dehydration with phosphorous pentoxide gave triphenyl-beta-styrylsilane (23 percent). Similarly, methyl-

⁴²N. G. Gaylord and E. I. Becker, Chem. Revs., 49, 413 (1951).

⁴³S. J. Cristol, J. R. Douglas and J. S. Meek, J. Am. Chem. Soc., 73, 816 (1951).

⁴⁴H. Gilman, D. Aoki and D. Wittenberg, ibid., in press (ca. 1958).

diphenylsilyllithium reacted with styrene oxide to give 1-phenyl-2-(methyldiphenylsilyl)-ethanol (48 percent). With cyclohexene oxide, triphenylsilyllithium and methyldiphenylsilyllithium gave rise to 2-(triphenylsilyl)-cyclohexanol (69 percent) and 2-(methyldiphenylsilyl)-cyclohexanol (72 percent), respectively. 2-(Triphenylsilyl)-cyclohexanol, by dehydration with phosphorous pentoxide, gave 1-cyclohexenyltriphenylsilane in 33 percent yield. This compound was synthesized⁴⁴ by the reaction of chlorotriphenylsilane with 1-cyclohexenyllithium.⁴⁵ With epibromohydrin,⁴⁴ triphenylsilyllithium gave hexaphenyldisilane instead of the expected coupling product (refer to the section on halogen-metal interconversion reactions). No hexaphenyldisilane was isolated from the reaction of triphenylsilyllithium with epichlorohydrin. Instead, a compound believed to be 2,5-bis(triphenylsilylmethyl)-1,4-dioxane was isolated.

In metalation reactions

Silylmetallic compounds metalate effectively only those compounds which have fairly acidic hydrogen atoms. Triphenylmethane⁴⁶ and fluorene,³⁸ for instance, are readily metalated

⁴⁵E. A. Braud and J. A. Coles, J. Chem. Soc., 2014 (1950).

⁴⁶A. G. Brook and H. Gilman, J. Am. Chem. Soc., 76, 2338 (1954).

by triphenylsilyllithium to give the metal salts, which by carbonation give triphenylacetic acid and 9-carboxyfluorene, respectively.

Diphenyl ether⁴⁴ and dibenzofuran³⁸ are metalated by triphenylsilyllithium in tetrahydrofuran to give, after carbonation, very low yields of 2,2'-dicarboxydiphenyl ether and 4-carboxydibenzofuran, respectively.

With triphenylsilane

A series of three papers describing the formation of tetraphenylsilane from the reactions of triphenylsilylmetallic compounds with triphenylsilane have appeared in the literature.

In the first of these, the formation of tetraphenylsilane⁴⁷ from the reactions of triphenylsilylpotassium with various alcohols was described. Support for the proposal that the formation of tetraphenylsilane in these reactions probably occurred through the reaction of triphenylsilylpotassium with triphenylsilane was furnished⁴⁸ by allowing triphenylsilylpotassium to react with preformed triphenylsilane. Tetraphenylsilane was isolated along with polymeric material of unknown nature. In an attempt to elucidate the

⁴⁷H. Gilman and T. C. Wu, ibid., 75, 2509 (1953).

⁴⁸A. G. Brook and H. Gilman, ibid., 76, 2333 (1954).

mechanism of this reaction, triphenylsilylpotassium was allowed to react with tri-p-tolylsilane. An equilibrium is established in which triphenylsilane and tri-p-tolylpotassium are formed, as evidenced by the formation of such products as tetraphenylsilane and phenyltri-p-tolylsilane.

In the third paper of this series,⁴⁶ the reaction of triphenylsilylpotassium with triphenylmethane gave tetraphenylsilane and triphenylmethylpotassium. Here again, triphenylsilane is presumably the intermediate in the formation of tetraphenylsilane.

In halogen-metal interconversion reactions

Incidental to the preparation of triphenylmethyltriphenylsilane⁴⁹ (refer to the section on analogs of hexaphenylethane), it was found that the interaction of triphenylsilylpotassium with chlorotriphenylmethane, followed by hydrolysis, gave, instead of the expected coupling product, a mixture containing hexaphenyldisilane and bis-triphenylmethyl peroxide. These results were interpreted as indicating that a halogen-metal interconversion reaction had taken place to give chlorotriphenylsilane and triphenylmethylpotassium. Coupling reactions between chlorotriphenylsilane and triphenylsilylpotassium to give hexaphenyldisilane and between triphenyl-

⁴⁹A. G. Brook, H. Gilman and L. S. Miller, ibid., 75, 4759 (1953).

methylpotassium and chlorotriphenylmethane to give hexaphenylethane (identified as the peroxide) were postulated.

Brook and Wolfe⁵⁰ have shown that the reaction of triphenylsilylpotassium with bromobenzene gave, in addition to the expected tetraphenylsilane, small amounts of hexaphenyl-disilane and biphenyl. The results were interpreted as meaning that a halogen-metal interconversion reaction had occurred to give bromotriphenylsilane and phenylpotassium.

The products isolated from the reactions of dimethylphenylsilyllithium and methyldiphenylsilyllithium with chlorotriphenylsilane³ were interpreted as having arisen via a halogen-metal interconversion reaction. However, another interpretation has now been worked out (refer to the Experimental and Discussion sections dealing with the cleavages of disilanes by silylmetallic compounds), which fits the experimental data more closely than the explanation based on a halogen-metal interconversion reaction.

Recently, Aoki and Dappen⁵¹ have demonstrated that halogen-metal interconversion is the predominant reaction between triphenylsilyllithium and alkyl and aryl bromides. The interaction of triphenylsilyllithium and n-butyl bromide gives

⁵⁰A. G. Brook and S. Wolfe, ibid., 79, 1431 (1957).

⁵¹D. Aoki and G. Dappen, Chemistry Dept., Iowa State College, Ames, Iowa. Private communication on halogen-metal interconversion reactions involving silylmetallic compounds. 1958.

hexaphenyldisilane in 80 percent yield and only a small amount of n-butyltriphenylsilane. In a like manner, hexaphenyldisilane was obtained as the main product from the reaction of triphenylsilyllithium and bromobenzene. Epibromohydrin reacts with triphenylsilyllithium to give hexaphenyldisilane⁴⁴ (refer to the Historical section dealing with the reactions of silylmetallic compounds with epoxides). Bromotriphenylsilane is apparently the intermediate in these reactions, which by coupling with triphenylsilyllithium gives hexaphenyldisilane.

n-Butyl chloride and allyl chloride gave only coupling products with triphenylsilyllithium. None of the easily detected hexaphenyldisilane was formed.

Since hexaphenyldisilane is the main product from the reaction of triphenylsilyllithium with bromobenzene in tetrahydrofuran⁵¹ and is formed in only small amounts from the reaction of triphenylsilylpotassium with bromobenzene in diethyl ether,⁵⁰ it appears that tetrahydrofuran as a solvent is more conducive to halogen-metal interconversion reactions than is diethyl ether.

In coupling reactions

Group IV-B analogs of hexaphenylethane. In the preparation of Group IV-B analogs of hexaphenylethane, coupling reactions involving silylmetallic compounds have been employed.

Triphenylmethyltriphenylsilane⁴⁹ is not formed cleanly from the reaction of triphenylsilylpotassium with chlorotriphenylmethane (refer to the section on halogen-metal interconversion reactions), but good yields of this compound were obtained from the interaction of triphenylmethylsodium with chlorotriphenylsilane.⁴⁹

Since hexaphenyldisilane is readily prepared^{52, 53} by the coupling of chlorotriphenylsilane with sodium in refluxing xylene, coupling reactions between triphenylsilylmetallic compounds and chlorotriphenylsilane to give this compound have been of little synthetic value. These reactions occur, however, with remarkable ease. Triphenylsilyllithium and chlorotriphenylsilane react⁵⁴ instantly at -70° in tetrahydrofuran to give hexaphenyldisilane in 88 percent yield.

Triphenylsilyltriphenylgermane was prepared⁵⁵ from the reactions of chloro- and bromotriphenylgermane with triphenylsilylpotassium. Attempts to prepare this compound from the reaction of triphenylgermylpotassium with chlorotriphenyl-

⁵²W. Schlenk, J. Renning and G. Racky, Ber., 44, 1178 (1911).

⁵³H. Gilman and G. E. Dunn, J. Am. Chem. Soc., 73, 5077 (1951).

⁵⁴See the Experimental section on miscellaneous reactions.

⁵⁵H. Gilman and C. W. Gerow, J. Am. Chem. Soc., 78, 5823 (1956).

silane gave mixtures of compounds which were not separated.

Triphenylsilyltriphenyltin was prepared successfully from either the reaction of triphenyltinlithium⁵⁶ with chlorotriphenylsilane or chlorotriphenyltin with triphenylsilylpotassium.¹⁴

Triphenylsilyltriphenyllead has not as yet been described.

Formation of polysilanes. The preparation of compounds containing two or more silicon atoms bonded together in a molecule is included in this section.

1,1,1-Trimethyl-2,2,2-triphenyldisilane has been prepared by the reactions of triphenylsilylpotassium,^{5,6} -lithium,^{3,7} -rubidium and -cesium¹⁴ with chlorotrimethylsilane. Similarly, 1,1,1-triethyl-2,2,2-triphenyldisilane has been prepared from triphenylsilylpotassium and chlorotriethylsilane.^{5,57}

A group of disilanes containing phenyl and p-tolyl groups has been synthesized⁵⁸ by coupling reactions involving silyl-metallic compounds.

Partially chlorinated disilanes have been prepared from

⁵⁶H. Gilman and S. D. Rosenberg, *ibid.*, 74, 531 (1952).

⁵⁷R. A. Benkeser, H. Landesman and D. J. Foster, *ibid.*, 74, 648 (1952).

⁵⁸H. Gilman and T. C. Wu, *ibid.*, 75, 3762 (1953).

reactions involving triphenylsilylpotassium.⁵⁹ From the reaction of triphenylsilylpotassium with one equivalent of dichlorodiphenylsilane, chloropentaphenyldisilane was obtained. From the reactions of one mole of silicon tetrachloride or one mole of trichlorophenylsilane with one mole of triphenylsilylpotassium, 1,1,1-trichloro-2,2,2-triphenyldisilane and 1,1-dichloro-1,2,2,2-tetraphenyldisilane, respectively, were isolated.⁵⁸

From the reaction of triphenylsilylpotassium in diethyl ether with one half equivalent of dichlorodiphenylsilane, octaphenyltrisilane was isolated.⁵⁹ Decaphenyltetrasilane was obtained by the action of sodium on chloropentaphenyldisilane in refluxing xylene.^{12,60}

With alkyl, aryl and aralkyl halides. Coupling reactions have been observed between triphenylsilylpotassium and bromobenzene,^{5,6,14,15,50,57} chloro- and fluorobenzene,¹⁴ benzyl chloride,¹⁴ *o*-bromotoluene and *o*-iodotoluene.¹⁴ Coupling reactions have also been observed between alkyl chlorides and triphenylsilyllithium,⁵¹ and, to a lesser extent, between alkyl bromides and triphenylsilyllithium⁵¹ (refer to the section on halogen-metal interconversion reactions).

⁵⁹H. Gilman, T. C. Wu, H. A. Hartzfeld, G. A. Guter, A. G. Smith, J. J. Goodman and S. H. Eidt, *ibid.*, 74, 561 (1952).

⁶⁰H. A. Hartzfeld, Chemistry Dept., Iowa State College, Ames, Iowa. Private communication to T. C. Wu. 1952.

With diphenyl sulfone and diphenyl sulfide

Both triphenylsilylpotassium and triphenylsilyllithium react with diphenyl sulfone to give tetraphenylsilane.⁶¹ Study of the reaction of triphenylsilylpotassium with diphenyl sulfone was abandoned in favor of the reaction between triphenylsilyllithium and diphenyl sulfone. It was reasoned that the formation of tetraphenylsilane could proceed through an initial metalation of diphenyl sulfone to give triphenylsilane. The reaction of triphenylsilane with triphenylsilylpotassium is known to occur fairly rapidly to give tetraphenylsilane.⁴⁸ The corresponding reaction of triphenylsilyllithium with triphenylsilane has, however, been shown to occur sluggishly.⁶²

A series of three papers^{57,63,64} has been published which describe the reactions of phenylsilicon hydrides with sodium-potassium alloy^{57,63} and with sodium in refluxing toluene.⁶⁴

⁶¹D. Wittenberg, T. C. Wu and H. Gilman, J. Org. Chem., in press (ca. 1958).

⁶²R. D. Gorsich. "Some cyclic organosilicon compounds and derivatives." Unpublished Ph.D. Thesis. Ames, Iowa, Iowa State College Library. 1957.

⁶³R. A. Benkeser and D. J. Foster, J. Am. Chem. Soc., 74, 4200 (1952).

⁶⁴R. A. Benkeser and D. J. Foster, ibid., 75, 5314 (1952).

These reactions give tetraphenylsilane and may involve the intermediate formation of silylmetallic compounds.

The products isolated from the reaction of triphenylsilyllithium with diphenyl sulfone⁶¹ vary considerably with the experimental conditions. At room temperature, the reactants in a 1:1 mole ratio give tetraphenylsilane (50 percent) and benzenesulfinic acid, while at -35° , followed by carbonation, the products isolated were benzoic acid (43 percent), triphenylsilanol (56 percent), benzenesulfinic acid and only a trace of tetraphenylsilane. When two or three moles of triphenylsilyllithium were reacted with one mole of diphenyl sulfone, a small amount of hexaphenyldisilane was isolated, along with tetraphenylsilane and m-phenylene-bis-(triphenylsilane). The mode of formation of the last mentioned compound is unknown.

Hydrolysis

The products formed from the hydrolysis of silylmetallic compounds depend on the hydrolytic conditions employed.

Benkeser and Severson⁵ have shown that hydrolysis of triphenylsilylpotassium with hydrochloric acid gives triphenylsilane. Only triphenylsilanol was obtained from the hydrolysis of triphenylsilylpotassium with water.¹⁴

It seems certain that the first step in the hydrolysis of a silylmetallic compound involves the formation of the

corresponding silicon hydride. If water is used for the hydrolysis, the metal hydroxide is formed, which in turn converts the silicon hydride to the corresponding silanol and hydrogen gas.⁶⁵ The extent of the conversion of the silane to the silanol under conditions of aqueous hydrolysis depends on the concentration of the silicon hydride, the concentration of hydroxide ion and the contact time. Excellent conversion of the silylmetallic compound to the silanol is achieved by carbonation, followed by prolonged exposure to aqueous base.²⁹

Color tests for silylmetallic compounds

Triphenylsilylpotassium,⁶ triphenylsilyllithium,^{4,7} and related silylmetallic compounds⁷ have been reported to give a positive Color Test I,⁴¹ and, under certain conditions, a positive Color Test IIA.⁶⁶

Since reactions involving silylmetallic compounds have received considerable attention recently, the need arose for a color test which distinguishes silylmetallic compounds from organometallic compounds. For this purpose the most promising

⁶⁵For a theoretical discussion of the conversion of silicon hydrides to silanols under conditions of aqueous hydrolysis, see H. Gilman and G. E. Dunn, ibid., 73, 3404 (1951).

