[Contribution from the Chemical Laboratory of Iowa State College]

THE PREPARATION AND CLEAVAGE STUDIES OF SOME ORGANOSILICON COMPOUNDS

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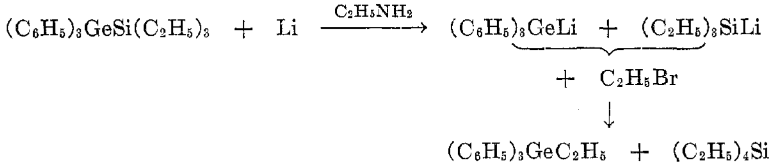
The only trialkylsilylmetallic compound which has been successfully synthesized and identified is triethylsilyllithium (1) prepared from triphenylgermyltriethylsilane and lithium in ethylamine.



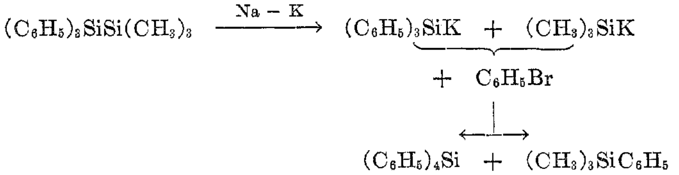
$$\begin{array}{r}(C_6H_5)_3GeSi(C_2H_5)_3 + Li \xrightarrow{C_2H_5NH_2} \underbrace{(C_6H_5)_3GeLi + (C_2H_5)_3SiLi} \\ + \; C_2H_5Br \qquad \\ \downarrow \qquad\quad \\ (C_6H_5)_3GeC_2H_5 + (C_2H_5)_4Si\end{array}$$

Triphenylsilylpotassium was first reported from the action of sodium-potassium alloy on phenylisopropyltriphenylsilane in ether (2). Concurrently, it was found that hexaphenyldisilane was cleaved smoothly with sodium-potassium alloy to give almost quantitative yields of triphenylsilylpotassium (3). Triphenylsilylpotassium was also formed from the cleavage of hexaphenyldisilane with potassium in di-*n*-butyl ether (3) and from the action of sodium-potassium alloy on triphenylethoxysilane (3), triphenylchlorosilane (3), triphenylsilane (4), and triphenylmethoxysilane (4). The reaction of hexaphenyldisilane with sodium-potassium alloy is advantageous since no by-products are formed and the yields are excellent.

$$(C_6H_5)_3SiSi(C_6H_5)_3 \xrightarrow{Na\text{-}K} 2\ (C_6H_5)_3SiK$$

In view of the ease of cleavage of the hexaaryldisilanes and the report of a reasonably stable trialkylsilyl-metallic compound, a study of cleavage reactions of hexaethyldisilane was initiated. Hexaethyldisilane has been prepared from the reaction of triethylbromosilane with sodium in a sealed tube (1); it was found that this compound could be prepared readily by refluxing triethylchlorosilane with sodium. Hexaethyldisilane seems to be unusually stable and all metallic cleavages thus far attempted have been unsuccessful.

Cleavage products have been isolated from the reaction of 1,1,1-triphenyl-2,2,2-trimethyldisilane, of 1,1,1-triphenyl-2,2,2-triethyldisilane, and of



$$\begin{array}{r}(C_6H_5)_3SiSi(CH_3)_3 \xrightarrow{Na - K} \underbrace{(C_6H_5)_3SiK + (CH_3)_3SiK} \\ + \; C_6H_5Br \qquad\quad \\ \longleftarrow\!\!\mid\!\!\longrightarrow \qquad\quad \\ (C_6H_5)_4Si + (CH_3)_3SiC_6H_5\end{array}$$

1,1,2,2-tetraphenyl-1,2-dimethyldisilane with sodium-potassium alloy. A possible explanation of the failure to cleave the hexaalkyldisilane may be the lack of resonance stabilization of the trialkylsilyl fragment as compared to the triphenylsilyl or diphenylalkylsilyl groupings.

