ml. of THF. The blue color acquired by the reaction mixture gradually changed to brown as the addition continued. After the addition was complete, Color Test I[8] was weakly positive. The reaction mixture was stirred for 3 hr. at room temperature and subsequently hydrolyzed with water. The organic layer was combined with ether extracts of the aqueous layer and dried over sodium sulfate. Evaporation of solvents left an oil which was dissolved in petroleum ether (b.p. 60–70°). On cooling, 0.15 g. of crystals, m. 160–170°, was deposited. These were recrystallized from petroleum ether (b.p. 60–70°) to give a small quantity of needles, m.p. 174–175°. A mixture melting point with an authentic sample of benzopinacol was not depressed, and the infrared spectra were identical. The petroleum ether from which the benzopinacol had deposited was evaporated. The resulting oil was dissolved in ethanol, from which 0.21 g. of white solid, m. 125–140°, was deposited. This material was recrystallized from ethanol to give 0.1 g. of diamond-shaped crystals, m.p. 142–144°, which was identified as 1,2-dimethyl-1,1,2,2-tetraphenyldisilane by a mixture melting point with an authentic sample. The ethanol solution, from which the 1,2-dimethyl-1,1,2,2-tetraphenyldisilane was isolated, was concentrated and chilled. There was deposited 1.09 g. (19%) of needles, m.p. 63–64°. Recrystallization from ethanol did not change the melting point. On the basis of an infrared spectrum which showed a broad Si–O band at 9.5 μ and Si–CH_3 bands at 8.0 and 12.7 μ, this product was assigned the structure of VI.

Anal. Calcd. for $C_{26}H_{24}OSi$: Si, 7.38. Found: Si, 7.35, 7.42.

Dimethylphenylsilyllithium (V) and Benzophenone.—To a solution of 6.75 g. (0.0370 mole) of benzophenone in 75 ml. of THF was added dropwise a solution of V prepared from 5.0 g. (0.0185 mole) of 1,1,2,2-tetramethyl-1,2-diphenyldisilane and 0.7 g. (0.1 g.-atom) of lithium in 75 ml. of THF; 10 hr. after the addition was complete, Color Test I[8] was negative. The reaction mixture was hydrolyzed with water. The organic layer was combined with ether extracts of the aqueous layer and dried over sodium sulfate. Evaporation of solvents left an oil which was dissolved in petroleum ether (b.p. 60–70°). There was formed 0.5 g. of diamond-shaped crystals, m. 170–176°. This material was recrystallized from benzene to give 0.25 g. of crystals, m.p. 181–183°, identified as benzopinacol on the basis of a mixture melting point and a comparison of the infrared spectrum with that of an authentic sample.

Evaporation of the petroleum ether from which the benzopinacol had deposited left an oil which was distilled at 0.05 mm. Two main fractions were collected. The first, 3.57 g., b.p. 104–107°, was dissolved in petroleum ether (b.p. 60–70°) and chilled. There was formed 0.4 g. (6%) of crystals, m.p. 67–68°, which was shown to be benzhydrol by a mixture melting point with an authentic sample and a comparison of the infrared spectra. The petroleum ether from which the benzhydrol had crystallized was evaporated. The presence of benzophenone in the resulting oil was shown by the formation of a 2,4-dinitrophenylhydrazone, 1.3 g., m.p. 238–240°. The infrared spectrum of the oil from which the benzophenone had been removed indicated the presence of some 1,1,2,2-tetramethyl-1,2-diphenyldisilane, but none was isolated.

The second fraction from the distillation consisted of 2.9 g., b.p. 139–143°, $n^{20}D$ 1.5705. This was redistilled at 0.05 mm. to give 2.36 g. (20%) of VII, b.p. 145–147°, $n^{20}D$ 1.5708. This oil crystallized slowly on standing for several days and melted at 36–38°. The infrared spectrum showed peaks at 9.5 μ (Si–O) and 8.0 μ (Si–CH_3). The product was too soluble in common solvents to be recrystallized.