⁶⁶H. Gilman and J. Swiss, ibid., 62, 1847 (1940).

color test has centered about the blue color developed in the reactions between silylmetallic compounds and benzophenone.^{4,6,22}

The test⁶⁷ consists of adding a few drops of the test solution to a 15 percent solution of benzophenone in dry benzene. A deep blue color, which fades on exposure to air or on hydrolysis, indicates the presence of a silylmetallic compound. The test is negative for ordinary organometallic compounds such as phenyllithium and butyllithium, but positive for stilbenedilithium or anthracenedilithium. Small pieces of lithium or sodium give a positive test, presumably due to the formation of a benzophenone ketyl.

Diphenyl sulfone and benzophenone anil have shown⁶⁷ some promise as color test reagents for silylmetallic compounds. Future research is planned with the aim of finding new and better color test reagents for silylmetallic compounds.

⁶⁷D. Wittenberg, Chemistry Dept., Iowa State College, Ames, Iowa. Private communication on color test reagents for silylmetallic compounds. 1958.

EXPERIMENTAL

Melting points and boiling points recorded are uncorrected. In general, melting points greater than 250° were taken in an electrically heated copper block while those below 250° were determined using an oil bath.

Reactions involving organometallic reactions were carried out under an atmosphere of dry, oxygen-free nitrogen in oven-dried glassware. The glassware was assembled while hot and flushed with a brisk stream of nitrogen during cooling.

Solvents were dried before use over sodium wire in the cases of ether, petroleum ether and benzene. Ethylene glycol dimethyl ether, used in a few experiments, was dried at the reflux temperature over sodium wire. A small amount of benzophenone was added at intervals until the characteristic blue color of diphenyl ketyl persisted for several minutes. Tetrahydrofuran was used in most experiments and was dried by refluxing, first over sodium wire, and then in the presence of lithium aluminum hydride. The solvent was collected immediately before use by distillation from the lithium aluminum hydride.

Silicon analyses were performed in weighed platinum crucibles on samples of 0.1 to 0.3 gram. The samples were decomposed with 10 to 20 drops of concentrated sulfuric acid and one drop of concentrated nitric acid. The crucibles were

heated over a low flame by means of a ring burner until dry. Subsequent treatment with fuming nitric acid gave a white ash which was heated with a Meeker burner for a period of about one hour. The crucibles were reweighed and the analyses reported as percent silicon.

The infrared data, reported in microns, were obtained on a Baird, model B, recording spectrophotometer.

Molar refractions were calculated using the values of Vogel, et al.^{68,69}

Preparation of Organosilylmetallic Compounds

Bis(triphenylsilyl)calcium (attempted)

To a mixture of 15.0 g. (0.029 mole) of hexaphenyldisilane and 8.1 g. (0.198 g. atom) of calcium was added sufficient tetrahydrofuran to form a thick paste. After stirring for two hours, with occasional heating, the mixture was light gray in appearance. A total of 140 ml. of tetrahydrofuran was added gradually. Color Test I⁴¹ was negative after the addition was complete. The calcium metal was destroyed by the cautious addition of water. From the organic layer was recovered 14.5 g. (96.5 percent) of hexaphenyldisilane,

⁶⁸A. I. Vogel, W. T. Cresswell, and J. Leicester, J. Phys. Chem., **58**, 174 (1954).

⁶⁹A. I. Vogel, W. T. Cresswell, G. H. Jeffrey and J. Leicester, J. Chem. Soc., 514 (1952).

m.p. 366-369°, identified by a mixed melting point.

In a second run using 15.0 g. (0.029 mole) of hexaphenyldisilane, 2.8 g. (0.0685 g. atom) of highly-pure calcium metal⁷⁰ and sufficient tetrahydrofuran to form a thick paste, this reaction was carried out under an atmosphere of helium. No cleavage was observed and 96.5 percent of the hexaphenyldisilane was recovered unchanged.

Bis(triphenylsilyl)magnesium (attempted)

Into a helium-filled flask was charged 15.0 g. (0.029 mole) of hexaphenyldisilane, 0.7 g. (0.0288 g. atom) of magnesium powder and sufficient tetrahydrofuran to form a thick paste. The paste was stirred for four hours and subsequently diluted to 25 ml. with tetrahydrofuran. The supernatant liquid gave a negative Color Test I.⁴¹ The magnesium was destroyed with dilute hydrochloric acid, and 96 percent of the hexaphenyldisilane was recovered from the organic layer.

Triethylsilyllithium (attempted)

Six attempts to prepare triethylsilyllithium in tetrahydrofuran were made. In a typical experiment, 5.0 g. (0.0217 mole) of hexaethyldisilane, 0.69 g. (0.1 g. atom) of

⁷⁰Kindly furnished by Dr. A. H. Daane of the Institute for Atomic Research, Iowa State College, Ames, Iowa.

lithium and five ml. of tetrahydrofuran were combined and stirred. The lithium coated over, and, after about 30 minutes, another five ml. of tetrahydrofuran was added. A red-brown color developed over a period of several minutes. When the stirrer was stopped to take Color Test I,⁴¹ which was positive, the color of the solution faded. When stirring was continued, the red-brown color again appeared. The reaction flask was cooled to -10° , and the color of the reaction mixture faded. The flask was allowed to warm to 0° , at which time the red color reappeared. The mixture was stirred for two hours at 0° , and subsequently an attempt was made to decant the solution into 5.0 g. of chlorotriphenylsilane in 50 ml. of tetrahydrofuran. However, most of the red color faded before the addition was complete. Water was added, the organic layer was dried, and solvent was evaporated. The residue was dissolved in petroleum ether (b.p. $60-70^{\circ}$) and chromatographed on an alumina column. The eluate yielded 3.67 g. (73 percent) of recovered hexaethyldisilane, identified by the infrared spectrum.

In the other five unsuccessful attempts to cleave hexaethyldisilane by lithium in tetrahydrofuran, the temperature and concentration were varied.⁷¹

One attempt was made to cleave hexaethyldisilane with

⁷¹M. B. Hughes¹⁹ was also unable to cleave hexaethyldisilane with lithium in tetrahydrofuran.

lithium in ethylene glycol dimethyl ether. A red color was formed as in the instances where tetrahydrofuran was used as a solvent, but the color faded when stirring was stopped. Recovery of hexaethyldisilane was 78 percent.

When the cleavage of hexaethyldisilane by lithium was attempted in triethylamine solution, no reaction was observed.

Cleavage of hexaphenyldisilane
by p-tolylolithium (attempted)

A solution of p-tolylolithium was prepared by the addition of 4.27 g. (0.025 mole) of p-bromotoluene in 25 ml. of tetrahydrofuran to a suspension of 0.208 g. (0.03 g. atom) of lithium in 10 ml. of tetrahydrofuran. The reaction was initiated at -40° and was held at -50° during the addition. Over a period of one hour following the addition, the reaction mixture was allowed to warm to -10° . Titration of an aliquot of the solution indicated a yield of 58 percent of p-tolylolithium. This solution (37 ml.) was added to a suspension of 5.0 g. (0.0097 mole) of hexaphenyldisilane in 20 ml. of tetrahydrofuran, cooled to -20° . The reaction mixture was held at 0° overnight by means of an ice bath (Dewar flask). Three ml. of chlorotrimethylsilane was added, and the reaction mixture was hydrolyzed with water. From the organic layer was obtained 4.87 g. (97.5 percent) of hexaphenyldisilane, m.p. $369-370^{\circ}$ (mixed m.p.).

Reactions of triphenylsilyllithium
with metal halides

Mercury (II) chloride. To a solution of 15.7 g. (0.058 mole) of mercury (II) chloride in 75 ml. of tetrahydrofuran was added a solution of triphenylsilyllithium (150 ml., 0.058 mole) during a period of 20 minutes. Color Test I⁴¹ was negative after the addition was complete. The solvent was distilled, and the residue was treated with anhydrous petroleum ether (b.p. 60-70°). The portion soluble in petroleum ether was filtered under nitrogen, and the solvent was removed by distillation to give an oil. This was distilled under reduced pressure to give 7.7 g. (45 percent) of chlorotriphenylsilane, b.p. 240-243° (35 mm.), which solidified immediately to give a white, crystalline solid, m.p. 95-97°. A mixed melting point with an authentic specimen of chlorotriphenylsilane was not depressed. The identity was further confirmed by a comparison of the infrared spectra, which were identical.

The portion insoluble in petroleum ether was washed thoroughly with water to remove unchanged mercury (II) chloride, and extracted repeatedly with hot benzene to give 2.7 g. (18.1 percent) of hexaphenyldisilane, m.p. 368-370° (mixed m.p.). The benzene insoluble residue was identified by qualitative tests as a mixture of mercury (I) chloride and metallic mercury.

Zinc chloride. To a solution of 5.26 g. (0.0386 mole) of freshly-fused zinc chloride in 100 ml. of tetrahydrofuran, maintained at -60° by means of a Dry Ice-acetone bath, was added 100 ml. of a tetrahydrofuran solution of triphenylsilyllithium prepared by cleavage of 10.0 g. (0.0193 mole) of hexaphenyldisilane with excess lithium. A light tan suspension resulted which gave a negative Color Test I.⁴¹ The suspension was allowed to warm to room temperature. The trace of suspended matter was allowed to settle, and the clear, yellow solution was decanted into an addition funnel.

One-half of the solution (100 ml.) was added to a solution of benzoyl chloride in 50 ml. of tetrahydrofuran at -60° . There was no evidence of reaction, even when the solution was allowed to warm to room temperature. The reaction mixture was hydrolyzed with saturated ammonium chloride. From the organic layer the only product identified was a small amount of triphenylsilanol, m.p. $152-153^{\circ}$.

The second half of the solution was added to 5.0 ml. of chlorotrimethylsilane in 50 ml. of tetrahydrofuran at -60° . There was no evidence of reaction. After warming to room temperature, the reaction mixture was hydrolyzed with water. None of the desired 1,1,1-trimethyl-2,2,2-triphenyldisilane was isolated from the organic layer.

In a second run, using the same quantities of triphenyl-

silyllithium and zinc chloride, the resulting yellow solution was added to a solution of 7.05 g. (0.0386 mole) of benzophenone in 100 ml. of tetrahydrofuran at -60° . There was no visible evidence of reaction. Hydrolysis, followed by the usual work-up failed to yield any pure derivatives.

Aluminum chloride. Addition of a tetrahydrofuran solution containing 0.0386 mole of triphenylsilyllithium to a solution of 5.15 g. (0.0386 mole) of aluminum chloride in 100 ml. of tetrahydrofuran resulted in an almost clear, colorless solution which gave a negative Color Test I.⁴¹ The tetrahydrofuran was removed by distillation and replaced by dry petroleum ether (b.p. $60-70^{\circ}$). Since the product was insoluble in petroleum ether, the solvent was again distilled and replaced by dry benzene. The benzene solution on cooling separated into two liquid phases. No crystalline products were isolated.

Cadmium chloride. One hundred milliliters of a tetrahydrofuran solution containing 0.0386 mole of triphenylsilyllithium was added, at room temperature, to a suspension of 7.05 g. (0.0386 mole) of oven-dried cadmium chloride. A black precipitate formed and the solution gave a negative Color Test I.⁴¹ The reaction mixture was filtered to give a clear solution which was dried over sodium sulfate. During the drying period of about one hour, a small amount of black precipitate formed. Evaporation of the solvent gave a

large amount of black material. Further attempts to work with this material were fruitless.

The original precipitate was extracted with hot benzene in a Soxhlet thimble. Only a small amount of impure hexaphenyldisiloxane was obtained in this manner. The insoluble black residue melted partially at 322° and bubbled slowly when treated with hydrochloric acid, confirming the presence of cadmium metal.

In a second run, the addition of triphenylsilyllithium to cadmium chloride (1:1 mole ratio) was carried out at -60° . The resulting mixture consisted of a yellow supernatant liquid and a white precipitate. Color Test I⁴¹ was negative. When the suspension was allowed to warm to room temperature, a black precipitate began to form about -10° . Work-up gave about the same results as in the previous run. Cadmium metal was again isolated but, as before, hexaphenyldisilane was not obtained.

In a third run, the reactants were mixed in a 1:1 mole ratio at -60° . To this suspension was added 5.0 ml. of benzoyl chloride. A blood-red solution resulted which, after warming to room temperature overnight, became yellow. The reaction mixture was hydrolyzed with water. The organic layer yielded an amorphous solid which resisted further purification. None of the desired triphenylsilylphenyl ketone was isolated.

In a fourth run, the reactants were mixed in a 1:1 mole ratio at -60° and dimethylsulfate was added. On warming, the reaction mixture again deposited cadmium metal. Following hydrolysis, no methyltriphenylsilane was isolated.

In a fifth run, a solution of triphenylsilyllithium prepared from 10.0 g. (0.0193 mole) of hexaphenyldisilane in 100 ml. of tetrahydrofuran was added, at room temperature, to a suspension of 3.54 g. (0.0193 mole) of cadmium chloride in 50 ml. of tetrahydrofuran. After the addition was complete, Color Test I⁴¹ was negative. The black cadmium deposit was removed by filtration, and the filtrate was dried over sodium sulfate and evaporated. The residue was treated with petroleum ether (b.p. $60-70^{\circ}$) to give 9.1 g. of a solid which decomposed from $200-205^{\circ}$ to a black melt. This product was recrystallized from a mixture of petroleum ether (b.p. $60-70^{\circ}$) and benzene to give 5.0 g. of yellow crystals which decomposed above 200° , again blackening. The infrared spectrum showed an O-H band at 2.8μ , indicating the possible presence of triphenylsilanol. The product was dissolved in benzene and chromatographed on an alumina column. No material resembling the original product could be eluted from the column. Only impure products of unknown composition, melting over wide ranges, were isolated.

Magnesium bromide. To a suspension of 1.5 g. (0.0617 g. atom) of magnesium in 25 ml. of tetrahydrofuran, cooled by

means of an ice bath, was added very slowly 9.3 g. (0.058 mole) of undissolved bromine. After the addition was complete, the suspension was heated to dissolve the magnesium bromide and decanted into a dry flask. On cooling, long needles of magnesium bromide formed.

To this suspension of magnesium bromide was added 100 ml. of a tetrahydrofuran solution containing 0.0386 mole of triphenylsilyllithium. There was no heat evolved and no visible evidence of reaction. Color Test I⁴¹ remained strongly positive. After stirring for 36 hours at room temperature, Color Test I was still positive, although somewhat weaker. A solution of 17.1 g. (0.058 mole) of chlorotriphenylsilane in 50 ml. of tetrahydrofuran was added. Color Test I was negative. Filtration gave 14.0 g. (70 percent) of hexaphenyldisilane, m.p. 364-366^o, identified by a mixed melting point.

Lead (II), tin (IV), or mercury (I) chlorides. The reactions of these anhydrous chlorides with triphenylsilyllithium in a 1:1 mole ratio were carried out and worked-up in the manner described for mercury (II) chloride.

From lead (II), tin (IV) and mercury (I) chlorides, the products obtained were hexaphenyldisilane in yields of 17 percent, 30 percent, and 33 percent, respectively; and chlorotriphenylsilane in yields of 17 percent, 25 percent, and 18 percent, respectively. The inorganic products isolated were metallic lead, identified by the melting point, tin (II)

chloride, identified by a qualitative test, and metallic mercury, identified by the boiling point.

Silver, copper (II), iron (III) or tin (II)⁷² chlorides.