Although hexaethyldisilane is resistant to metallic cleavage, it was found to be readily cleaved by both bromine and iodine to give the corresponding triethylhalosilane.

EXPERIMENTAL[1]

Triethylsilane. To a 500-ml., three-necked flask were added 200 ml. of dry ether and a small amount of lithium aluminum hydride to insure dryness. Then 85.5 g. (0.567 mole) of triethylchlorosilane and 15.0 g. (0.40 mole) of lithium aluminum hydride were added and the mixture was refluxed for 7 hours. After cooling, the mixture was carefully hydrolyzed, first with wet ether, followed by water, and finally 1:1 hydrochloric acid. The layers were separated, the ether layer was dried over sodium sulfate, and the ether was removed by distillation. The remaining liquid was fractionally distilled to give 36.3 g. (55%) of a clear liquid boiling at 103.5–104.5° (735 mm.), n_D^{20} 1.4100. A boiling point of 107° (733 mm.), n_D^{20} 1.4117 has been reported for triethylsilane (5).

Hexaethyldisilane. In a 250-ml. flask were placed 67.6 g. (0.45 mole) of triethylchlorosilane and 22.2 g. (0.965 g.-atom) of sodium. The mixture was heated and as soon as the sodium had melted, stirring was started; there immediately developed a deep purple coloration. The mixture was heated at the reflux temperature overnight. After cooling, 200 ml. of dry ether was added and the resulting mixture was filtered. The ether was distilled from the filtrate and the resulting oil subsequently was distilled to give 28.0 g. (54%) of a clear liquid boiling at 248–250° (735 mm.).[2] The reported boiling point is 255° (760 mm.) (1).

Phenyltrimethylsilane. To a mixture of 53.2 g. (0.45 mole) of trimethylethoxysilane and 50 ml. of dry ether was added an ethereal solution containing 0.46 mole of phenyllithium at a rate to maintain a constant reflux. The mixture was stirred for 8 hours following the completion of the phenyllithium addition. Subsequent to the addition of benzene to decrease the solubility of the lithium salts, the mixture was filtered and the ether and benzene were removed by distillation. The remaining liquid was fractionally distilled to yield 45.3 g. (72%) of phenyltrimethylsilane boiling at 166–167° (735 mm.), n_D^{20} 1.4896. The reported boiling point of phenyltrimethylsilane is 171.1–173.3° (758.4 mm.) (6).

Phenyltriethylsilane. An ethereal solution containing 0.20 mole of phenyllithium was added dropwise to 30.0 g. (0.20 mole) of triethylchlorosilane dissolved in 100 ml. of dry ether at a rate to maintain refluxing. After stirring for 16 hours the mixture was filtered and the ether was distilled from the filtrate. The residual material was twice distilled to give 12.0 g. (31.2%) of phenyltriethylsilane boiling at 231–232° (735 mm.). The product was redistilled under reduced pressure to yield a colorless liquid boiling at 71–72° (0.45 mm.), n_D^{20} 1.5024, d_{20} 0.8816, MR_D 64.5 (Calc'd, 64.0). The reported boiling point for phenyltriethylsilane is 238.3–238.5° (762.1 mm.) (7).

Benzyltriethylsilane. A solution containing 63.3 g. (0.50 mole) of benzyl chloride in 50 ml. of dry ether was added to a mixture of 200 ml. of dry ether and 12.3 g. (0.51 g.-atom) of magnesium turnings at a rate to maintain refluxing. The mixture was stirred for 12 hours following this addition and subsequently was cooled with an ice-salt bath. To the cooled solution was added dropwise 37.6 g. (0.25 mole) of triethylchlorosilane in 50 ml. of ether. The mixture was then warmed to reflux and there maintained for 46 hours. After cooling, the mixture was hydrolyzed with dilute hydrochloric acid; the ether layer was separated and dried over sodium sulfate. The ether and toluene were distilled off and the remaining liquid was vacuum-distilled, b.p. 69–71° (~0.1 mm.). The distillate was redistilled at 735 mm. to

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[1] The reactions herein described were run in an inert atmosphere of nitrogen. All melting and boiling points are uncorrected.