Anal. Calcd. for $C_{21}H_{22}OSi$: C, 79.19; H, 6.96; *MR*,[9] 99.01. Found: C, 79.27, 79.17; H, 6.98, 6.86; *MR*, 99.19.

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(9) The values used in the calcd. *MR* were those of Vogel, *et al.*, *Chem. Ind.* (*London*), 358 (1950); and Vogel, *et al.*, *Chem. Ind.* (*London*), 19 (1953).

AMES, IOWA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Cleavage of Symmetrically Substituted Disilanes by Lithium in Tetrahydrofuran

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The cleavage of symmetrically substituted disilanes containing methyl and phenyl groups by lithium in tetrahydrofuran is reported. From $(CH_3)_2C_6H_5SiSiC_6H_5(CH_3)_2$ was obtained $(CH_3)_2C_6H_5SiLi$ while $CH_3(C_6H_5)_2SiSi(C_6H_5)_2CH_3$ gave $CH_3(C_6H_5)_2SiLi$. Derivatives were prepared with chlorotrimethylsilane and with chlorotriphenylsilane under conditions where the chlorosilane was present in excess. Addition of chlorotriphenylsilane to either silylmetallic resulted in a halogen-metal interconversion reaction in which hexaphenyldisilane and other coupling products were obtained.

The formation of silylmetallic compounds in which the metal is sodium, potassium or lithium has been reported by several investigators. Triphenylsilylpotassium was prepared[1] by Benkeser and Severson by way of the cleavage of phenylisopropyltriphenylsilane by sodium–potassium alloy in diethyl ether. Subsequent to this work, the formation of triphenylsilylpotassium was demonstrated[2] as a result of the cleavage of hexaphenyldisilane by sodium–potassium alloy in diethyl ether. The desirability of eliminating the use of sodium–potassium alloy led to an investigation[3] which showed that hexaphenyldisilane was cleaved readily by lithium, sodium or potassium in ethylene glycol dimethyl ether (GDME). These triphenylsilylmetallic solutions, however, suffered from a serious disadvantage in that they were unstable over extended periods of time.

As an extension of the study of the formation and reactions of silylmetallic compounds, we have carried out cleavages of symmetrically substituted disilanes containing methyl and phenyl groups by lithium in tetrahydrofuran (THF).

Solutions of II in THF were found to be fairly stable over extended periods of time at room temperature, a distinct advantage over the use of GDME as a solvent. The yield of the derivative 1,1,1-trimethyl-2,2,2-triphenyldisilane, prepared by

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(1) R. A. Benkeser and R. G. Severson, THIS JOURNAL, **73**, 1424 (1951).

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

(3) (a) A. G. Brook and H. Gilman, *ibid.*, **76**, 278 (1954); (b) see also A. G. Brook, *Chem. in Can.*, **7**, 43 (1955).

reaction of II with chlorotrimethylsilane, only decreased from 79 to 74% after the reagent had been allowed to stand for 20 hr. at room temperature. Under conditions of reflux, however, decomposition of II to unidentified products was rapid.

$$\underset{\text{I}}{(C_6H_5)_3SiSi(C_6H_5)_3} \xrightarrow[\text{THF}]{\text{Li}} \underset{\text{II}}{2(C_6H_5)_3SiLi} \quad \text{(1a)}$$

$$\underset{\text{III}}{CH_3(C_6H_5)_2SiSi(C_6H_5)_2CH_3} \xrightarrow[\text{THF}]{\text{Li}} \underset{\text{IV}}{2CH_3(C_6H_5)_2SiLi} \quad \text{(1b)}$$

$$\underset{\text{V}}{(CH_3)_2C_6H_5SiSiC_6H_5(CH_3)_2} \xrightarrow[\text{THF}]{\text{Li}} \underset{\text{VI}}{2(CH_3)_2C_6H_5SiLi} \quad \text{(1c)}$$