The reactions of these anhydrous chlorides with triphenylsilyllithium in a 1:1 mole ratio were carried out in the manner described for mercury (II) chloride.

The products isolated, under anhydrous conditions, were hexaphenyldisilane in yields of 41 percent, 26 percent, 20 percent, and 16 percent, respectively; and triphenylsilane in yields of 3 percent, 29 percent, 30 percent, and trace amounts, respectively. No chlorotriphenylsilane was isolated in these cases.

Reactions of Organosilylmetallic Compounds

Silylamines

1-(Triphenylsilyl)morpholine. To a solution of 3.4 g. (0.0386 mole) of morpholine in 50 ml. of tetrahydrofuran was added 100 ml. of a tetrahydrofuran solution of triphenylsilyllithium prepared from 10.0 g. (0.0193 mole) of hexaphenyldisilane and excess lithium. Color Test I⁴¹ was negative after the addition was complete. The tetrahydrofuran was distilled, and a few ml. of ethanol was added cautiously. When the evo-

⁷²Kindly furnished by the Metal and Thermite Corporation.

lution of hydrogen had subsided, 100 ml. of ethenol was added. 1-(Triphenylsilyl)morpholine weighing 11.1 g. (83 percent) was separated by filtration. The melting point, 179-181^o, was not changed by recrystallization from a benzene, petroleum ether (b.p. 60-70^o) mixture.

Anal. Calcd. for C₂₂H₂₃ONSi: Si, 8.13. Found: Si, 8.14, 8.03.

1-(Triphenylsilyl)piperidine. To a solution of 3.44 g. (4.0 ml., 0.04 mole) of piperidine in 50 ml. of tetrahydrofuran was added 100 ml. of a tetrahydrofuran solution of triphenylsilyllithium prepared from 10.0 g. (0.0193 mole) of hexaphenyldisilane and excess lithium. After the addition was complete, Color Test I⁴¹ was negative. The tetrahydrofuran was distilled and ethanol was added cautiously. When the evolution of hydrogen had subsided, 100 ml. of ethanol was added. 1-(Triphenylsilyl)piperidine weighing 11.4 g. (86 percent) was separated by filtration. The melting point, 130-132^o, was raised to 131-132^o by recrystallization from cold petroleum ether (b.p. 60-70^o).

Anal. Calcd. for C₂₃H₂₅NSi: Si, 8.18. Found: Si, 8.27, 8.17.

1,4-Bis(triphenylsilyl)piperazine. To a solution of 0.0386 mole of triphenylsilyllithium in 100 ml. of tetrahydrofuran was added a solution of 1.46 g. (0.017 mole) of piperazine in 50 ml. of tetrahydrofuran. Color Test I⁴¹ was

positive. 1,4-Bis(triphenylsilyl)piperazine weighing 9.55 g. (93 percent) was filtered from the reaction mixture, washed with tetrahydrofuran and petroleum ether (b.p. 60-70°) and dried in a vacuum desiccator at 0.01 mm. The melting point, 288-290°, was changed to 287-288° after recrystallization from xylene.

Anal. Calcd. for $C_{40}H_{38}N_2Si_2$: Si, 9.32. Found: Si, 9.45, 9.38.

N,N-Dibutyl-1-methyl-1,1-diphenylsilylamine. To a solution of 1.53 g. (2.0 ml., 0.0119 mole) of di-n-butylamine in 30 ml. of tetrahydrofuran was added 45 ml. of a tetrahydrofuran solution of methyldiphenylsilyllithium prepared by the cleavage of 2.04 g. (0.00518 mole) of 1,1-dimethyl-1,1,2,2-tetraphenyldisilane with excess lithium. Color Test I⁴¹ was negative after the addition was complete. Ten ml. of ethanol was added to destroy the lithium hydride which had formed. The solvents were distilled and replaced by petroleum ether (b.p. 60-70°). The gelatinous lithium ethoxide was removed by suction filtration. The petroleum ether was stripped from the filtrate and distillation afforded 1.38 g. (41 percent) of N,N-dibutyl-1-methyl-1,1-diphenylsilylamine, b.p. 117-118° (0.02 mm.), n_D^{20} 1.5337, d_{20}^{20} 0.963.

Anal. Calcd. for $C_{21}H_{31}NSi$: Si, 8.65; MR_D , 105.7.
Found: Si, 8.90, 8.83; MR_D , 105.4.

N,N-Dibutyl-1,1-dimethyl-1-phenylsilylamine. To a solu-

tion of 4.78 g. (0.0370 mole) of di-n-butylamine in 50 ml. of tetrahydrofuran was added 50 ml. of a tetrahydrofuran solution of dimethylphenylsilyllithium prepared from 5.0 g. (0.0185 mole) of 1,1,2,2-tetramethyl-1,2-diphenyldisilane and excess lithium. Color Test I⁴¹ was negative after the addition was complete. Work-up in the manner described for the previous experiment gave 2.86 g. (29 percent) of N,N-dibutyl-1,1-dimethyl-1-phenylsilylamine, b.p. 72-74° (0.04 mm), n_D^{20} 1.4933, d_4^{20} 0.902.

Anal. C₁₆H₂₉NSi: C, 72.93; H, 11.09; MR_D, 85.6. Found: C, 72.67, 72.55; H, 10.62, 10.33; MR_D, 84.8.

N,N-Dibutyl-1,1,1-triphenylsilylamine. To 100 ml. of a tetrahydrofuran solution containing 0.0386 mole of triphenylsilyllithium was added a solution of 10.0 ml. of di-n-butylamine in 50 ml. of tetrahydrofuran. After the addition was complete, Color Test I⁴¹ was negative. Twenty milliliters of ethanol was added cautiously, and the solvents were distilled. Ethanol was added and the solution was cooled in an ice bath to give 8.03 g. (53.5 percent) of N,N-dibutyl-1,1,1-triphenylsilylamine, m.p. 64-65°. Concentration of the mother liquor gave another 1.09 g. (7.3 percent) of product, m.p. 62-64°. A mixed melting point with an authentic sample of N,N-dibutyl-1,1,1-triphenylsilylamine, prepared from the reaction of

lithiodibutylamide with triphenylsilane,⁷³ was not depressed.

N,N-Diphenyl-1,1,1-triphenylsilylamine (attempted). To a solution of 0.0386 mole of triphenylsilyllithium in 100 ml. of tetrahydrofuran was added 6.53 g. (0.0386 mole) of diphenylamine in 50 ml. of tetrahydrofuran. The brown color of the triphenylsilyllithium was discharged; Color Test I⁴¹ was negative. Addition of ethanol gave a slow but steady evolution of hydrogen gas. Distillation of the solvents, followed by addition of ethanol and cooling, gave none of the desired product. Following hydrolysis, the only product isolated was triphenylsilanol, 6.77 g. (64 percent), m.p. 152-154^o, identified by a mixed melting point.

N-Butyl-1,1,1-triphenylsilylamine. A solution of triphenylsilyllithium, prepared from 10.0 g. (0.0193 mole) of hexaphenyldisilane and excess lithium in 100 ml. of tetrahydrofuran, was added to an excess of n-butylamine in 50 ml. of tetrahydrofuran. Color Test I⁴¹ was negative after the addition was complete. The tetrahydrofuran was distilled and replaced by dry petroleum ether (b.p. 60-70^o). Filtration of the suspension gave a clear solution from which the petroleum ether was strip distilled. The resulting oil was distilled to give 7.16 g. (56 percent) of N-butyl-1,1,1-

⁷³H. Gilman, B. Hofferth, H. W. Melvin and G. E. Dunn, J. Am. Chem. Soc., 72, 5767 (1950).

triphenylsilylamine, b.p. 138-139^o (0.02 mm), which solidified on standing to give a waxy solid.⁷⁴ The infrared spectrum showed a strong N-H band at 2.9 .

Anal. Calcd. for C₂₂H₂₅NSi: Si, 8.48. Found: Si, 8.37, 8.44.

N-Butyl-1,1,1-triphenylsilylamine with methanol or ethanol. A small amount of N-butyl-1,1,1-triphenylsilylamine was dissolved in warm methanol. The odor of n-butylamine became intense. The solution was cooled to give crystals of methoxytriphenylsilane, m.p. 42-43^o (reported, 55^o)^{29,57}. The infrared spectrum of this compound was almost superimposable with that of a sample of methoxytriphenylsilane, m.p. 55.⁷⁵

Anal. Calcd. for C₁₉H₁₈OSi (m.p. 42-43^o): Si, 9.67. Found: Si, 9.58, 9.60.

A methanol solution of the 42-43^o form was seeded with the 55^o form and cooled to give crystals, m.p. 55^o. Attempts to reverse this technique by seeding a solution of the 55^o degree form with the 42-43^o form gave only the higher melting modification.⁷⁶

⁷⁴A melting point of 47-48^o has been reported for N-ethyl-1,1,1-triphenylsilylamine.¹³

⁷⁵The author is indebted to Dr. A. G. Brook of the Department of Chemistry, University of Toronto, Toronto, Canada, for a sample of the higher melting modification.

⁷⁶Dr. Brook, in a private communication, has informed us that he also was able to raise the melting point of the 42-43^o modification to that of the higher melting form, but was unable to reverse the procedure.

Ethoxytriphenylsilane, m.p. 65° (reported $63-64^{\circ}$),⁷⁷ was obtained by a similar procedure using ethanol. No dimorphism was observed.

Methoxytriphenylsilane from chlorotriphenylsilane and sodium methoxide. To a solution of sodium methoxide, prepared by addition of 0.415 g. (0.018 g. atom) of sodium to 50 ml. of methanol, was added 5.0 g. (0.0175 mole) of chlorotriphenylsilane. The reaction mixture was allowed to cool to room temperature, and the suspended sodium chloride was removed by filtration. The clear, colorless filtrate was cooled without seeding to give 2.15 g. (41 percent) of methoxytriphenylsilane, m.p. $42-43^{\circ}$. The product was shown, by the method of mixed melting points and a comparison of the infrared spectra, to be identical to the methoxytriphenylsilane prepared in the previous experiment.

Cleavage of N,N-dibutyl-1,1,1-triphenylsilylamine by phenyllithium (attempted). To a solution of 2.0 g. (0.00514 mole) of N,N-dibutyl-1,1,1-triphenylsilylamine in 25 ml. of ether was added 25 ml. of an ethereal solution containing 0.0095 mole of phenyllithium. The solution remained clear after 48 hours, indicating no tetraphenylsilane had formed. The ether was distilled and replaced by ethanol. Cooling gave 1.2 g. (60 percent) of recovered silylamine, m.p. $64-65^{\circ}$,

⁷⁷H. Gilman and G. N. R. Smart, J. Org. Chem., 19, 441 (1954).

identified by a mixed melting point.

With some aza-aromatic heterocycles

9-(Triphenylsilyl)acridan. To a solution of 6.9 g. (0.0386 mole) of recrystallized acridine in 50 ml. of tetrahydrofuran was added 100 ml. of a tetrahydrofuran solution of triphenylsilyllithium prepared from 10.0 g. (0.0193 mole) of hexaphenyldisilane and excess lithium. The resulting dark solution gave a negative Color Test I.⁴¹ The reaction mixture was hydrolyzed with water, and the organic layer was dried over sodium sulfate. The tetrahydrofuran was distilled, and crystallization of the residue from petroleum ether (b.p. 77-115°) gave a yellow powder, m.p. 177-190°. Recrystallization from the same solvent gave 4.63 g. (27 percent) of 9-(triphenylsilyl)acridan, m.p. 179-181°. Since the product discolored on prolonged exposure to air, it was dried under reduced pressure at 0.01 mm. The infrared spectrum showed a strong N-H band at 2.9 μ .

Anal. Calcd. for C₃₁H₂₅NSi: Si, 6.39. Found: Si, 6.33, 6.58.

10-Methyl-9-(triphenylsilyl)acridan. Using the same technique and molar quantities as described for the preceding reaction, excess methyl sulfate was added to the reaction mixture prior to hydrolysis. From the dried organic layer was obtained a solid which on treatment with ethanol gave 10.6 g.

(60 percent) of 10-methyl-9-(triphenylsilyl)acridan, m.p. 173-177°. Recrystallization from the same solvent raised the melting point to 179-181°. The infrared spectrum showed no N-H band at 2.9 . A mixed melting point with 9-(triphenylsilyl)acridan gave a large depression.

Anal. Calcd. for $C_{32}H_{27}NSi$: Si, 6.20. Found: Si, 6.42, 6.45.

9-(Triphenylsilyl)acridine. Using the same technique and molar quantities as described for the previous reaction, oxygen gas was passed above the solution. Considerable heat was evolved, and a heavy yellow precipitate formed. After about 30 minutes, the reaction had subsided and the suspension was filtered to give 5.3 g. (31 percent) of 9-(triphenylsilyl)acridine, m.p. 287-290°. Recrystallization from a benzene-petroleum ether (b.p. 60-70°) mixture gave bright, yellow crystals, m.p. 287-289°. An unsuccessful attempt was made to obtain additional product from the original filtrate.

Attempts to prepare 9-(triphenylsilyl)acridine by oxidation of 9-(triphenylsilyl)acridan with either nitrobenzene or ferric chloride failed.

Reduction of 9-(triphenylsilyl)acridine. Dry hydrogen chloride was passed for several hours over the surface of a benzene solution of 1.0 g. (0.00229 mole) of 9-(triphenylsilyl)acridine in contact with 10.0 g. (0.153 g. atom) of powdered zinc. The suspension was filtered. The filtrate

was neutralized with aqueous sodium carbonate and dried over solid sodium carbonate. A black tar left by evaporation of the benzene was dissolved in petroleum ether (b.p. 77-115°) and cooled. A black tar separated, which was removed by filtration and discarded. The clear filtrate was seeded with 9-(triphenylsilyl)acridan and set aside in the cold. The slow-forming crystals weighed 0.1 g. (10 percent), m.p. 179-182°. A mixed melting point with 9-(triphenylsilyl)acridan was not depressed, and the infrared spectra were practically indistinguishable.

Alternate synthesis of 10-methyl-9-(triphenylsilyl)-acridan. To a solution of 0.4 g. (0.00205 mole) of 10-methylacridan in 20 ml. of ether was added 2.5 ml. of an ethereal solution containing 0.0025 mole of *n*-butyllithium.⁷⁸ The solution became bright red in color. To this solution was added 0.71 g. (0.0025 mole) of undissolved chlorotriphenylsilane. The red color was discharged. Ether was added to increase the volume of the reaction mixture, and hydrolysis was effected by water. The organic layer was dried over sodium sulfate and evaporated. The solid was recrystallized from ethanol to give 0.75 g. (81 percent) of 10-methyl-9-(triphenylsilyl)acridan, m.p. 179-181°. A mixed melting

⁷⁸H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn and L. S. Miller, J. Am. Chem. Soc., 71, 1499 (1949).

point with a sample prepared by the first procedure was not depressed. The infrared spectra were identical.

10-Methyl-9-(triphenylsilyl)acridan from 9-(triphenylsilyl)acridan. Five milliliters of an ethereal solution containing 0.005 mole of *n*-butyllithium⁷⁸ was added to a solution of 1.5 g. (0.00342 mole) of 9-(triphenylsilyl)acridan in 20 ml. of ether, followed by an excess of dimethyl sulfate. Ether was added to increase the volume of the reaction mixture, which was subsequently hydrolyzed with water. The organic layer was dried over sodium sulfate and evaporated. Recrystallization of the solid from ethanol gave 0.92 g. (59 percent) of 10-methyl-9-(triphenylsilyl)acridan, m.p. 179-181°. A mixed melting point with a sample prepared by the first method was not depressed. The infrared spectra were identical.