[2] Hexaethyldisilane was also distilled at 2.5 mm., boiling at 87–89°; it is a colorless, odorless liquid, d^{20} 0.8300, n_D^{20} 1.4759, MR_D Calc'd 78.8, Found 78.3.

give 38.0 g. (47%) of benzyltriethylsilane, b.p. 250–252°, n_D^{20} 1.5030. The reported boiling point of benzyltriethylsilane is 267–269° (760 mm.) (1).

1,2-Diphenyl-1,1,2,2-tetramethyldisilane. To a 500-ml., three-necked flask fitted with a dropping-funnel, stirrer, and condenser were added 105.0 g. (0.620 mole) of freshly distilled phenyldimethylchlorosilane, 35.0 g. (1.52 g.-atom) of sodium, and 200 ml. of dry xylene. The mixture was warmed to reflux; soon after the sodium had melted a deep blue color developed. The mixture was stirred at reflux temperature for 25 hours and subsequently was cooled and filtered. The solvent was distilled from the colorless filtrate. The residual material was distilled (735 mm.) to yield 2.0 g. of liquid boiling from 216–289° and 61.8 g. of distillate boiling from 289–302°. The latter fraction was twice redistilled to give 37.0 g. (44%) of product boiling at 128–130° (1.8 mm.) and melting at 34–35°.

Anal.[3] Calc'd for $C_{16}H_{22}Si_2$: Si, 20.75. Found: Si, 20.74, 21.00.

1,1,2,2-Tetraphenyl-1,2-dimethyldisilane. An ethereal solution containing 0.715 mole of phenyllithium in 615 ml. of ether was added dropwise to 76.0 g. (0.358 mole) of freshly distilled methyltriethoxysilane dissolved in 400 ml. of dry ether. The mixture was refluxed for 16 hours, after which time about 700 ml. of ether was removed by distillation and 500 ml. of dry petroleum ether (b.p. 60–70°) was added. Distillation was continued until the temperature of the vapors reached 45°. The gray mixture was cooled, filtered, and the solvent distilled from the orange filtrate. Vacuum-distillation of the residual material gave 70.0 g. of colorless liquid distilling over the range of 80–110° (0.2–1.0 mm.). This fraction was redistilled to give 60.0 g. (69.5%) of diphenylmethylethoxysilane boiling at 100–102° (0.3 mm.), n_D^{20} 1.5380. The reported boiling point is 171° (16 mm.), n_D^{20} 1.5440 (8).

Diphenylmethylchlorosilane was prepared in 92% yield from the above diphenylmethylethoxysilane by the method of Daudt and Hyde (8).

To 51.0 g. (0.219 mole) of diphenylmethylchlorosilane in 100 ml. of dry toluene was added 7.0 g. (0.33 g.-atom) of sodium. The mixture was warmed to reflux and stirring was begun when the sodium had melted; a purple color developed. Refluxing and stirring were continued for 2 days; the reaction mixture was then cooled and filtered. The toluene was distilled from the filtrate leaving 42.0 g. of a brown, semi-solid residue. This residue was dissolved in 50 ml. of hot benzene; 100 ml. of ethanol was added and the mixture was cooled and filtered to give 27.7 g. of colorless crystals melting at 140–142°. Two additional recrystallizations from a benzene-ethanol solution gave 22.8 g. of product melting at 145–146°. Another 6.0 g. of material of the same purity was obtained from the filtrate by concentration and recrystallization from benzene-ethanol. The total yield of 1,1,2,2-tetraphenyl-1,2-dimethyldisilane was 28.8 g. (66.7%).