Derivatives of IV and VI were prepared by reaction with chlorotriphenylsilane and with chlorotrimethylsilane.

$$(CH_3)_2C_6H_5SiLi + (C_6H_5)_3SiCl \longrightarrow (CH_3)_2C_6H_5SiSi(C_6H_5)_3\ (45\%) + (C_6H_5)_3SiSi(C_6H_5)_3\ (2.3\%) \quad \text{(2a)}$$

$$(CH_3)_2C_6H_5SiLi + (CH_3)_3SiCl \longrightarrow (CH_3)_2C_6H_5SiSi(CH_3)_3\ (47\%) \quad \text{(2b)}$$

$$CH_3(C_6H_5)_2SiLi + (C_6H_5)_3SiCl \longrightarrow CH_3(C_6H_5)_2SiSi(C_6H_5)_3\ (52\%) \quad \text{(2c)}$$

$$CH_3(C_6H_5)_2SiLi + (CH_3)_3SiCl \longrightarrow CH_3(C_6H_5)_2SiSi(CH_3)_3\ (74\%) \quad \text{(2d)}$$

When derivatization was carried out by a reaction with chlorotriphenylsilane, the mode of addition was found to be important. The results given above were obtained by the addition of the silylmetallic compound to chlorotriphenylsilane and to chlorotrimethylsilane. Addition of chlorotriphenylsilane to the silylmetallic compound gave rise to different results as

$$(C_6H_5)_3SiCl + (CH_3)_2C_6H_5SiLi \longrightarrow (C_6H_5)_3SiSi(C_6H_5)_3\ (35\%) + (CH_3)_2C_6H_5SiSiC_6H_5(CH_3)_2\ (71\%) \quad \text{(3a)}$$

$$(C_6H_5)_3SiCl + CH_3(C_6H_5)_2SiLi \longrightarrow (C_6H_5)_3SiSi(C_6H_5)_3\ (27\%) + CH_3(C_6H_5)_2SiSi(C_6H_5)_2CH_3{}^4 + CH_3(C_6H_5)_2SiSi(C_6H_5)_3{}^4 \quad \text{(3b)}$$

Formation of the products of (3a) and (3b) is explained readily on the basis of a halogen–metal interconversion reaction. Thus reaction 3b may be interpreted as

$$CH_3(C_6H_5)_2SiLi + (C_6H_5)_3SiCl \longrightarrow CH_3(C_6H_5)_2SiCl + (C_6H_5)_3SiLi \quad \text{(4a)}$$

Accompanying this halogen–metal interconversion reaction are the various possible coupling reactions

$$CH_3(C_6H_5)_2SiCl + (C_6H_5)_3SiLi \longrightarrow CH_3(C_6H_5)_2SiSi(C_6H_5)_3 \quad \text{(4b)}$$

$$(C_6H_5)_3SiCl + (C_6H_5)_3SiLi \longrightarrow (C_6H_5)_3SiSi(C_6H_5)_3 \quad \text{(4c)}$$

$$CH_3(C_6H_5)_2SiCl + CH_3(C_6H_5)_2SiLi \longrightarrow CH_3(C_6H_5)_2SiSi(C_6H_5)_2CH_3 \quad \text{(4d)}$$

It is surprising that the unsymmetrical coupling product, $(CH_3)_2C_6H_5SiSi(C_6H_5)_3$, could not be obtained from reaction 3a. This result leads one to believe that the first step of this reaction is a rapid halogen–metal interconversion

$$(CH_3)_2C_6H_5SiLi + (C_6H_5)_3SiCl \longrightarrow (CH_3)_2C_6H_5SiCl + (C_6H_5)_3SiLi \quad \text{(5a)}$$

which in the presence of a large excess of VI leads to immediate coupling as

$$(CH_3)_2C_6H_5SiLi + (CH_3)_2C_6H_5SiCl \longrightarrow (CH_3)_2C_6H_5SiSiC_6H_5(CH_3)_2 \quad \text{(5b)}$$

As the process depicted by equations 5a and 5b continues, triphenylsilyllithium (II) builds up in the system, and the formation of I becomes important as shown by equation 4c. In this way the unsymmetrical coupling reaction

$$(CH_3)_2C_6H_5SiCl + (C_6H_5)_3SiLi \longrightarrow (CH_3)_2C_6H_5SiSi(C_6H_5)_3 \quad \text{(5c)}$$

has little chance to occur.