Addition of triphenylsilyllithium to isoquinoline (attempted). To a solution of 0.0386 mole of triphenylsilyllithium in 100 ml. of tetrahydrofuran was added 5.0 ml. (5.45 g., 0.043 mole) of isoquinoline. A vigorous reaction ensued, and Color Test I⁴¹ was negative. Oxygen gas was passed over the surface of the reaction mixture; the color of the solution faded. Work-up by the usual method gave an oil which was dissolved in petroleum ether (b.p. 60-70°) and chromatographed on an alumina column. The column was eluted with

petroleum ether (b.p. 60-70°), and the resulting solution was evaporated. On treatment with ether, the residue gave some yellow powder, m.p. 162-172°. Recrystallization from petroleum ether (b.p. 60-70°) gave 0.6 g. of crystals, m.p. 171-173°. The identity of this compound is not known.

Anal. Calcd. for $C_{27}H_{21}NSi$: Si, 7.25. Found: Si, 6.40.

Addition of triphenylsilyllithium to phenanthridine (attempted). To a solution of 6.9 g. (0.0386 mole) of phenanthridine in 25 ml. of tetrahydrofuran was added 100 ml. of a tetrahydrofuran solution containing 0.0386 mole of triphenylsilyllithium. After a period of 12 hours, Color Test I⁴¹ was still positive. Excess methyl sulfate was added to the reaction mixture, followed by water. Work-up in the usual way failed to give any pure products.

Addition of triphenylsilyllithium to phenazine (attempted). To a solution of 3.5 g. (0.0193 mole) of phenazine in 50 ml. of tetrahydrofuran was added 50 ml. of a tetrahydrofuran solution containing 0.0193 mole of triphenylsilyllithium. Color Test I⁴¹ was negative after the addition was complete. Excess methyl sulfate was added, and the tetrahydrofuran was distilled and replaced by petroleum ether (b.p. 60-70°). The green suspension was filtered to remove inorganic salts, and the filtrate was chromatographed on an alumina column. Elution with petroleum ether gave 1.9 g.

(38 percent) of an oil which crystallized when seeded with triphenylsilane and was shown by the infrared spectrum to be this compound. Elution of the column with carbon tetrachloride gave some dark oil which crystallized from a mixture of benzene and petroleum ether (b.p. 60-70°) to give a small amount of yellow-green needles, m.p. 204-206°. The identity of this compound is unknown. The column was eluted with benzene and acetone to give dark, tarry materials which resisted further purification.

Anal. Calcd. for $C_{31}H_{26}N_2Si$: Si, 6.18. Found: Si, 5.46.

Thiosilanes

(Methylthio)triphenylsilane. To a stirred suspension of 0.62 g. (0.0193 g. atom) of sulfur in 25 ml. of tetrahydrofuran was added 50 ml. of a tetrahydrofuran solution of triphenylsilyllithium prepared from 5.0 g. (0.00965 mole) of hexaphenyldisilane and excess lithium. Heat was evolved during the addition, and the solution became almost black in appearance. After the addition was complete, Color Test I⁴¹ was negative, indicating that the triphenylsilyllithium had reacted completely. Addition of excess methyl iodide caused heat to be evolved and an immediate discharge of the black color. The tetrahydrofuran was stripped off, and the remaining oil was distilled to give 4.05 g. (76 percent) of crude

(methylthio)triphenylsilane, b.p. 145-150° (0.06 mm), which crystallized on standing. The product was recrystallized from anhydrous petroleum ether (b.p. 60-70°) to give 3.07 g. (52 percent) of rhomboidal crystals, m.p. 83-84°.

Anal. Calcd. for C₁₉H₁₈SSi: Si, 9.15. Found: Si, 9.33, 9.28.

(Benzylthio)triphenylsilane. To the reaction mixture of triphenylsilyllithium and sulfur, prepared in the manner described for the previous reaction, was added excess benzyl chloride. The dark color of the reaction mixture was discharged over a period of approximately 30 minutes. The tetrahydrofuran was stripped off to leave a dark oil. This was distilled to give 3.33 g. (45 percent) of crude (benzylthio)-triphenylsilane, b.p. 172-177° (0.015 mm). Two recrystallizations from anhydrous petroleum ether (b.p. 60-70°) gave 2.7 g. (36 percent) of crystals, m.p. 92-94°.

Anal. Calcd. for C₂₅H₂₂SSi: Si, 7.33. Found: Si, 7.08, 7.27.

(Benzoylthio)triphenylsilane. To a solution of the lithium salt of triphenylsilanethiol, prepared in the manner described for the preceding experiments, was added 3.05 g. (0.0217 mole) of benzoyl chloride. The dark color of the solution was discharged immediately, and heat was evolved. The tetrahydrofuran was stripped off, and the resulting oil was distilled to give 4.48 g. (59 percent) of crude (benzoyl-

thio)triphenylsilane, b.p. 183-189° (0.01 mm). Recrystallization from dry petroleum ether (b.p. 60-70°) gave 2.75 g. (36 percent) of yellow needles, m.p. 128-129°. The infrared spectrum of this compound showed a normal carbonyl peak at 5.9 μ .

Anal. Calcd. for C₂₅H₂₀OSSi: Si, 7.08. Found: Si, 7.10, 6.87.

Cleavage of (methylthio)triphenylsilane by phenyllithium.

To a stirred solution of 2.0 g. (0.00653 mole) of (methylthio)triphenylsilane in 20 ml. of ether was added 32 ml. of an ethereal solution containing 0.00978 mole of phenyllithium. The reaction mixture was hydrolyzed with water and filtered to give 1.97 g. (89 percent) of tetraphenyldisilane, m.p. 233-235°, identified by a mixed melting point. The filtrate was highly obnoxious in odor, presumably due to the presence of methyl mercaptan.

Hexaphenyldisilthiane or 1,1,1-trimethyl-2,2,2-triphenyldisilthiane (attempted). Addition of either chlorotriphenylsilane or chlorotrimethylsilane to the lithium salt of triphenylsilanethiol, prepared in the manner described above, resulted in no observable reaction, even after an extended period of time.

Cleavage studies involving organosilicon compounds

Hexaphenyldisilane by dimethylphenylsilyllithium. To a stirred suspension of 9.85 g. (0.019 mole) of hexaphenyldisilane in 50 ml. of tetrahydrofuran was added 30 ml. of a tetrahydrofuran solution of dimethylphenylsilyllithium prepared by the cleavage of 2.57 g. (0.0095 mole) of 1,1,2,2-tetramethyl-1,2-diphenyldisilane with excess lithium. Two hours after the addition was complete, the reaction mixture was hydrolyzed with water. From the organic layer was obtained 6.4 g. (65 percent) of recovered hexaphenyldisilane, m.p. 365-367° (mixed m.p.). The organic layer was dried and evaporated. The residual oil was treated with petroleum ether (b.p. 60-70°) to give 2.2 g. (21 percent) of triphenylsilanol, m.p. 154-156° (mixed m.p.). The petroleum ether was stripped off, and distillation afforded 1.43 g. (56 percent) of 1,1,2,2-tetramethyl-1,2-diphenyldisilane, b.p. 73° (0.01 mm). The distillate solidified on seeding with an authentic specimen of 1,1,2,2-tetramethyl-1,2-diphenyldisilane. The infrared spectra were identical.

1,1-Dimethyl-1,2,2,2-tetraphenyldisilane by dimethylphenylsilyllithium. To a solution of 10.0 g. (0.0254 mole) of 1,1-dimethyl-1,2,2,2-tetraphenyldisilane in 50 ml. of tetrahydrofuran was added 40 ml. of a tetrahydrofuran solution of dimethylphenylsilyllithium prepared from 3.43 g.

(0.0127 mole) of 1,1,2,2-tetramethyl-1,2-diphenyldisilane and excess lithium. After stirring overnight, the reaction mixture was hydrolyzed with water. From the dried organic layer was obtained an oil which on treatment with petroleum ether (b.p. 60-70°) gave 1.55 g. (22 percent) of triphenylsilanol, m.p. 154-156° (mixed m.p.). From the petroleum ether filtrate was obtained an oil which on distillation afforded 4.32 g. (63 percent) of 1,1,2,2-tetramethyl-1,2-diphenyldisilane, b.p. 76-81° (0.005 mm). The distillate solidified on seeding with an authentic specimen of 1,1,2,2-tetramethyl-1,2-diphenyldisilane. The infrared spectra were identical. The distillation residue was treated with ethanol to give 2.6 g. (26 percent) of recovered 1,1-dimethyl-1,2,2,2-tetra-phenyldisilane, m.p. 81.5-83° (mixed m.p.).

Hexaphenyldisilane by methyldiphenylsilyllithium. To a stirred suspension of 7.9 g. (0.0152 mole) of hexaphenyldisilane in 25 ml. of tetrahydrofuran was added 80 ml. of a tetrahydrofuran solution of methyldiphenylsilyllithium prepared by the cleavage of 6.0 g. (0.0152 mole) of 1,2-dimethyl-1,1,2,2-tetra-phenyldisilane with excess lithium. One hour after the addition was complete, water was added, and filtration of the organic layer gave 1.73 g. (22 percent) of recovered hexaphenyldisilane, m.p. 365-367° (mixed m.p.). The residue from the dried filtrate was dissolved in hot petroleum ether (b.p. 60-70°) and chromatographed on an alumina

column. Two petroleum ether fractions were collected. The first was evaporated to dryness and treated with ethanol to give 1.57 g. (26 percent) of 1,2-dimethyl-1,1,2,2-tetraphenyldisilane, m.p. 142-146°, identified by a mixed melting point with an authentic specimen. A mixed melting point with methylpentaphenyldisilane was depressed. The second petroleum ether fraction was treated similarly with ethanol to give 1.78 g. (ca. 29 percent) of solid, m. 121-133°. The melting point was not improved by recrystallization from ethanol. The infrared spectrum indicated this material was a mixture of 1,2-dimethyl-1,1,2,2-tetraphenyldisilane and methylpentaphenyldisilane. The ethanol filtrates were combined and evaporated to give an oil. When this oil was chilled and seeded with triphenylsilane, the entire mass crystallized. The product weighed 4.7 g. (59.5 percent), m.p. 43-45°, and was shown by the infrared spectrum and a mixed melting point to be triphenylsilane.

1,2-Dimethyl-1,1,2,2-tetraphenyldisilane by dimethylphenylsilyllithium. To a solution of 11.7 g. (0.0296 mole) of 1,2-dimethyl-1,1,2,2-tetraphenyldisilane in 75 ml. of tetrahydrofuran was added 70 ml. of a tetrahydrofuran solution of dimethylphenylsilyllithium prepared by the cleavage of 8.0 g. (0.0296 mole) of 1,1,2,2-tetramethyl-1,2-diphenyldisilane with excess lithium. Thirty minutes after the addition was complete, the reaction mixture was poured into cold

hydrochloric acid. From the dried organic layer was obtained an oil which was distilled to give 9.06 g. (77.5 percent) of methyldiphenylsilane, b.p. 79° (0.1 mm), n_D^{20} 1.5694 (reported b.p. $82^{\circ}/0.15$ mm, n_D^{20} 1.5747;⁶⁴ b.p. $137-139^{\circ}/14$ mm, n_D^{20} 1.5724⁶²). The identity of the silane was further confirmed by the infrared spectrum, which showed a strong Si-H absorption peak at 4.7μ . A second fraction boiling at $96-98^{\circ}$ (0.1 mm), 3.6 g. (45 percent), crystallized on seeding with 1,1,2,2-tetramethyl-1,2-diphenyldisilane and was shown to be this compound by the infrared spectrum.

Triphenylmethyltriphenylsilane by triphenylsilyllithium (attempted). To a stirred suspension of 3.0 g. (0.00597 mole) of triphenylmethyltriphenylsilane in 20 ml. of tetrahydrofuran was added 25 ml. of a tetrahydrofuran solution containing 0.008 mole of triphenylsilyllithium. After one hour, the reaction mixture was carbonated by pouring jet-wise into a slurry of Dry Ice and ether. The carbonated mixture was allowed to stand for two hours to ensure complete decomposition of the lithium salt of triphenylsilanecarboxylic acid to carbon monoxide and the lithium salt of triphenylsilanol.²⁹ The mixture was then shaken with 10 percent sodium hydroxide. Acidification of the basic extract gave no acid. From the organic layer was filtered 2.71 g. (90 percent) of recovered triphenylmethyltriphenylsilane, m.p. $317-325^{\circ}$ (decomp.). A mixed melting point with an authentic specimen was not

depressed.

Hexaphenyldigermene by triphenylsilyllithium. To a stirred suspension of 3.0 g. (0.00494 mole) of hexaphenyldigermene in 30 ml. of tetrahydrofuran was added 50 ml. of a tetrahydrofuran solution of triphenylsilyllithium prepared by cleavage of 5.13 g. (0.00988 mole) of hexaphenyldisilane with excess lithium. After 12 hours, the reaction mixture was hydrolyzed and filtered to give 2.63 g. (quantitative, based on hexaphenyldigermene) of hexaphenyldisilane, m.p. 367-369°. Recrystallization from benzene raised the melting point to 372-373°.

Anal. Calcd. for $C_{36}H_{30}Si_2$: Si, 10.81. Found: Si, 10.78, 10.82.

The filtrate was dried and evaporated. Addition of petroleum ether (b.p. 60-70°) gave 2.24 g. (41 percent) of triphenylsilanol, m.p. 152-158°. Recrystallization raised the melting point to 158-159° (mixed m.p.).

The petroleum ether mother liquor was chromatographed on an alumina column. Evaporation of the solvent from the eluate gave an oil which crystallized when cooled and melted 44-47°, 2.1 g. (70 percent), identified by the infrared spectrum as triphenylgermane. The Ge-H and Ge-phenyl bands were located at 4.9μ and 9.2μ , a shift of 0.2μ to a longer wavelength than the corresponding silicon bonds. The spectrum was superimposable with that of an authentic specimen

of triphenylgermane.

Triphenylsilyltriphenyltin by triphenylgermyllithium (attempted). To a suspension of 6.04 g. (0.0099 mole) of triphenylsilyltriphenyltin in 20 ml. of tetrahydrofuran was added 30 ml. of a tetrahydrofuran solution containing 0.0099 mole of triphenylgermyllithium. Some heat was evolved, and after the addition was complete, Color Test I⁴¹ was weakly positive. After 16 hours, the solution had become yellow and Color Test I was still slightly positive. Excess ethyl iodide was added, and the reaction mixture was stirred overnight. Following hydrolysis with water, filtration gave 4.21 g. of powder, m. 324-350° (decomp.). Recrystallization from benzene raised the melting point to 336-350° (decomp.). Further purification of this material was not attempted.

In a second run, using 2.0 g. (0.00329 mole) of triphenylsilyltriphenyltin and 0.00758 mole of triphenylgermyllithium, no pure products were isolated.