Anal. Calc'd for $C_{26}H_{26}Si_2$: Si, 14.22. Found: Si, 14.29, 14.39.

1,1,1,2-Tetraphenyl-2,2-dimethyldisilane. An ethereal suspension containing 0.0308 mole of triphenylsilylpotassium was added dropwise to 7.3 g. (0.043 mole) of phenyldimethylchlorosilane in 50 ml. of dry ether. A white solid was formed with the evolution of heat. After stirring for 10 minutes, the mixture was hydrolyzed with wet ether. The mixture was filtered and the filtrate was washed with water; the ether layer was separated and dried over sodium sulfate. The ether was distilled off leaving a liquid which partially solidified on standing. This material was crystallized from 95% ethanol to yield 8.3 g. (68.4%) of a white solid melting at 79–81°. Three additional recrystallizations from 95% ethanol gave 5.8 g. of crystals melting at 85–86°.

Anal. Calc'd for $C_{26}H_{26}Si_2$: Si, 14.22. Found: Si, 14.19, 14.10.

Attempted metallic cleavage of hexaethyldisilane. A mixture of 8.3 g. (0.036 mole) of hexaethyldisilane and 5 ml. of sodium-potassium alloy (9) was stirred for 2 days. The light blue mixture was amalgamated (9) and force-siphoned into another flask with the aid of dry ether. Color Test I (10) of this blue solution was negative; the solution was hydrolyzed, first with wet ether and subsequently with water. There was no visible sign of reaction during

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[3] The silicon analyses were carried out by the procedure of Gilman, Hofferth, Melvin, and Dunn, *J. Am. Chem. Soc.*, **72**, 5767 (1950).

TABLE I

ATTEMPTED CLEAVAGE REACTIONS OF HEXAETHYLDISILANE

AMT. OF Et_6Si_2	REAGENT	AMT. OF REAGENT	SOLVENT	TEMP., °C.	TIME, hrs.	RECOVERY, %
0.036 mole	Na-K alloy	5 ml. of 1:5 alloy	None	Room temp.	48	73
.036 mole	Na-K alloy	2 ml. of 1:5 alloy	None	150	64	79
.036 mole	Na-K alloy plus 15 drops of tetrahydrofuran[a]	5 ml. of 1:5 alloy	Et_2O	32	48	71[b]
.036 mole	Na-K alloy	2 ml. of 1:5 alloy	Ethylene glycol dimethyl ether[c]	84	48	69[b]
.157 mole	Na	0.279 g.-atom	Liq. NH_3	−33	37	99
.012 mole	Rb	.024 g.-atom	None[d]	50	22	49
.20 mole	C_6H_5Li	.20 mole	Et_2O	Room temp.	17	70

[a] Tetrahydrofuran has recently been found in these laboratories to have a catalytic action on the cleavage of Si-Si and Ge-Ge bonds. [b] Triphenylchlorogermane was added prior to hydrolysis; no triphenylgermyl-triethylsilane (reference 1) was isolated. [c] This solvent has been found to be effective for the cleavage of certain Si-Si compounds; Brook and Gilman, *J. Am. Chem. Soc.*, **75**, in press. [d] After 22 hours the mixture was cooled, 10 ml. of dry ethyl ether and 10 ml. of dry isopropyl ether were added, and refluxing was continued for an additional 24 hours.

hydrolysis, except for the disappearance of the blue color. The layers were separated, the ether layer was dried over sodium sulfate, and the ether was removed by distillation. The residual liquid was distilled to yield 6.0 g. (73% recovery) of hexaethyldisilane, boiling at 74–75° (1.1–1.2 mm.), n_D^{20} 1.4770. A summary of additional attempted cleavages of hexaethyldisilane by procedures similar to that above is given in Table I.