As a check of the postulates just made concerning the reaction of VI and chlorotriphenylsilane, an experiment was carried out in which one mole equivalent of chlorotriphenylsilane was added to a mixture of one mole equivalent of II and one mole equivalent of VI. The products were I (65%) and V (61%). Again none of the unsymmetrical coupling product was obtained. It was noted during the addition of the chlorotriphenylsilane that compound I did not begin to precipitate until approximately 0.5 mole equivalent of the chlorotriphenylsilane had been added. During this first part of the addition, reactions 5a and 5b were probably taking place exclusive of (5c) and (4c).

The increase in resonance stabilization afforded by the interchange presumably acts as a driving force for the halogen–metal interconversion reactions given here. Halogen–metal interconversion in these cases occurs quickly in the presence of excess silylmetallic compound, and only to a slight extent, if at all, in the presence of excess chlorotriphenylsilane.

Halogen–metal interconversion reactions of a similar nature have been reported. Hexaphenyldisilane and hexaphenylethane were obtained[5] by the interaction of triphenylsilylpotassium and chlorotriphenylmethane. Hexaphenyldigermane has been reported[6] as one of the products obtained from the reaction of triphenylgermyllithium with chlorotriphenyltin. From triphenylgermylpotassium and chlorotriphenylsilane these workers[7] obtained hexaphenyldisilane.

Experimental[8]

Materials.—Chlorodimethylphenylsilane and chloromethyldiphenylsilane were kindly supplied by the General Electric Company. Compounds I,[9] III[10] and V[10] were prepared in accordance with reported directions. THF (Eastman Kodak Co. white label) was dried by distilling from sodium wire into a flask containing powdered lithium aluminum hydride. Redistillation from the lithium aluminum hydride ensured complete dryness.

Cleavage of Hexaphenyldisilane (I).—To a rapidly stirred mixture of 15 g. (0.029 mole) of hexaphenyldisilane

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[4] Only a partial separation of these two compounds was made.

[5] A. G. Brook, H. Gilman and L. S. Miller, THIS JOURNAL, **75**, 4759 (1953).

[6] H. Gilman and C. W. Gerow, *J. Org. Chem.*, **22**, 334 (1957).

[7] H. Gilman and C. W. Gerow, THIS JOURNAL, **78**, 5823 (1956).

[8] All reactions were carried out under an atmosphere of dry nitrogen using oven-dried glassware. All melting points are uncorrected.

[9] H. Gilman and G. E. Dunn, THIS JOURNAL, **73**, 5077 (1951).

[10] A. G. Smith, Masters Thesis, Iowa State College, 1953.

and 3.0 g. (0.43 g. atom) of finely cut lithium wire was added sufficient THF to form a thick paste. A yellow color formed immediately which gradually became more intense. A total of 150 ml. of THF was added dropwise. After stirring for about 3 hr. at room temperature, the cleavage was complete as evidenced by the complete dissolution of hexaphenyldisilane. The orange-brown solution was filtered through glass wool into an addition funnel. A 25-ml. aliquot was added to a stirred solution of 2.0 ml. of chlorotrimethylsilane in 25 ml. of THF. The orange-brown color was discharged immediately to give a colorless solution and a negative Color Test I.[11] The reaction mixture was hydrolyzed with water. The THF layer was combined with ether extracts of the aqueous layer and dried over sodium sulfate. Evaporation of solvents left a solid material which was crystallized from ethanol to give 2.54 g. (79%) of 1,1,1-trimethyl-2,2,2-triphenyldisilane, m.p. 108–109°. This product was identified by a mixed melting point and by comparison of the infrared spectrum with that of an authentic sample.