Tetraphenylsilane by dimethylphenylsilyllithium (attempted). To a stirred suspension of 3.72 g. (0.0111 mole) of tetraphenylsilane in 30 ml. of tetrahydrofuran was added 30 ml. of a tetrahydrofuran solution of dimethylphenylsilyllithium prepared from 3.0 g. (0.0111 mole) of 1,1,2,2-tetramethyl-1,2-diphenyldisilane and excess lithium. After 16 hours, water was added and filtration gave 2.35 g. (78.4 percent) of recovered tetraphenylsilane, m.p. 236-238°. Concen-

tration of the mother liquor gave another 0.48 g. of solid, m.p. 230-233°. Both crops were identified as tetraphenylsilane by the method of mixed melting points.

Tetraphenylsilane by methyldiphenylsilyllithium (attempted). To a suspension of 5.52 g. (0.0152 mole) of tetraphenylsilane in 45 ml. of tetrahydrofuran was added 45 ml. of a tetrahydrofuran solution of methyldiphenylsilyllithium prepared from 3.0 g. (0.0076 mole) of 1,2-dimethyl-1,1,2,2-tetraphenyldisilane and excess lithium. After 24 hours, the reaction mixture was hydrolyzed with water and filtered to give 4.71 g. (85 percent) of recovered tetraphenylsilane, m.p. 237-238° (mixed m.p.).

Tetraphenylgermane by triphenylsilyllithium (attempted). To a suspension of 1.9 g. (0.005 mole) of tetraphenylgermane in 15 ml. of tetrahydrofuran was added 30 ml. of a tetrahydrofuran solution containing 0.0116 mole of triphenylsilyllithium. After one hour, the reaction mixture was carbonated by addition to a Dry Ice-ether slurry and allowed to stand overnight. From the organic layer was obtained 1.75 g. (92 percent) of recovered tetraphenylgermane, m.p. 235-237°, identified by a mixed melting point and a comparison of the infrared spectrum with that of an authentic sample.

Hexaphenyldisilane and triphenylmethyllithium (attempted). A 0.5 mole run of n-butyllithium, starting with butyl

chloride, was prepared according to a published technique.⁷⁹ This solution (400 ml. in tetrahydrofuran) was added quickly to a solution of 61 g. (0.25 mole) of triphenylmethane in 75 ml. of tetrahydrofuran. The reaction mixture was allowed to stand for four hours at room temperature to ensure complete decomposition of the excess *n*-butyllithium.⁷⁹ Color Test I⁴¹ was positive at this time, although Color Test I performed on a small portion of the *n*-butyllithium solution, held back for this purpose, was negative. Carbonation of an aliquot (total volume 475 ml.) gave an 86 percent yield of triphenylacetic acid.

To a suspension of 5.0 g. (0.00965 mole) of hexaphenyldisilane in 25 ml. of tetrahydrofuran was added 50 ml. (0.023 mole) of the triphenylmethyllithium solution. After 18 hours, water was added and filtration gave 4.84 g. (96.8 percent) of recovered hexaphenyldisilane, m.p. 372-373° (mixed m.p.).

Miscellaneous reactions

Triphenylsilyllithium and chlorotriphenylsilane. To a solution of 5.66 g. (0.0192 mole) of chlorotriphenylsilane in 50 ml. of tetrahydrofuran, cooled to -60° by means of a Dry Ice-acetone bath, was added a solution of 0.0193 mole of

⁷⁹H. Gilman and B. Gaj, J. Org. Chem., 22, 1165 (1957).

triphenylsilyllithium in 50 ml. of tetrahydrofuran. Immediately after the addition was complete, Color Test I⁴¹ was negative. After warming to room temperature, the reaction mixture was hydrolyzed with water and filtered to give 8.8 g. (88 percent) of hexaphenyldisilane, m.p. 366-369° (mixed m.p.).

Triphenylsilyllithium and ketene. Ketene vapors, produced by pyrolysis of acetone in a standard ketene generator, were passed through an ice cooled condenser and then over the surface of a stirred solution of 0.0386 mole of triphenylsilyllithium in 100 ml. of tetrahydrofuran, cooled by means of a Dry Ice-acetone bath. After one hour, the ketene supply was disconnected, and the reaction mixture was allowed to warm to room temperature overnight. Hydrolysis was effected with dilute hydrochloric acid. From the dried organic layer was obtained a dark, viscous oil which would not crystallize. This was dissolved in benzene and chromatographed on an alumina column. The first benzene fraction was evaporated and distilled to give 2.28 g. (23 percent) of triphenylsilane, b.p. 114° (0.003 mm), m.p. 40-44°, identified by the infrared spectrum. The second benzene fraction crystallized from ethanol to give 0.75 g. of crystals, m.p. 149-152°. Recrystallization from the same solvent raised the melting point to 152-153°. This product was later shown to be identical to 2-(triphenylsilyl)-2-propanol, prepared from tri-

phenylsilyllithium and acetone.²⁴ Apparently, the ketene supply was contaminated with some acetone.

Triphenylsilyllithium and benzalacetophenone. To a stirred solution of 8.15 g. (0.0386 mole) of benzalacetophenone in 50 ml. of tetrahydrofuran was added a solution of 0.0386 mole of triphenylsilyllithium in 100 ml. of tetrahydrofuran. Color Test I⁴¹ was then negative. Following hydrolysis with ammonium chloride solution, filtration gave 4.56 g. (45.5 percent) of hexaphenyldisilane, m.p. 363-366° (mixed m.p.). The organic layer of the filtrate was dried and evaporated to give a heavy oil. This was dissolved in ether and on standing gave some white powder, 0.4 g., m. 195-290°. The ether filtrate was cooled to give 0.45 g. of powder, m.p. 188-189°, which showed a strong O-H band in the infrared spectrum at 2.9 μ . This compound was shown to be identical to the pinacol formed by bimolecular reduction of benzalacetophenone with zinc and acetic acid, according to the directions of Russell.⁸⁰ The ether mother liquor was evaporated to dryness. The resulting oil was dissolved in benzene and chromatographed on an alumina column. The benzene eluate was evaporated and treated with hot ethanol. On cooling, some amorphous powder deposited. Efforts to crystallize this material were fruitless. After several depositions

⁸⁰A. Russell, J. Chem. Soc., 218 (1934).

from ethanol, the solid liquified over the range 80-120°. The infrared spectrum of this material was nearly identical to that of 2-phenyl-2-triphenylgermylethylphenyl ketone, m.p. 119-120°, ⁸¹ except for shifts due to the substitution of silicon for germanium.

Anal. Calcd. for C₃₃H₂₈OSi: C, 84.57; H, 6.02. Found: C, 83.88, 83.73; H, 5.51, 5.61.

Triphenylsilylaldehyde (attempted)

From triphenylsilyllithium and ethyl orthoformate.

To a solution of 5.72 g. (0.0386 mole) of ethyl orthoformate in 50 ml. of tetrahydrofuran was added a solution of 0.0386 mole of triphenylsilyllithium in 100 ml. of tetrahydrofuran. There was no evidence of reaction. The solution was refluxed for 16 hours, at which time Color Test I⁴¹ was still positive. The reaction mixture was hydrolyzed with ammonium chloride solution and filtered to give 4.25 g. (42.5 percent) of hexaphenyldisilane, m.p. 365-367° (mixed m.p.). The organic filtrate was dried, evaporated, dissolved in petroleum ether (b.p. 60-70°) and chromatographed on an alumina column. The products isolated were 1.5 g. (15 percent) of triphenylsilane, eluted with petroleum ether (b.p. 60-70°), and 0.4 g. of impure 4-(triphenylsilyl)-butanol, m.p. 102-105°, eluted

⁸¹C. W. Gerow. "The preparation and cleavage of some organogermanium compounds." Unpublished Ph.D. Thesis. Ames, Iowa, Iowa State College Library. 1956.

with acetone.

From triphenylsilyllithium and N,N-dimethylformamide. To a solution of 3.0 g. (0.042 mole) of N,N-dimethylformamide in 50 ml. of tetrahydrofuran was added 100 ml. of a tetrahydrofuran solution containing 0.0386 mole of triphenylsilyllithium. Heat was evolved, and Color Test I⁴¹ was negative after the addition was complete. The reaction mixture was hydrolyzed with ammonium chloride solution, and the organic layer was dried over sodium sulfate. The tetrahydrofuran was distilled to give an oil, which, when treated with petroleum ether (b.p. 60-70°) gave 5.8 g. (54 percent) of triphenylsilanol, m.p. 149-153° (mixed m.p.). The petroleum ether was distilled from the filtrate. The resulting oil was refluxed with 5.0 g. of hydroxylamine hydrochloride, 25 ml. of pyridine and 25 ml. of ethanol. On cooling, no oxime crystallized.

In a second run, hydrolysis was effected by pouring the reaction mixture into cold hydrochloric acid. The organic layer was dried over sodium sulfate, and the tetrahydrofuran was stripped off. The resulting oil was dissolved in 100 ml. of ethanol and treated with a mixture of 10.0 g. of 2,4-dinitrophenylhydrazine, 50 ml. of sulfuric acid, 30 ml. of water and 200 ml. of ethanol. No crystals formed on cooling. Dilution with a large volume of water gave 7.2 g. (67 percent)

of crude triphenylsilanol, m.p. 141-146^o, identified by a mixed melting point.

Reaction of mercury (II) chloride with triphenylsilane.

To a solution of 21.3 g. (0.0708 mole) of mercury (II) chloride in 100 ml. of tetrahydrofuran was added 50 ml. of a tetrahydrofuran solution containing 10.0 g. (0.0384 mole) of triphenylsilane. A white precipitate formed during the 30 minute addition period, and the solution was distinctly acidic to litmus. Solvent from the reaction mixture was removed by distillation. The residue was extracted with anhydrous petroleum ether (b.p. 60-70^o). The petroleum ether was removed by distillation, and the residual liquid was distilled under reduced pressure to give 7.5 g. (66 percent) of chlorotriphenylsilane, b.p. 224-226^o (20 mm). The distillate solidified promptly and melted at 94-96^o. A mixed melting point with an authentic specimen of chlorotriphenylsilane was not depressed. The identity of the product was further confirmed by a comparison of the infrared spectra, which were superimposable. The petroleum ether insoluble portion was washed with water to remove any unchanged mercury (II) chloride. The remaining white solid was identified as mercury (I) chloride, 16.9 g. (91 percent).

There was no observable reaction between mercury (I), tin (IV), and lead (II) chlorides with triphenylsilane.

DISCUSSION

Organosilylmetallic compounds have only recently achieved stature as intermediates in the synthesis of organosilicon compounds. As pointed out earlier, the first true organosilylmetallic compound to be isolated was described by Benkeser and Severson⁵ in 1951.

The present investigation has demonstrated that organosilylmetallic compounds are useful as intermediates for the synthesis of a variety of new organosilicon compounds, many of which contain functional groups.

Preparative Methods

Early in this investigation, it was found that the use of tetrahydrofuran as a solvent for organosilylmetallic compounds increased greatly the utility of these reagents as intermediates for the synthesis of new organosilicon compounds. The two previous solvents which had been employed suffered from certain disadvantages and limitations. The use of diethyl ether as a solvent gave undesirable suspensions of triphenylsilylpotassium^{5,6} and involved the somewhat troublesome handling of sodium-potassium alloy. Ethylene glycol dimethyl ether, on the other hand, gave solutions of triphenylsilylalkali metal compounds which decompose rapidly by attacking the solvent to give products which were not

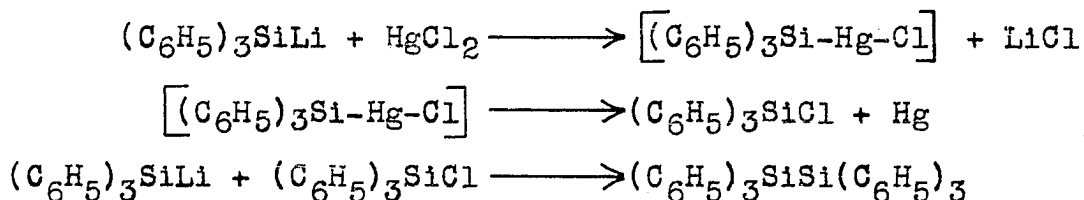
identified.

Both the advantages of solubility and stability were realized through the use of tetrahydrofuran as a solvent. Triphenylsilyllithium,⁴ prepared in this solvent by cleavage of hexaphenyldisilane with lithium, was both soluble and stable. In addition, methyldiphenylsilyllithium and dimethylphenylsilyllithium were readily prepared in tetrahydrofuran by the lithium cleavages of the corresponding disilanes.

It was found that the rate of cleavage of symmetrical disilanes with lithium increased as the number of phenyl groups attached to the silicon atoms increased. Thus, 1,1,2,2-tetramethyl-1,2-dipenyldisilane requires five to six hours for complete cleavage, whereas 1,2-dimethyl-1,1,2,2-tetraphenyldisilane is cleaved in less than one hour. Hexaphenyldisilane, which on the basis of this trend should cleave in a few minutes, requires three to four hours. The extreme insolubility of hexaphenyldisilane in tetrahydrofuran no doubt accounts for the slowness of cleavage. 1,2-Dimethyl-1,1,2,2-tetraphenyldisilane and 1,1,2,2-tetramethyl-1,2-dipenyldisilane are soluble in tetrahydrofuran.

A possible approach to the synthesis of organosilyl-metallic compounds containing different metals is through the reactions of silyllithium compounds with anhydrous metal halides. Analogous reactions between organosodium, -lithium

and -magnesium compounds are well known.^{82,83} From the reaction of mercury (II) chloride with triphenylsilyllithium in a 1:1 mole ratio, the products isolated were chlorotriphenylsilane (18 percent), hexaphenyldisilane (45 percent) and a mixture of mercury (I) chloride and metallic mercury. The most plausible explanation for the formation of these products centers about an unstable silicon-mercury intermediate. Disproportionation of this intermediate would give chlorotriphenylsilane and mercury. A simple coupling reaction between chlorotriphenylsilane and triphenylsilyllithium would give rise to the hexaphenyldisilane isolated.



Support for this theory concerning the formation of an unstable silicon-mercury intermediate was furnished by Dr. M. V. George,⁸⁴ who, in some significant studies, obtained tetraphenylsilane (73 percent), hexaphenyldisilane (6 percent)

⁸²R. G. Jones and H. Gilman, Chem. Revs., 54, 835 (1954).

⁸³H. Gilman. "Organic chemistry, an advanced treatise", Vol. I. New York, N.Y., John Wiley and Sons, Inc. 1938. pp. 406-489.

⁸⁴Dr. M. V. George, Chemistry Dept., Iowa State College, Ames, Iowa. Information concerning the reactions of triphenylsilyllithium with organomercury compounds. Private communication. 1958.

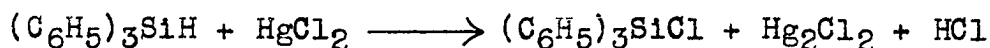
and free mercury from the reaction of phenylmercuric bromide with triphenylsilyllithium. Tetraphenylsilane (69 percent) and benzoic acid (74 percent) were isolated from the reaction of diphenylmercury with triphenylsilyllithium in a 1:1 mole ratio, followed by carbonation of the reaction mixture.⁸⁴ Similarly, the reaction of di-*p*-tolylmercury with triphenylsilyllithium gave, after carbonation and hydrolysis, *p*-toluic acid (71 percent) and triphenyl-*p*-tolylsilane (88 percent).