Reaction of 1,1,1-triphenyl-2,2,2-trimethyldisilane with sodium-potassium alloy. To a solution containing 15.7 g. (0.0477 mole) of 1,1,1-triphenyl-2,2,2-trimethyldisilane (3) in 100 ml. of dry ether was added 6.5 ml. of a 1:5 sodium-potassium alloy. A deep green color soon appeared, accompanied by the formation of a solid green material. Color Test I was positive. The green color of the mixture deepened and after 5.5 hours, 15.7 g. (0.10 mole) of bromobenzene in 40 ml. of dry ether was added, with a resulting evolution of heat. The mixture was carefully hydrolyzed with water and filtered, leaving a solid residue weighing 13.2 g. From this residue there was obtained 1.5 g. (12%) of hexaphenyldisilane melting at 354–357° and 7.3 g. (45%) of tetraphenylsilane melting at 231–232°. The products were separated by the use of benzene[4] and were identified by mixture melting points. The original filtrate was separated and the solvent was evaporated from the ethereal layer; distillation of the resulting liquid gave 0.6 g. (8%) of colorless product boiling at 164–166° (735 mm.), n_D^{20} 1.5155. An infrared spectrum[5] of this liquid, when compared with that of an authentic sample of phenyltrimethylsilane, indicated the substance to be phenyltrimethylsilane and a small amount of bromobenzene.

TABLE II

ADDITIONAL ATTEMPTED CLEAVAGE REACTIONS OF ORGANOSILICON COMPOUNDS WITH SODIUM-POTASSIUM ALLOY[a]

COMPOUND	AMT., moles	AMT. OF ALLOY, ml.	TIME	RECOVERY, %
Triethylsilane	0.07	5	26 hrs.	43
Phenyltrimethylsilane	.062	7	8 days	38
Benzyltriethylsilane	.05	5.5	8 days	83

[a] These experiments were carried out at room temperature; anhydrous ethyl ether was used as a solvent.

In a second run, using 18.0 g. of 1,1,1-triphenyl-2,2,2-trimethyldisilane, and 2.0 ml. of sodium-potassium alloy followed by 27.4 g. of iodobenzene there were isolated 9.3 g. (50%) of tetraphenylsilane melting at 230–231° and 2.9 g. of a liquid boiling at 172–175° (735 mm.). No hexaphenyldisilane was obtained from this run.

Reaction of 1,1,1-triphenyl-2,2,2-triethyldisilane and sodium-potassium alloy. To a mixture of 20.0 g. (0.0535 mole) of 1,1,1-triphenyl-2,2,2-triethyldisilane (9) and 6.5 ml. of 1:5 sodium-potassium alloy was added 60 ml. of dry ether. On stirring, the mixture became dark green. After 5 minutes sufficient green precipitate had formed to make stirring difficult; an additional 80 ml. of dry ether was added. After 7 hours, 19.5 g. (0.124 mole) of bromobenzene was added and the mixture subsequently was hydrolyzed with water. Filtration gave 12.0 g. of solid; the material was recrystallized from benzene-ethanol to give 7.0 g. (39%) of tetraphenylsilane melting at 234.5–235° (mixture m.p. not depressed).

From the ethereal filtrate there was obtained 3.0 ml. of a clear liquid boiling at 82° (0.23 mm.), n_D^{20} 1.4987. The infrared spectrum of this liquid was identical with that of authentic phenyltriethylsilane except for a band at 9.35 μ with the former.

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[4] Tetraphenylsilane is soluble in benzene, while hexaphenyldisilane is insoluble in this solvent.

[5] The authors are grateful to Dr. V. A. Fassel and Mr. M. Margoshes for the infrared absorption data.