The remaining triphenylsilyllithium solution was allowed to stand at room temperature for a period of 20 hr. Repetition of the procedure just described gave 2.38 g. (74%), m.p. 108–109°.

The bulk of the solution was refluxed for 24 hr. Derivatization of a 25-ml. aliquot as before gave only 0.2 g. (6%) of impure product, m. 101–108°. Recrystallization did not improve the melting point.

Cleavage of 1,1,2,2-Tetramethyl-1,2-diphenyldisilane (V).—To a rapidly stirred mixture of 10.0 g. (0.037 mole) of V and 1.4 g. (0.2 g. atom) of lithium was added sufficient THF to form a thick paste. After about 30 min. a yellow color began to form. A total of 100 ml. of THF was added dropwise over a period of 1 hr. The solution gradually became brown. The course of the cleavage was followed by periodically titrating 1-ml. aliquots of the reaction mixture with standard acid. After stirring for 5.5 hr. at room temperature, there was no further increase in the titration value, and the muddy-brown solution (92 ml.) was filtered through glass wool into an addition funnel.

Forty-six ml. of the solution was added to a stirred solution of 25 g. (0.085 mole) of distilled chlorotriphenylsilane (95% by titration) in 100 ml. of THF. Some heat was evolved during the addition, and Color Test I[11] was negative immediately after the addition was complete. The reaction mixture was hydrolyzed with water and filtered to give 0.46 g. (2.3%) of hexaphenyldisilane, m.p. 367–369° (mixed melting point). The organic layer was dried over sodium sulfate. Evaporation of the solvent left a solid which was swirled with petroleum ether (b.p. 60–70°) and filtered. There was obtained 12.2 g. of triphenylsilanol, m.p. 153–156°, identified by a mixed melting point. Evaporation of the petroleum ether left a pasty mass which was recrystallized from ethanol to give 6.6 g. (45%) of crude 1,1-dimethyl-1,2,2,2-tetraphenyldisilane, with m.p. 79–84°. Several recrystallizations from ethanol gave 4.6 g. (32%), m.p. 84–85°. A mixed melting point with an authentic sample, m.p. 84–85°, was not depressed, and the infrared spectra were identical.

Forty-six ml. of the dimethylphenylsilyllithium solution was added dropwise to a stirred solution of 5.0 ml. of chlorotrimethylsilane in 50 ml. of THF. During the addition considerable heat was evolved. The color of the silylmetallic was discharged, and Color Test I[11] was negative after the addition was complete. After hydrolysis of the reaction mixture with water, the aqueous layer was extracted with ether, and the combined organic layer was dried over sodium sulfate. Evaporation of the solvents left a thin oil which was distilled to give 3.61 g. (47%) of pentamethylphenyldisilane, b.p. 112–115° (30 mm.), $n^{20}_{\rm D}$ 1.5055. Redistillation gave 3.1 g. (40%) of product, b.p. 113–114.5° (25 mm.), $n^{20}_{\rm D}$ 1.5056, d^{20}_{20} 0.8738.

Anal. Calcd. for $C_{11}H_{20}Si_2$: C, 63.38; H, 9.65; *MR*,[12] 70.89. Found: C, 63.52, 63.54; H, 9.44, 9.71; *MR*, 70.82.