The reactions of a series of anhydrous metal chlorides with triphenylsilyllithium were carried out. One group, mercury (I) chloride, lead (II) chloride, and tin (IV) chloride reacted with triphenylsilyllithium to give chlorotriphenylsilane (18 percent, 17 percent and 25 percent, respectively); and hexaphenyldisilane (33 percent, 17 percent, and 30 percent, respectively), thus resembling mercury (II) chloride in their mode of reaction.

A second group of anhydrous metal chlorides: namely, iron (III) chloride, copper (II) chloride, silver chloride and tin (II) chloride, reacted with triphenylsilyllithium to give triphenylsilane (30 percent, 29 percent, 3 percent and trace amounts, respectively); and hexaphenyldisilane (41 percent, 26 percent, 20 percent, and 16 percent, respectively). Chlorotriphenylsilane was not isolated in these reactions. The mode of formation of triphenylsilane is not known. For

the present it may be stated that water was excluded as far as possible during the reactions and subsequent work-ups, suggesting the possible role of tetrahydrofuran as a hydrogen donor.

It was recognized that the formation of chlorotriphenylsilane from the reactions of mercury (II), mercury (I), tin (IV), and lead (II) chlorides with triphenylsilyllithium could arise through the initial formation of triphenylsilane, which by reduction with the metal chlorides could yield chlorotriphenylsilane. However, of the four metal chlorides mentioned, only mercury (II) chloride was capable of converting triphenylsilane to chlorotriphenylsilane. This is in line with the observation that mercury (II) chloride is the strongest oxidizing agent of this group.



Fritz⁸⁵ has treated mercury (II) chloride with Si-H compounds in aqueous solution to give mercury (I) chloride and the corresponding silanols. Anderson treated triethylgermane⁸⁶ and triethylstannane⁸⁷ with transition metal halides to give triethylgermyl halides and triethyltin halides, respectively.

⁸⁵G. Fritz, Z. anorg. u. allgem. chem., 280, 134 (1955).

⁸⁶H. H. Anderson, J. Am. Chem. Soc., 79, 326 (1957).

⁸⁷H. H. Anderson, ibid., 79, 4913 (1957).

Triphenylsilyllithium reacted instantly with either fused zinc chloride or anhydrous aluminum chloride. The nature of the products is not known. Solutions obtained from the reactions of triphenylsilyllithium and zinc chloride were treated with benzoyl chloride, chlorotrimethylsilane and benzophenone, but no reactions were observed. An attempt to isolate the products from the reaction of triphenylsilyllithium with aluminum chloride failed. It is suggested that the products from the reactions of zinc chloride or aluminum chloride with triphenylsilyllithium are complex ions.

Triphenylsilyllithium reacted with cadmium chloride in a 1:1 mole ratio at room temperature to give metallic cadmium and unidentified products. Hexaphenyldisilane was not formed. At -70° , again in a 1:1 mole ratio, no cadmium metal was deposited. As the reaction mixture warmed, cadmium metal began to precipitate at about -10° . When the reaction was carried out at -70° , followed by addition of benzoyl chloride, a blood-red solution formed, which on warming to room temperature became yellow and did not deposit cadmium metal. Attempts to isolate the desired triphenylsilylphenyl ketone failed. When the reaction of triphenylsilyllithium and cadmium chloride in a 1:2 mole ratio was carried out at room temperature, followed by hydrolysis, a compound decomposing above 200° with the deposition of cadmium metal was isolated. This compound is believed to be bis(triphenylsilyl)cadmium,

but the structure has not been established definitely.

Six attempts were made to prepare triethylsilyllithium by the cleavage of hexaethylidisilane with lithium⁸⁸ in tetrahydrofuran. Red solutions were obtained which gave a positive Color Test I,⁴¹ but the red color was unstable. When stirring was discontinued for a moment for the purpose of performing Color Test I, the red color faded. Lowering the temperature of the reaction mixture caused the color to fade instead of stabilizing it. It is possible that triethylsilyllithium is forming slowly in these reactions and attacking the solvent immediately. Attempted cleavages of hexaethylidisilane with lithium in either ethylene glycol dimethyl ether or triethylamine failed.

Attempts to cleave hexaphenyldisilane with calcium or magnesium gave no observable reaction. The reaction with calcium was carried out under an atmosphere of helium in order to avoid the formation of calcium nitride.

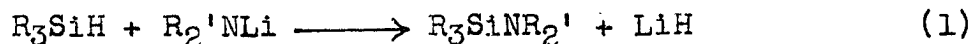
Reactions of Organosilylmetallic Compounds

Silylamines

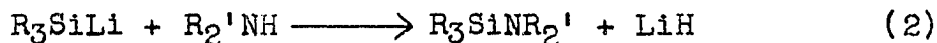
The reactions of chlorosilanes with amines, the classi-

⁸⁸H. McNinch, Chemistry Dept., Iowa State College, Ames, Iowa. The type of lithium employed may profoundly influence certain cleavage reactions, in particular the cleavage of benzyl ethers. Private communication. 1958.

cal method for the formation of silylamines,⁸⁹ were unsuccessful for the preparation of triarylsilylamines.⁹⁰ As an alternative, a series of triarylsilylamines was prepared⁹⁰ from the reactions of triphenylsilane with lithium dialkylamides.



In this study, a variety of silylamines was synthesized from the reactions of silyllithium compounds with primary and secondary amines. Thus, triphenylsilyllithium, methyl-diphenylsilyllithium, and dimethylphenylsilyllithium³ react with di-*n*-butylamine to give N,N-dibutyl-1,1,1-triphenylsilylamine, N,N-dibutyl-1-methyl-1,1-diphenylsilylamine and N,N-dibutyl-1,1-dimethyl-1-phenylsilylamine, respectively. In like manner, triphenylsilyllithium reacts with morpholine, piperidine, and piperazine to give 1-(triphenylsilyl)morpholine, 1-(triphenylsilylsilyl)piperidine, and 1,4-bis(triphenylsilyl)piperazine, respectively, in high yields.

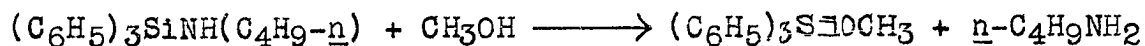


From the reaction of triphenylsilyllithium with *n*-butylamine, N-butyl-1,1,1-triphenylsilylamine was isolated by distillation. This waxy solid is cleaved rapidly by methanol

⁸⁹E. G. Rochow. "Chemistry of the silicones". New York, N.Y., John Wiley and Sons, Inc. 1951.

⁹⁰H. Gilman, B. Hofferth, H. W. Melvin and G. E. Dunn, *J. Am. Chem. Soc.*, **72**, 5767 (1950).

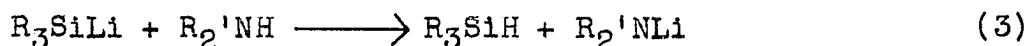
or ethanol to give the corresponding alkoxy silanes.⁹¹ Methoxytriphenylsilane obtained in this manner melted at 42-43° (reported, 55°).^{29,57} Methoxytriphenylsilane obtained from the reaction of chlorotriphenylsilane with sodium



methoxide also melted at 42-43°. The lower melting form (42-43°) was readily converted to the higher melting form⁷⁶ (55°) by a simple seeding technique. Attempts to reverse this procedure failed. Apparently the higher melting isomer is the stable form. When admixed, the two forms gave no melting point depression. The infrared spectra were practically superimposable.

The silylamines derived from secondary amines were highly resistant to alcoholysis.

It is probable that the overall reaction (equation 2) for the formation of silylamines takes place in two fast steps, an initial metalation of the amine (equation 3) fol-



lowed by coupling (equation 1). In support of this view, it was found that triphenylsilyllithium metalated diphenylamine, but no silylamine was isolated. Similarly, N-diphenylmethyl-

⁹¹Similar cleavages of hexamethyldisilazine by alcohols were reported recently by S. H. Langer, S. Connell and I. Wender, *J. Org. Chem.*, 23, 50 (1958).

aniline was metalated³⁴ by triphenylsilyllithium to give, after hydrolysis, triphenylsilane (70 percent), N-diphenylmethylaniline (66 percent) and none of the silylamine.

Apparently, the presence of a phenyl group on the nitrogen atom reduces the nucleophilicity of the lithium amide to a degree where it is not capable of displacing a hydride ion from triphenylsilane. It has been reported⁹⁰ that lithium diphenylamide does not react with triphenylsilane.

While silicon-oxygen⁸⁹ and silicon-sulfur^{92,93} bonds are cleaved by organolithium compounds, the silicon-nitrogen bond was found to be remarkably stable. Treatment of N,N-dibutyl-1,1,1-triphenylsilylamine with phenyllithium resulted in a 60 percent recovery of the rather soluble silylamine. No tetraphenylsilane, easily detected by its insolubility, was formed.

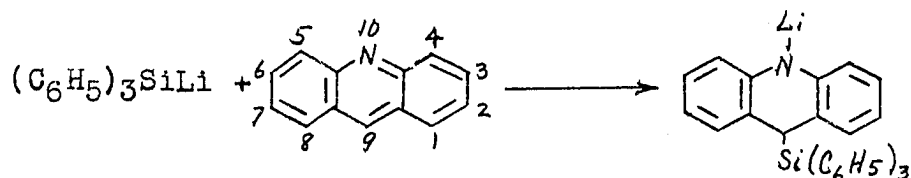
Derivatives of aza-aromatic heterocycles

Acridine. As a part of the study of the addition of silylmetallic compounds to aza-aromatic heterocycles, the mode of addition of triphenylsilyllithium to acridine was investigated.

⁹²D. Wittenberg and H. Gilman, J. Am. Chem. Soc., 79, 6339 (1957).

⁹³Refer to the Experimental section on thiosilanes.

Alkyl- and aryllithium compounds have been reported to undergo addition to acridine^{94,95,96} in the 9,10-positions.



9,10-Addition takes place to give 10-lithio-9-(triphenylsilyl)acridan, which by hydrolysis gives 9-(triphenylsilyl)acridan, by reaction with oxygen⁹⁷ gives the totally aromatic compound, 9-(triphenylsilyl)acridine, and by reaction with methyl sulfate gives 10-methyl-9-(triphenylsilyl)acridan. The last mentioned compound was also obtained by treatment of 9-(triphenylsilyl)acridan with *n*-butyllithium,⁷⁸ followed by methyl sulfate. 9-(Triphenylsilyl)acridine is reduced to 9-(triphenylsilyl)acridan by zinc and hydrogen chloride in benzene solution. Attempts to oxidize 9-(triphenylsilyl)acridan to 9-(triphenylsilyl)acridine with either nitrobenzene or ferric chloride failed.

The structure of 10-methyl-9-(triphenylsilyl)acridan was established by an alternate synthesis. Treatment of 10-

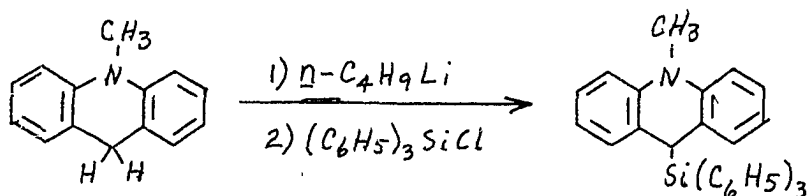
⁹⁴E. Bergmann, O. Blum-Bergmann and A. F. Christiani, Ann., 483, 80 (1930).

⁹⁵K. Ziegler and H. Zeiser, ibid., 485, 174 (1931).

⁹⁶H. Gilman and D. A. Shirley, J. Am. Chem. Soc., 72, 2181 (1952).

⁹⁷H. Gilman and J. T. Edward, Can. J. Chem., 31, 457 (1953).

methyl-acridan with *n*-butyllithium⁷⁸ gave 9-lithio-10-methyl-acridan, which by coupling with chlorotriphenylsilane gave 10-methyl-9-(triphenylsilyl)acridan in an excellent yield.



These derivatives of acridine are currently under investigation with regard to their possible use as antioxidants containing silicon.

Isoquinoline. The only pure product obtained from the reaction of triphenylsilyllithium with isoquinoline, followed by the passage of oxygen through the solution, was a very small quantity of crystals, m.p. 171-173°. The silicon analysis was low for 1-(triphenylsilyl)isoquinoline, although the infrared spectrum indicated that this could be the structure. The identity of the compound has not been established.

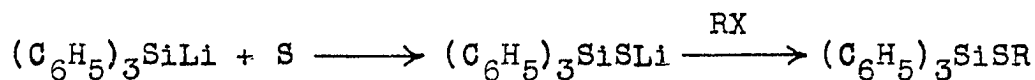
Phenanthridine. The reaction of phenanthridine with triphenylsilyllithium in a 1:1 mole ratio was not complete after 12 hours. Subsequent addition of methyl sulfate failed to give any pure products.

Phenazine. From the reaction of triphenylsilyllithium with phenazine, followed by methyl sulfate, the only pure

product isolated was a small amount of yellow-green crystals, m.p. 204-206°. The silicon analysis was low for 10-methyl-5-(triphenylsilyl)phenazine, although the infrared spectrum indicated that this could be the structure. The identity of the product has not been established.

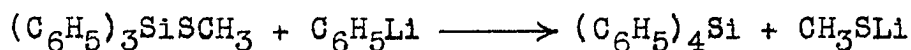
Thiosilanes

Solutions of triphenylsilyllithium³ in tetrahydrofuran react smoothly with sulfur to give the lithium salt of triphenylsilanethiol. Subsequent reactions of this intermediate with methyl iodide, benzyl chloride or benzoyl chloride give rise to (methylthio)triphenylsilane, (benzylthio)triphenyl-



silane, and (benzoylthio)triphenylsilane, respectively, in good yields. To our knowledge, the last mentioned compound is the first reported to contain the Si-S-CO- linkage. These thiosilanes were isolated by distillation, followed by recrystallization from a chemically inert solvent.

(Methylthio)triphenylsilane is cleaved by phenyllithium to give tetraphenylsilane in a reaction analogous to the



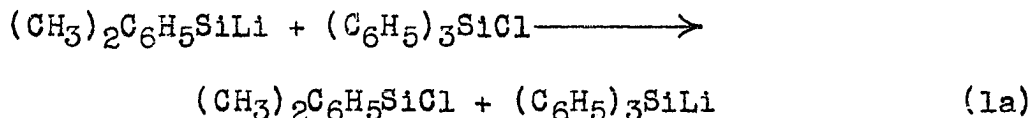
well known cleavages of alkoxy silanes by organometallic reagents.⁸⁹

No observable reaction was noted between the lithium

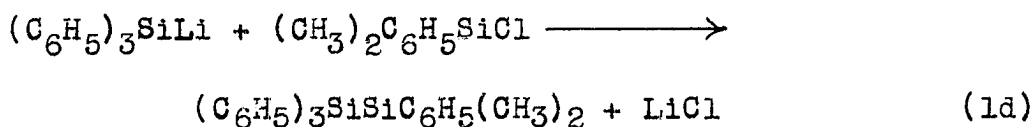
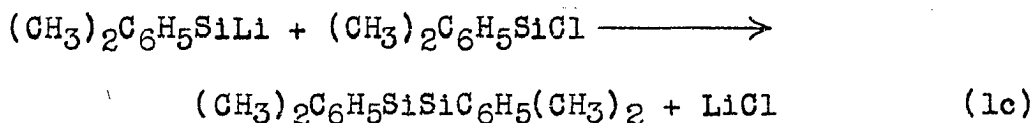
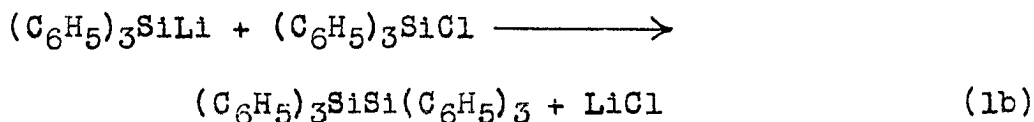
salt of triphenylsilanethiol and iodobenzene, chlorotri-
methylsilane, or chlorotriphenylsilane, although a prompt
coupling reaction has been reported by Hyde and coworkers⁹⁸
between the sodium salt triphenylsilanol and chlorosilanes.
This difference in reactivity may be rationalized on the
basis that the sodium salt of triphenylsilanol should be a
stronger nucleophile than the lithium salt of triphenyl-
silanethiol.