Reaction of 1,1,2,2-tetraphenyl-1,2-dimethyldisilane and sodium-potassium alloy. A mixture of 10.0 g. (0.0254 mole) of 1,1,2,2-tetraphenyl-1,2-dimethyldisilane, 4 ml. of sodium-potassium alloy, and 20 ml. of dry ether was placed in a 500-ml. flask. As soon as stirring was started, a golden yellow color developed. This color gradually deepened and after 5 minutes an additional 50 ml. of dry ether was added. Twenty-four hours later the mixture had become greenish-brown in color. To the mixture was added 23.0 g. (0.15 mole) of bromobenzene dissolved in 100 ml. of dry ether. The color changed from greenish-brown to a deep maroon with the evolution of heat. Following hydrolysis with dilute hydrochloric acid, the ether layer was separated and dried over sodium sulfate. The ether was distilled off and heating was continued until the vapors reached 160°. There remained 14.0 g. of a brown liquid. This liquid was dissolved in refluxing 95% ethanol, and was filtered hot, cooled, and refiltered to give a sticky solid. Repeated recrystallizations of this solid from 95% ethanol yielded 0.86 g. of a light yellow solid melting at 64–66°. An additional recrystallization from 95% ethanol raised the melting point of the 0.5 g. (4%) of white solid to 66–67°. A mixture melting point with an authentic triphenylmethylsilane sample was not depressed.

A summary of attempted cleavages of additional organosilicon compounds by procedures similar to those above is given in Table II.

Cleavage of hexaethyldisilane by halogens. (a) With bromine. To 16.6 g. (0.074 mole) of hexaethyldisilane was added 15.6 g. (0.098 mole) of bromine dissolved in ether. The reddish color disappeared after stirring for 15 minutes. The ether was distilled off and the remaining liquid was distilled (735 mm.) to give 24.4 g. (87%) of triethylbromosilane boiling at 162–165°. The reported boiling point is 162–163° (760 mm.) (11).

(b) With iodine. To a solution of 16.6 g. (0.074 mole) of hexaethyldisilane in 50 ml. of carbon tetrachloride was added 19 g. (0.075 mole) of iodine dissolved in 50 ml. of carbon tetrachloride. There was no noticeable evolution of heat. After stirring for 3 days, the solution was still deep purple in color. The solution was cooled with an ice-bath, 15.0 g. (0.16 g.-atom) of powdered copper was added, heat was liberated, and the liquid became colorless. The carbon tetrachloride was distilled off and the remaining liquid was distilled to give 20 g. of a liquid boiling over the range 182–203° (735 mm.). As the liquid was distilled, it gradually became pink and deepened in color; the liquid was decolorized and remained colorless when stored over copper powder. This material was redistilled to give 19.0 g. (86%) of crude triethyliodosilane boiling over the range 185–195° (735 mm.). The reported boiling point of triethyliodosilane is 191.5° (752.4 mm.) (12).

To a suspension of 0.0308 mole of triphenylsilylpotassium in ether was added 10.0 g. of the above liquid dissolved in 50 ml. of ether. Heat was liberated and subsequent to hydrolysis with water, removal of the ether and crystallization from 95% ethanol, there was obtained 9.2 g. (80%) of 1,1,1-triphenyl-2,2,2-triethyldisilane melting at 96.5–97.5° (mixture m.p. not depressed).

SUMMARY

The preparations of triethylsilane, benzyltriethylsilane, and hexaethyldisilane from triethylchlorosilane are reported. Phenyltrimethylsilane and phenyltriethylsilane have been prepared from the corresponding trialkylethoxysilanes. 1,2-Diphenyl-1,1,2,2-tetramethyldisilane, 1,1,1,2-tetraphenyl-2,2-dimethyldisilane, and 1,1,2,2-tetraphenyl-1,2-dimethyldisilane have been synthesized.

A study has been made of the possibility of metallic cleavage of hexaethyldisilane; those cleavages attempted were unsuccessful. However, hexaethyldisilane was found to be cleaved readily by halogens. Products indicative of cleavage have been isolated from the reaction of 1,1,1-triphenyl-2,2,2-trimethyldisilane, 1,1,1-triphenyl-2,2,2-triethyldisilane, and 1,1,2,2-tetraphenyl-1,2-dimethyldisilane with sodium-potassium alloy.

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