Addition of Chlorotriphenylsilane to Dimethylphenylsilyllithium (VI).—To a stirred solution of VI prepared by the method described above from 5.0 g. (0.0185 mole) of 1,1,2,2-tetramethyl-1,2-diphenyldisilane (V) and 0.7 g. (0.1 g. atom) of lithium in 50 ml. of THF was added dropwise a solution of 14.2 g. (0.048 mole) of chlorotriphenylsilane in 50 ml. of THF. When the addition was complete, Color Test I[11] was negative. After hydrolysis with water, filtration gave 7.32 g. (38%) of hexaphenyldisilane, m.p. 367–369°, identified by a mixed melting point. The organic layer was combined with ether extracts of the aqueous layer and dried over sodium sulfate. Evaporation of the solvents left an oil which did not deposit crystals from ethanol, indicating that 1,1-dimethyl-1,2,2,2-tetraphenyldisilane was absent. The ethanol was evaporated. The resulting oil was swirled with petroleum ether (b.p. 60–70°) and filtered to give 3.02 g. of triphenylsilanol, m.p. 154–157°, identified by a mixed melting point. Evaporation of the petroleum ether left an oil which was distilled at 0.005 mm. After collecting a 0.31-g. forerun, b.p. 74–77°, the main fraction, 2.59 g., b.p. 77–81°, was obtained. Both fractions crystallized quickly when seeded with V and melted at 33–35°. The combined yield of V was 58%. The residue from the distillation could not be crystallized.

In a second run, 75 ml. of a solution of dimethylphenylsilyllithium was prepared from 7.0 g. (0.026 mole) of V and 0.7 g. (0.1 g. atom) of lithium in 70 ml. of THF.

To 54 ml. of this solution was added a solution of 14.2 g. (0.048 mole) of chlorotriphenylsilane in 50 ml. of THF. Work-up was the same as in the previous run. There was obtained 6.71 g. (35%) of hexaphenyldisilane, m.p. 366–368° (mixed melting point), and 3.53 g. (71%) of V, b.p. 101–102.5° (0.1 mm.), m.p. 33–35°.

The remaining 21 ml. of the dimethylphenylsilyllithium solution was hydrolyzed with water. The organic layer, after drying over sodium sulfate, was evaporated. The resulting oil was dissolved in petroleum ether (b.p. 60–70°) and chromatographed on an alumina column. Evaporation of the petroleum ether left 0.2 g. of an oil which could not be induced to crystallize. An infrared spectrum of this oil was almost identical with a spectrum of V. There was no Si–O–Si band present at 9.5 μ.

Addition of Chlorotriphenylsilane to a Mixture of Triphenylsilyllithium (II) and Dimethylphenylsilyllithium (VI).—To a stirred solution of II and VI prepared from 3.84 g. (0.0074 mole) of hexaphenyldisilane (I) and 0.7 g. (0.1 g. atom) of lithium in 50 ml. of THF and 2.0 g. (0.0074 mole) of 1,1,2,2-tetramethyl-1,2-diphenyldisilane (V) and 0.7 g. (0.1 g. atom) of lithium, respectively, was added a solution of 4.35 g. (0.0148 mole) of chlorotriphenylsilane in 30 ml. of THF. After about half of the chlorotriphenylsilane solution had been added, Compound I began to precipitate. After the addition was complete, the reaction mixture was stirred for 1 hr. Color Test I[11] was strongly positive. After hydrolysis with water, 5.0 g. (65%) of hexaphenyldisilane, m.p. 366–368° (mixed melting point), was obtained by filtration. The organic layer was dried over sodium sulfate and subsequently evaporated. The resulting oil was swirled with petroleum ether (b.p. 60–70°) and filtered to give 1.0 g. of triphenylsilanol, m.p. 147–150°, identified by a mixed melting point. Evaporation of the petroleum ether left an oil which was dissolved in hot ethanol. Since no crystals were formed as the solution cooled, the ethanol was evaporated. Distillation of the resulting oil at 0.1 mm. gave a 0.27-g. forerun, b.p. 102–105°, and a 0.94-g. fraction, b.p. 105–110°. Both fractions crystallized when seeded with V and melted at 33–35°. The combined yield was 61%. The residue from the distillation deposited a trace of unidentified solid from ethanol, m. 160–230°.