Cleavage studies involving organosilicon compounds

Disilanes by silylmetallic compounds. It was postu-
lated³ that the formation of hexaphenyldisilane from the
reactions of either methyldiphenylsilyllithium or dimethyl-
phenylsilyllithium with chlorotriphenylsilane was thought to
occur via a halogen-metal interconversion reaction. For
instance, the reaction of dimethylphenylsilyllithium with
chlorotriphenylsilane was illustrated in the following way
(1a). The various possible coupling reactions could then



⁹⁸J. F. Hyde, O. K. Johannson, W. K. Daudt, R. F. Fleming, H. B. Laudenslager and M. P. Roche, J. Am. Chem. Soc., 75, 5615 (1953).

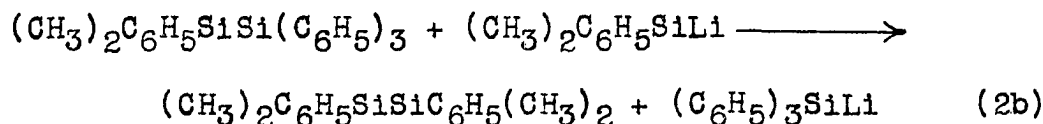
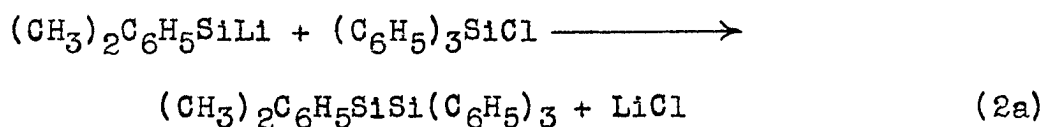


give rise to hexaphenyldisilane, 1,1,2,2-tetramethyl-1,2-diphenyldisilane, and 1,1-dimethyl-1,2,2,2-tetraphenyldisilane (1b, 1c, 1d). The last mentioned product was not isolated when the reaction was carried out by addition of chlorotriphenylsilane to dimethylphenylsilyllithium. By reversing the direction of addition, *i.e.*, adding dimethylphenylsilyllithium to chlorotriphenylsilane, good yields of 1,1-dimethyl-1,2,2,2-tetraphenyldisilane were isolated along with a small amount of hexaphenyldisilane.

In a similar manner, addition of methyl-diphenylsilyllithium to chlorotriphenylsilane gave good yields of methyl-pentaphenyldisilane, whereas reversing the direction of addition gave hexaphenyldisilane, methylpentaphenyldisilane and 1,2-dimethyl-1,1,2,2-tetraphenyldisilane. While the concept of a halogen-metal interconversion reaction explains the formation of the products in these reactions, the importance of the direction of addition is left unanswered. In light of new evidence, an explanation based on the cleavage of

disilanes by silylmetallic compounds may be advanced.

The reaction of dimethylphenylsilyllithium with chlorotriphenylsilane probably involves an initial coupling reaction to give 1,1-dimethyl-1,2,2,2-tetraphenyldisilane (2a), regardless of the direction of addition. In the presence of excess dimethylphenylsilyllithium, a second reaction (2b) takes place involving the cleavage of 1,1-dimethyl-1,2,2,2-tetraphenyldisilane by dimethylphenylsilyllithium to give

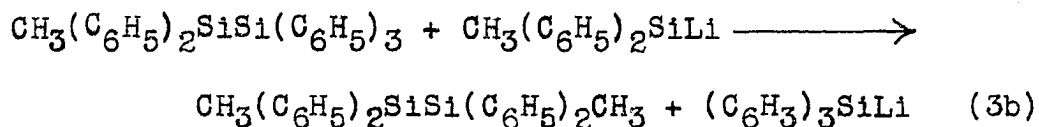
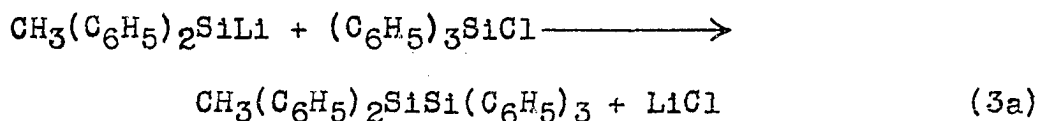


1,1,2,2-tetramethyl-1,2-diphenyldisilane and triphenylsilyllithium. Hence, the failure to isolate 1,1-dimethyl-1,2,2,2-tetraphenyldisilane is not surprising. Hexaphenyldisilane arises through the reaction of triphenylsilyllithium with chlorotriphenylsilane (1b). When dimethylphenylsilyllithium is added to chlorotriphenylsilane, the latter compound is present in excess. The unsymmetrical coupling product, 1,1-dimethyl-1,2,2,2-tetraphenyldisilane, which forms does not undergo further cleavage and may be obtained in good yields.

A similar argument may be presented for the formation of the products isolated from the addition of chlorotriphenylsilane to methylphenylsilyllithium. Methylpentaphenyldi-

silane, formed by an initial coupling reaction (3a), is cleaved further by methyldiphenylsilyllithium to give 1,2-dimethyl-1,1,2,2-tetraphenyldisilane and triphenylsilyllithium (3b).

In this case, however, methylpentaphenyldisilane was isolated,

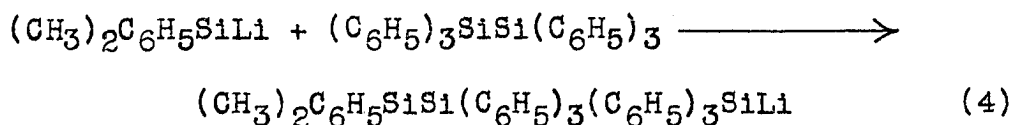


which would indicate the cleavage of this compound by methyldiphenylsilyllithium is kinetically slower than the cleavage of 1,1-dimethyl-1,2,2,2-tetraphenyldisilane by dimethylphenylsilyllithium. This explanation is in line with the activity series for silyllithium compounds, to be presented later in this section, in which methyldiphenylsilyllithium is shown to be less reactive than dimethylphenylsilyllithium. Hexaphenyldisilane is again formed by the reaction of chlorotriphenylsilane with triphenylsilyllithium (1b). Addition of methyldiphenylsilyllithium to chlorotriphenylsilane gave only the coupling product, methylpentaphenyldisilane.

Support for the hypotheses presented concerning the cleavage of disilanes by silyllithium compounds was obtained by cleavage of preformed disilanes by silyllithium reagents.

The addition of dimethylphenylsilyllithium to an equimolar suspension of hexaphenyldisilane in tetrahydrofuran

gave a prompt reaction from which the products isolated were 1,1,2,2-tetramethyl-1,2-diphenyldisilane (56 percent), triphenylsilanol (21 percent), and hexaphenyldisilane (65 percent recovery). The formation of these products may be visualized as having occurred through the initial cleavage of hexaphenyldisilane by dimethylphenylsilyllithium to give 1,1-dimethyl-1,2,2,2-tetraphenyldisilane and triphenylsilyllithium (4). Cleavage of 1,1-dimethyl-1,2,2,2-tetraphenyl-



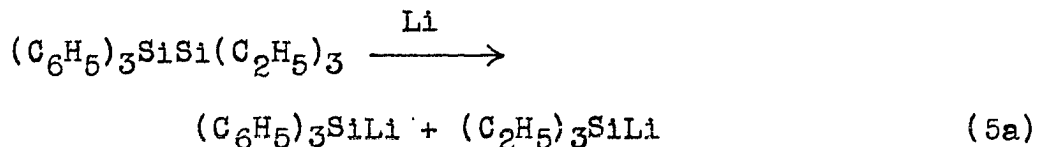
disilane by a second molecule of dimethylphenylsilyllithium gives 1,1,2,2-tetramethyl-1,2-diphenyldisilane and triphenylsilyllithium (2b). Failure to isolate 1,1-dimethyl-1,2,2,2-tetraphenyldisilane may be attributed to the difference in solubility of 1,1-dimethyl-1,2,2,2-tetraphenyldisilane and hexaphenyldisilane. The former compound is soluble in tetrahydrofuran and is cleaved as soon as it forms by dimethylphenylsilyllithium in preference to the highly insoluble hexaphenyldisilane.

Treatment of 1,1-dimethyl-1,2,2,2-tetraphenyldisilane with one equivalent of dimethylphenylsilyllithium gave, after hydrolysis, triphenylsilanol (22 percent), 1,1,2,2-tetramethyl-1,2-diphenyldisilane (63 percent), and 1,1-dimethyl-1,2,2,2-tetraphenyldisilane (26 percent recovery).

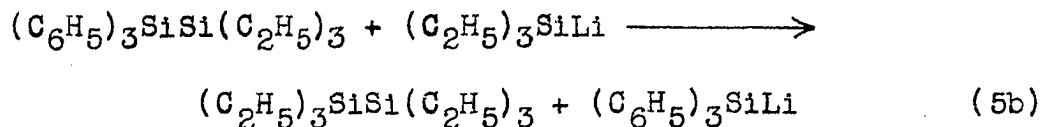
From the reaction of methyldiphenylsilyllithium with hexaphenyldisilane (2:1 mole ratio), the products isolated were 1,2-dimethyl-1,1,2,2-tetraphenyldisilane (26 percent), triphenylsilane (59 percent), hexaphenyldisilane (22 percent recovery), and ca. 29 percent of a mixture of 1,2-dimethyl-1,1,2,2-tetraphenyldisilane and 1,1-dimethyl-1,2,2,2-tetraphenyldisilane.

Addition of dimethylphenylsilyllithium to 1,2-dimethyl-1,1,2,2-tetraphenyldisilane (2:1 mole ratio) gave, after acid hydrolysis, 1,1,2,2-tetramethyl-1,2-diphenyldisilane (45 percent) and methyldiphenylsilane (77 percent).

Evidence for the existence of a transient trialkylsilyl-metallic compound is afforded by the cleavage of 1,1,1-triethyl-2,2,2-triphenyldisilane by lithium⁹⁹ (5a) in tetrahydrofuran. The products isolated from this reaction were, after acid hydrolysis, hexaethyldisilane (14 percent), triethylsilane (11 percent) and triphenylsilane (92 percent). Isolation of the first compound indicates the formation of triethylsilyllithium (5a) which, by cleavage of 1,1,1-triethyl-2,2,2-triphenyldisilane, gives hexaethyldisilane (5b).



⁹⁹D. Wittenberg, Chemistry Dept., Iowa State College, Ames, Iowa. Private communication on the cleavage of 1,1,1-triethyl-2,2,2-triphenyldisilane by lithium. 1958.



Assuming that the silicon-silicon bond strength remains about constant with varying numbers of alkyl and aryl substituents on the silicon atoms, on the basis of the reactions described, silyllithium compounds may be arranged in a reactivity series.



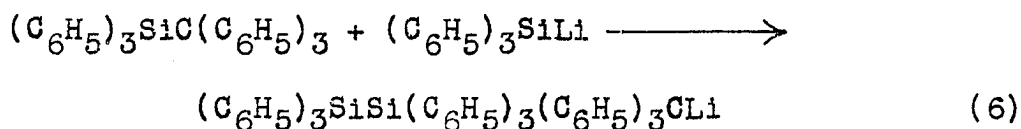
The clean-cut cleavages of disilanes by silyllithium compounds indicates that side reactions such as the cleavage of silicon-phenyl bonds by the silylmetallic compounds does not take place. In line with this reasoning, it was found that tetraphenylsilane is not cleaved by either methyldiphenylsilyllithium or dimethylphenylsilyllithium. It was assumed that the silicon-phenyl bonds in tetraphenylsilane are equivalent to the silicon-phenyl bonds in disilanes as far as their ease of cleavage by silyllithium compounds is concerned.

Although disilanes are cleaved readily by silylmetallic compounds, they are resistant to cleavage by organolithium compounds. This study has shown that hexaphenyldisilane is unaffected by *p*-tolylsilyllithium in tetrahydrofuran. Previous attempts to cleave hexaphenyldisilane by phenylsilyllithium in

diethyl ether¹⁰⁰ were unsuccessful.

Triphenylmethyltriphenylsilane by triphenylsilyllithium.

It has been reported⁴⁹ that the reaction of triphenylsilyl-potassium with chlorotriphenylmethane, followed by carbonation of the reaction mixture, gives hexaphenyldisilane, hexaphenylethane (identified as the peroxide), and triphenylacetic acid. The formation of these products was postulated as having occurred via a halogen-metal interconversion reaction, followed by various coupling reactions. It is possible, however, to visualize these products as having arisen by way of a cleavage reaction (6) similar to those described

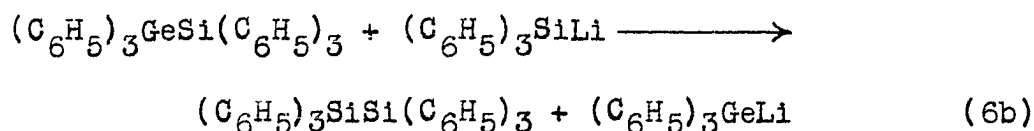
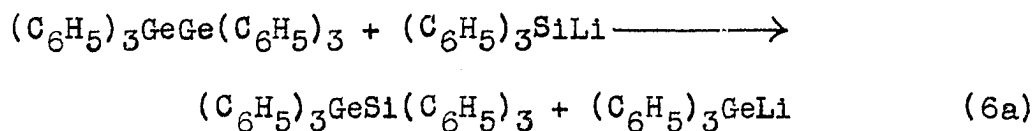


in the preceding section for disilanes. This alternative was tested by the addition of triphenylsilyllithium to triphenylmethyltriphenylsilane, followed by carbonation of the reaction mixture. Following hydrolysis, however, no triphenylacetic acid was obtained from the aqueous layer. Recovery of triphenylmethyltriphenylsilane was 90 percent. It appears, therefore, that the products isolated from the reaction of triphenylsilylpotassium with chlorotriphenyl-

100G. E. Dunn. "Relationships between some organosilicon compounds and their carbon analogs." Unpublished Ph.D. Thesis. Ames, Iowa, Iowa State College Library. 1951.

methane⁴⁹ did indeed arise as the result of a halogen-metal interconversion reaction.

Hexaphenyldigermene by triphenylsilyllithium. From the reaction of an excess of two moles of triphenylsilyllithium with one mole of hexaphenyldigermene was obtained a quantitative yield of hexaphenyldisilane and triphenylgermane (70 percent). The reaction proceeds through the initial cleavage



of hexaphenyldigermene by triphenylsilyllithium to give triphenylsilyltriphenylgermane and triphenylgermyllithium (6a). Cleavage of triphenylsilyltriphenylgermane by a second molecule of triphenylsilyllithium gives hexaphenyldisilane and triphenylgermyllithium (6b).¹⁰¹

Considering the equations (6a and 6b) as written, the formation of triphenylgermyllithium from a cleavage reaction with triphenylsilyllithium would at first glance indicate that triphenylsilyllithium is more reactive than triphenyl-

¹⁰¹Dr. M. V. George, Dept. of Chemistry, Iowa State College, Ames, Iowa, in related studies, has found that preformed triphenylsilyltriphenylgermane is indeed cleaved by triphenylsilyllithium. Private communication. 1958.

germyllithium. However, the Ge-Ge bond strength is less than the silicon-silicon bond strength. Therefore, no conclusion can be drawn on the basis of this experiment concerning the relative reactivities of triphenylsilyllithium and triphenylgermyllithium.

The specificity of this reaction should signify that the germanium-phenyl bonds in hexaphenyldigermene are not cleaved by triphenylsilyllithium.¹⁰² Tetraphenylgermane was, in accordance with this assumption, recovered unchanged after treatment with triphenylsilyllithium.

Triphenylsilyltriphenyltin by triphenylgermyllithium. It was anticipated that the reaction of triphenylsilyltriphenyltin with triphenylgermyllithium would give triphenylsilyltriphenylgermane and triphenyltinlithium. However, no pure products were isolated. The difficulty may be that the reaction is not specific, *i.e.*, cleavage of the tin-phenyl bond by triphenylgermyllithium may be taking place.

Hexaphenyldisilane by triphenylmethyllithium. As would be expected on the basis of the low reactivity of triphenylmethyllithium, no cleavage of hexaphenyldisilane by this reagent was observed. Hexaphenyldisilane was recovered in almost quantitative yield.

¹⁰²D. Wittenberg, Chemistry Dept., Iowa State College, Ames, Iowa, has shown that tetraphenyltin is cleaved by an excess of two moles of triphenylsilyllithium to give hexaphenyldisilane. Private communication. 1958.

Relative Reactivities of Organometallic and Organosilylmetallic Compounds

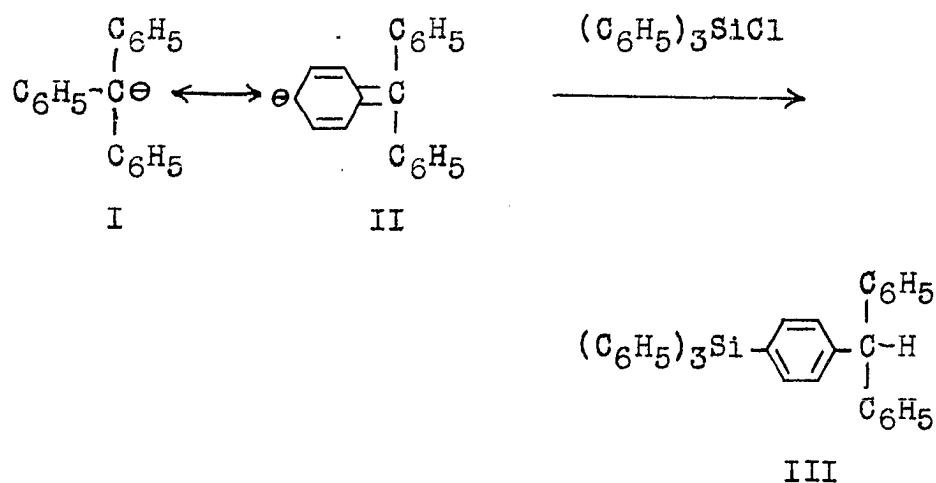
Although it is possible to compare the relative reactivities of organometallic and silylmetallic compounds toward specific functional groups, there appears to be no general way in which their relative reactivities may be related. For instance, *n*-butyllithium is a much better metalating agent than triphenylsilyllithium (refer to the historical section on metalation reactions), but in a competitive coupling reaction between phenyllithium and triphenylsilyllithium and chlorotriphenylsilane at -50° ,¹⁰³ hexaphenyldisilane is formed in 85 percent yield and tetraphenylsilane in only five percent yield. This section has, therefore, been subdivided so that specific comparisons between organometallic and organosilylmetallic compounds can be made.

Triphenylmethylmetallic and triphenylsilylmetallic compounds

The high order of reactivity of triphenylsilylmetallic compounds as compared to triphenylmethylmetallic compounds is due in large part to the ability of carbon to form stable multiple bonds. The triphenylmethyl anion may be represented by a total of 10 resonance structures, two of which are given

¹⁰³D. Wittenberg, Chemistry Dept., Iowa State College, Ames, Iowa. Private communication. 1958.

below. Isolation of *p*-triphenylsilylphenyldiphenylethane(III)



from the reaction of triphenylmethylsodium with chlorotriphenylsilane is strong evidence that structures such as II contribute greatly to the ground state of triphenylmethyl anion.

Reactions analogous to the formation of *p*-triphenylsilylphenyldiphenylmethane⁴⁹ are not known for silylmetallic compounds. This difference can be attributed to the inability of silicon to form stable multiple bonds. A smaller distribution of the negative charge in the triphenylsilyl anion renders it more nucleophilic (more reactive) than the triphenylmethyl anion.

There is evidence, however, that the triphenylsilyl anion receives some stabilization of the type described for triphenylmethyl anion. Cleavage of disilanes by silyllithium compounds to give new disilanes and less reactive silyl-

lithium compounds is best explained by postulating that the driving force for the cleavage is furnished by the increased stabilization derived in going from one silyllithium compound to another containing a larger number of phenyl groups. A second line of evidence for the resonance stabilization of silyllithium compounds is derived from the lithium cleavages of symmetrically substituted disilanes³ in tetrahydrofuran solution. It was found that as the methyl groups on the disilane were replaced by phenyl groups, the rate of cleavage by lithium to give the silyllithium compound increased markedly.

Triphenylsilylmetallic compounds react with benzophenone to give, after hydrolysis, benzhydryloxytriphenylsilane.^{4,22} However, the corresponding reaction of triphenylmethylsodium¹⁰⁴ or -magnesium bromide¹⁰⁵ gives hexaphenylethane and benzopinacol.

Triphenylmethylsodium¹⁰⁴ reacts with aliphatic ketones to give triphenylmethane by abstraction of the hydrogen atom alpha to the carbonyl group. The more reactive (and apparently less selective) triphenylsilyllithium adds to aliphatic ketones to give alpha-silylcarbinols as the main product and triphenylsilane as the by-product.²⁴

¹⁰⁴W. Schlenk and R. Ochs, Ber., 49, 608 (1916).

¹⁰⁵H. Gilman and R. E. Fothergill, J. Am. Chem. Soc., 51, 3149 (1929).

Cleavage of ethers

On the basis of present evidence, it appears likely that the cleavage of ethers is more readily effected by organometallic compounds than by silylmetallic compounds. Organosodium and -potassium compounds cleave diethyl ether readily, and for this reason are not ordinarily prepared in this solvent. Triphenylsilylpotassium,^{5,6} on the other hand, is obtained as a suspension in diethyl ether and appears to be quite stable in this medium. Phenyllithium decomposes rapidly in tetrahydrofuran solution⁷⁹ whereas triphenylsilyllithium³ decomposes at the rate of only about five percent per day in this solvent.

Reactions with chlorosilanes

It has been observed³⁸ that, generally speaking, the minimum temperature at which organolithium will couple with trialkyl- or triarylchlorosilanes is about -20° . This investigation has shown, on the other hand, that triphenylsilyllithium and chlorotriphenylsilane react instantly at -70° to give hexaphenyldisilane in 90 percent yield (refer to the Experimental section). Since these results would indicate that silyllithium compounds are more reactive toward chlorosilanes than organolithium compounds, a competitive reaction¹⁰³ was carried out at -50° between a mixture of phenyl-

lithium and triphenylsilyllithium and chlorotriphenylsilane. Hexaphenyldisilane was isolated in 85 percent yield as contrasted to only a five percent yield of tetraphenylsilane. These results clearly indicate that in coupling reactions involving chlorosilanes, silylmetallic compounds are more reactive than organometallic compounds.

Cleavage of disilanes

As pointed out earlier (refer to the Experimental and Discussion sections dealing with the cleavage of disilanes by silylmetallic compounds), disilanes are readily cleaved by silyllithium compounds to give new disilanes and less reactive silyllithium compounds. No reaction was observed, however, between phenyllithium in diethyl ether¹⁰⁰ or p-tollyllithium in tetrahydrofuran (this thesis, Experimental section) with hexaphenyldisilane. These results clearly demonstrate a higher order of reactivity for silyllithium compounds than for aryllithium compounds in the cleavage of disilanes.

Metalation reactions

Organolithium compounds in diethyl ether are well known for their excellent properties as metalating agents.¹⁰⁶

¹⁰⁶For a general discussion of metalation reactions involving organolithium compounds see H. Gilman and J. W. Morton, Org. Reactions, VIII, Chap. 6 (1954).

Recently it has been shown that the yields of 4-carboxy-dibenzofuran, obtained by metalation of dibenzofuran with *n*-butyllithium⁷⁸ in diethyl ether, followed by carbonation, are considerably improved by employing a mixture of diethyl ether and tetrahydrofuran.¹⁰⁷ Although tetrahydrofuran has thus been shown to enhance metalation reactions, treatment of diphenyl ether⁴⁴ or dibenzofuran³⁸ with triphenylsilyllithium in this solvent, followed by carbonation, gave only very low yields of the corresponding acids. Organolithium compounds thus appear to be more reactive in metalation reactions than silyllithium compounds. This may be due in part to greater bond strength of the carbon-hydrogen linkage as compared to the silicon-hydrogen linkage formed in metalation reactions.

Suggestions for Future Research

Further work should be done in an attempt to form new bonds between silicon and other elements. A possible approach would be through the reactions of silylmetallic compounds with various metal and nonmetal halides. A second approach would be through the reactions of silylmetallic compounds with the free elements. It is possible that reactive intermediates could be obtained in this way, which by further reaction with organic halides could give rise to new organosilicon

¹⁰⁷H. Gilman and R. D. Gorsich, J. Org. Chem., 22, 687 (1957).

compounds containing a variety of elements.

Further work should be carried out with the aim of isolating in a pure form the compound believed to be bis(triphenylsilyl)cadmium. Treatment of this compound with hydrogen chloride in benzene solution should give triphenylsilane and cadmium chloride, which would constitute a proof of structure. An attempt should be made to react the compound with benzoyl chloride or benzoic anhydride to give triphenylsilylphenyl ketone as an extension of the useful procedure for the preparation of ketones developed earlier in these laboratories for the carbon analogs.¹⁰⁸

Triphenylsilyltriphenyllead, the one remaining silicon-containing analog of hexaphenylethane which has not been described, can perhaps be prepared from the reaction of triphenylsilyllithium in tetrahydrofuran with chlorotriphenyllead.

Since triphenylsilyllithium⁴ and -potassium²² have been shown to react with benzophenone to give, after hydrolysis, benzhydryloxytriphenylsilane, it should be of interest to determine the mode of reaction of triphenylsilyllithium with thiobenzophenone. If the reaction occurs in a manner analogous to the reaction of triphenylsilyllithium and benzophenone,⁴ benzhydrylthiotriphenylsilane would be isolated.

¹⁰⁸H. Gilman and J. F. Nelson, Rec. trav. chim., 55, 518 (1936).

The possibility exists, however, that triphenylsilyldiphenylthiol may be isolated.

Recent interest in the relative reactivities of Group IV-B metallic compounds has created the need for a method of determining the relative reactivities of these reagents. A possible approach to determining the relative reactivities of triphenylsilyllithium and triphenylgermyllithium would be by taking advantage of their different mode of reaction with benzophenone. Triphenylgermyllithium gives rise to triphenylgermyldiphenylcarbinol¹⁰⁹ in contrast to the alkoxysilane obtained on addition of triphenylsilyllithium to benzophenone.⁴ Thus, addition of one equivalent of benzophenone to a mixture of one equivalent of triphenylsilyllithium and one equivalent of triphenylgermyllithium in tetrahydrofuran should give products which are easily separable by chromatography and from which the desired relative reactivities can be determined.

¹⁰⁹H. Gilman and G. W. Gerow, J. Am. Chem. Soc.; 77, 5740 (1955).

SUMMARY

This thesis has dealt with the formation and reactions of organosilylmetallic compounds.

A survey of the literature has been presented which includes published and unpublished work up to August, 1958.

In the synthesis of silylmetallic compounds, the use of tetrahydrofuran as a solvent was found to be particularly advantageous. Solutions of triphenylsilyllithium, methyl-diphenylsilyllithium and dimethylphenylsilyllithium were prepared in this solvent by lithium cleavage of the corresponding symmetrical disilanes. These solutions were found to be fairly stable over extended periods of time.

In attempting to prepare silylmetallic compounds containing metals other than the commonly encountered alkali metals, triphenylsilyllithium was reacted with a number of anhydrous metal halides. Of these, mercury (I), mercury (II), tin (IV) and lead (II) chlorides reacted with triphenylsilyllithium to give chlorotriphenylsilane in what appeared to involve the formation and disproportionation of silicon-metal bonds. A second group of metal chlorides, i.e., iron (III), tin (II), silver and copper (II) chlorides reacted with triphenylsilyllithium to give triphenylsilane. The mode of formation of triphenylsilane in these reactions is not known. Since water was excluded as far as possible from the reaction mixtures,

the role of tetrahydrofuran as a hydrogen donor is suggested. However, the chance that trace amounts of water were responsible for the formation of triphenylsilane cannot be excluded. Triphenylsilyllithium reacted with either zinc or aluminum chloride to give solutions from which no pure products were isolated. From the reaction of triphenylsilyllithium with cadmium chloride, a compound believed to be the significant bis(triphenylsilyl)cadmium was isolated. More work is needed to isolate this compound in pure form and to prove its structure.

Silylamines were isolated as the result of reactions between silyllithium compounds and primary and secondary amines. Isolation of these silylamines was in most cases remarkably simple.

The lithium salt of triphenylsilanethiol was prepared by the reaction of triphenylsilyllithium with elemental sulfur. This intermediate coupled with reactive organic halides to give the corresponding thiosilanes in good yields.

A series of silicon-containing acridine compounds was synthesized by the addition of triphenylsilyllithium to acridine. These stable silicon derivatives of acridine are currently under investigation with regard to their possible use as high temperature antioxidants.

It was demonstrated that disilanes are readily cleaved by silyllithium compounds to give new disilanes and less re-

active silyllithium compounds. On the basis of these results, a reactivity series for silyllithium compounds has been advanced. In like manner, hexaphenyldigermene is cleaved by two moles of triphenylsilyllithium to give hexaphenyldisilane in quantitative yield and triphenylgermyllithium.

In some related studies, tetraphenylsilane was unaffected by either methyldiphenylsilyllithium or dimethylphenylsilyllithium. Neither was tetraphenylgermane cleaved by triphenylsilyllithium. Triphenylmethyltriphenylsilane was recovered unchanged after treatment with triphenylsilyllithium as was hexaphenyldisilane after exposure to triphenylmethyllithium.

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