Cleavage of 1,2-Dimethyl-1,1,2,2-tetraphenyldisilane (III).—To a rapidly stirred mixture of 5.0 g. (0.0127 mole) of III and 0.7 g. (0.1 g. atom) of lithium was added a few drops of THF. A brown color formed immediately, and heat was evolved. A total of 70 ml. of THF was added dropwise. After 1 hr., there was no further increase in the titration value of a 1-ml. aliquot of the reaction mixture. The solution (76 ml.) was decanted through glass wool.

Thirty ml. of methyldiphenylsilyllithium solution was added to a stirred solution of 3.0 g. (0.010 mole) of chlorotriphenylsilane in 50 ml. of THF. Heat was evolved, and immediately after the addition was complete, Color Test I[11] was negative. After hydrolysis with water, the organic layer was dried over sodium sulfate. Removal of solvent left 3.0 g. (66%) of crude product, m. 132–140°. Recrystallization from ethanol gave 2.4 g. (52%) of methylpentaphenyldisilane, m.p. 148–149°, identified by a mixed melting point and comparison of the infrared spectrum with that

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[11] H. Gilman and F. Schulze, THIS JOURNAL, **47**, 2002 (1925).

[12] The values used for the calcd. *MR* are those of Warrick, *ibid.*, **68**, 2455 (1946).

of an authentic sample, the preparation of which will be described later in this paper.

Anal. Calcd. for $C_{31}H_{28}Si_2$: Si, 12.3. Found: Si, 12.46, 12.38.

Forty-six ml. of the methyldiphenylsilyllithium solution was added to a stirred solution of 3.0 ml. of chlorotrimethylsilane in 50 ml. of THF. Heat was evolved, and Color Test I[11] was negative after the addition was complete. The reaction mixture was hydrolyzed with water, the aqueous layer extracted with ether, and the combined organic layer dried over sodium sulfate. The oil left by evaporation of solvents was dissolved in petroleum ether (b.p. 60–70°) and chromatographed on an alumina column. Removal of the petroleum ether left an oil which was distilled at 0.01 mm. After collecting a first fraction, 0.26 g., b.p. 79–81°, the main fraction, 2.8 g., b.p. 81–82°, $n^{20}D$ 1.5618, was collected. The combined yield was 74%. The main fraction was redistilled at 0.01 mm. to give 2.4 g. of 1,2,2,2-tetramethyl-1,1-diphenyldisilane, b.p. 81.5–82°, $n^{20}D$ 1.5606, $d^{20}{}_{20}$ 0.9678.

Anal. Calcd. for $C_{16}H_{22}Si_2$: C, 71.07; H, 8.20; *MR*,[12] 90.71. Found: C, 70.85, 71.04; H, 8.06, 8.21; *MR*, 90.45.

Addition of Chlorotriphenylsilane to Methyldiphenylsilyllithium (IV).—A solution of 3.24 g. (0.011 mole) of chlorotriphenylsilane in 35 ml. of THF was added to a stirred solution of IV prepared from 1.82 g. (0.00463 mole) of 1,2-dimethyl-1,1,2,2-tetraphenyldisilane (III) and 0.25 g. (0.036 g. atom) of lithium in 35 ml. of THF. After about half of the chlorotriphenylsilane solution had been added, Compound I began to precipitate; 15 min. after the addition was complete, Color Test I[11] was negative. The reaction mixture was hydrolyzed with water and filtered to give 0.93 g. (19%) of hexaphenyldisilane, m.p. 365–368° (mixed melting point). The organic layer was dried over sodium sulfate and then evaporated. The resulting solid was recrystallized from ethanol to give 0.6 g. of white solid, m. 124–135°.

In a second run, a solution of 7.15 g. (0.0242 mole) of chlorotriphenylsilane in 75 ml. of THF was added to a stirred solution of IV prepared from 4.0 g. (0.0102 mole) of III and 0.7 g. (0.1 g. atom) of lithium in 60 ml. of THF. Work-up by the procedure described in the first run gave 2.86 g. (27%) of hexaphenyldisilane, m.p. 361–364° (mixed melting point), and 3.7 g. of solid material, m. 111–122°. Attempts to separate this mixture by fractional crystallization and by chromatography failed. Distillation of the mixture at 0.01 mm. gave three small fractions, b.p. 150–192°, totaling 0.4 g., each melting at 134–138°. These fractions were combined and recrystallized three times from ethanol to give 0.1 g. of crystals, m.p. 141–143°. A mixed melting point with 1,2-dimethyl-1,1,2,2-tetraphenyldisilane (III) (m.p. 145–146°) was not depressed. A mixed melting point with methylpentaphenyldisilane (m.p. 148–149°) was greatly depressed. The main fraction from the distillation, b.p. 192–196°, 0.73 g., melted at 118–132°. The residue from the distillation was dissolved in hot ethanol and cooled to give 0.1 g. of crystals, m.p. 144–146°. A mixed melting point with methylpentaphenyldisilane was not depressed. A mixed melting point with III was greatly depressed.

Methylpentaphenyldisilane.—To a solution of 20 ml. of methyllithium in diethyl ether prepared from 2.3 g. (0.0161 mole) of methyl iodide and 0.7 g. (0.1 g. atom) of lithium was added a suspension of 3.0 g. (0.0063 mole) of chloropentaphenyldisilane, prepared by a described procedure.[13] After stirring for 1 hr., the reaction mixture was hydrolyzed with water. The organic layer and ether extracts of the aqueous layer were combined and dried over sodium sulfate. Removal of the ether left a solid which was recrystallized from ethanol to give 1.21 g. (42%) of methylpentaphenyldisilane, m.p. 146–148°. Recrystallization from ethanol gave white, fluffy crystals, m.p. 147–148°. A mixed melting point with the methylpentaphenyldisilane obtained from the reaction of methyldiphenylsilyllithium with chlorotriphenylsilane was not depressed. The infrared spectra of the two samples were identical.

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

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The Preparation of Cyclohexyltriphenylsilane

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Cyclohexyltriphenylsilane (a compound which could not be prepared in earlier work from the reaction of triphenylsilylpotassium with cyclohexyl bromide or by reaction of cyclohexylmagnesium bromide with chlorotriphenylsilane) has now been prepared by two different procedures. The two successful preparations utilized, respectively, the reaction of cyclohexyllithium with chlorotriphenylsilane, and the reaction of phenyllithium with trichlorocyclohexylsilane. However, the compound was not formed by the attempted addition of triphenylsilane to cyclohexene in the presence of benzoyl peroxide and only to a very small extent in a similar reaction using platinum chloride as the catalyst.

In a recent article[1] it was reported that two different procedures for the preparation of cyclohexyltriphenylsilane failed to yield any of the desired product. Repetition of this work by us confirmed their results, but we have found that this elusive compound can be prepared by modification of the original conditions and reagents. One of the reported procedures[1] utilized either "normal" or "inverse" addition of a solution of triphenylsilylpotassium in ether to cyclohexyl bromide. The fact that none of the usual coupling product, cyclohexyltriphenylsilane, was formed and that high yields of other products including hexaphenyldisilane, triphenylsilane, bicyclohexyl, cyclohexene and cyclohexyl bromide were obtained was used as supplementary evidence[2] for the occurrence of the halogen–metal interconversion reaction (well established in organic chemical systems[3]) when organosilicon-metallic compounds are allowed to react with organic halides.

The second reported procedure[1] utilized the reaction of cyclohexylmagnesium bromide with

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[1] A. G. Brook and S. Wolfe, THIS JOURNAL, **79**, 1431 (1957).

[2] See A. G. Brook, H. Gilman and L. S. Miller, *ibid.*, **75**, 4759 (1953), for the first recorded instance of halogen–metal interconversion in organosilicon systems.

[3] See R. G. Jones and H. Gilman's chapter in R. Adams, "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 339.