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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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

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.

chlorotriphenylsilane and yielded triphenylsilane, cyclohexene and triphenylsilanol. The formation of these "reduction" products was explained by use of a "quasi-ring" complex. A similar complex was used to explain some of the products of the triphenylsilylpotassium–cyclohexyl bromide reaction mentioned previously. Such "reduction" reactions are commonly noted when sterically hindered ketones and Grignard reagents are allowed to react[4] and the occurrence of the above and related reactions in cyclohexylsilane systems has been taken as indicative of steric hindrance to the formation of some cyclohexyl–silicon bonds.[1,5,6]

Steric hindrance in cyclohexyl compounds is not new. In 1904, it was found[7] that cyclohexylmagnesium chloride and phosgene yielded dicyclohexylmethanol and that dicyclohexyl ketone reacted with cyclohexylmagnesium chloride to give dicyclohexylmethanol and cyclohexene; these same two products were obtained later by Gray and Marvel[4] from the reaction of ethyl cyclohexanecarboxylate with cyclohexylmagnesium bromide. Neither is steric hindrance new to organosilicon compounds containing cyclohexyl groups. Kipping and Cusa[5] found that cyclohexylmagnesium bromide and trichlorophenylsilane reacted to yield the reduction product dicyclohexylphenylsilane. Recently,[6] this reaction was confirmed and extended to include reactions of other organometallic compounds, such as isopropylmagnesium chloride, with phenyltrichlorosilane. In addition to the dialkylphenylsilane reduction product, there was isolated in each case the corresponding olefin. An attempt was made in 1949[8] to prepare tetracyclohexylsilane by reaction of cyclohexyllithium with silicon tetrachloride. The product, however, was chlorotricyclohexylsilane. This product could not be made to react with methyllithium, ethyllithium or phenyllithium or with methylmagnesium iodide.

In 1954, despite the work just mentioned, two successful preparations of "tetracyclohexylsilane" were reported.[9,10] Reaction of cyclohexyllithium with either gaseous silicon tetrafluoride[9] or with dicyclohexylfluorosilane[9] yielded, respectively, 7.95 and 11.3% of "tetracyclohexylsilane," m.p. 194°. Hydrogenation of tetraphenylsilane[10] using 50–100 atmospheres of hydrogen at 80–150°, a Raney nickel catalyst and a reaction time of 7 hr. yielded 63% of "tetracyclohexylsilane," m.p. 279–281°. Analytical data reported for the two "tetracyclohexylsilanes" agree with the theoretical values and the two materials may be examples of stereoisomers such as are noted with tetra-*o*-tolylsilane.[11]

In work related to one of the attempted preparations reported herein, cyclohexyltriphenylgermane has been successfully prepared[12] by addition of triphenylgermane to the double bond of cyclohexene in the presence of benzoyl peroxide.

Results

As noted previously, reaction of cyclohexylmagnesium bromide with chlorotriphenylsilane[1] failed to give any of the desired product, cyclohexyltriphenylsilane. It has been found that cyclohexyllithium (prepared from the alkyl chloride) reacts normally with chlorotriphenylsilane to give approximately 20% of cyclohexyltriphenylsilane after several recrystallizations. Difficulty was encountered in the preparation of cyclohexyllithium and yields of this organometallic compound were only 28–30%.

A much better procedure for the preparation of the desired compound is the reaction of trichlorocyclohexylsilane with three equivalents of phenyllithium. Although yields of the pure product are only of the order of 28%, the intermediate phenyllithium is much easier to obtain in high yields than is cyclohexyllithium. Crude yields of *ca.* 100% were obtained in all of the reactions using phenyllithium in ether, but purification required multiple recrystallizations. Each sample prepared was contaminated by a higher melting product, perhaps hexaphenyldisiloxane, but no pure sample of this contaminant could be obtained even after several recrystallizations. In the phenyllithium reaction both ether and tetrahydrofuran were employed as the solvent in separate reactions. The use of tetrahydrofuran did not increase the yield of pure material; the crude yield was *ca.* 76% when this solvent was used.

The experiments of Brook and Wolfe[1] were repeated, using cyclohexylmagnesium chloride instead of cyclohexylmagnesium bromide for the reaction with chlorotriphenylsilane, and using triphenylsilyllithium in tetrahydrofuran solution instead of triphenylsilylpotassium in ether suspension for the reaction with cyclohexyl bromide. The results of Brook and Wolfe[1] were similar to those encountered in the present study, and these experiments have been excluded from the Experimental part.

Since cyclohexyltriphenylgermane had been prepared[12] by the addition of triphenylgermane to cyclohexene using benzoyl peroxide as the catalyst, an investigation was made of the addition of triphenylsilane to cyclohexene. No addition was obtained when benzoyl peroxide was used as the catalyst. A recent report[13] has indicated the usefulness of platinum chloride dissolved in isopropyl alcohol as a catalyst for the addition of Si–H compounds to olefins. Employment of a procedure similar to that reported[13] yielded only traces of impure material. An infrared spectrum of this substance indicated it to be impure cyclohexyltriphenylsilane.

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(4) A. Gray and C. S. Marvel, THIS JOURNAL, **47**, 2796 (1925); see also, M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Non-metallic Substances," Prentice-Hall, Inc., New York, N. Y., 1954, pp. 145–147.

(5) F. S. Kipping and N. W. Cusa, *J. Chem. Soc.*, 1040 (1933).

(6) M. C. Harvey, W. H. Nebergall and J. S. Peake, THIS JOURNAL, **79**, 2762 (1957).

(7) P. Sabatier and A. Mailhe, *Compt. rend.*, **139**, 343 (1904).

(8) W. H. Nebergall and O. H. Johnson, THIS JOURNAL, **71**, 4022 (1949); see also, *ibid.*, **70**, 1706 (1948), and **71**, **1720** (1949), for work related to the attempted preparation of tetracyclohexylgermane.

(9) A. D. Petrov and T. I. Chernysheva, *Zhur. Obshchei Khim.*, **24**, 1189 (1954) [*C. A.*, **49**, 12276 (1955)]; *J. Gen. Chem., U.S.S.R.*, **24**, 1179 (1954) (Engl. translation).

(10) M. Kanazahi and M. Takakusa, *Bull. Chem. Soc. Japan*, **27**, 441 (1954) (in English); see V. N. Ipatieff and B. N. Dolgov, *Ber.*, **62B**, 1220 (1929), for an early attempt at non-catalytic reduction of tetraphenylsilane.

(11) G. N. R. Smart, H. Gilman and H. W. Otto, THIS JOURNAL, **77**, 5193 (1955).

(12) R. Fuchs and H. Gilman, *J. Org. Chem.*, **23**, in press (1958).

(13) J. L. Speier, J. A. Webster and G. H. Barnes, THIS JOURNAL, **79**, 974 (1957).

Experimental[14]

Cyclohexyltriphenylsilane. A. From Trichlorocyclohexylsilane and Phenyllithium in Ethyl Ether.—To trichlorocyclohexylsilane (10.7 g., 0.05 mole) was added slowly, with stirring, 125 ml. (0.15 mole) of 1.25 *N* phenyllithium in ether. After stirring for 2 hr., Color Test I[15] was negative. An additional 55 ml. (0.08 mole) of phenyllithium solution was added and the mixture stirred for 1 hr. Hydrolysis with 100 ml. of water and work-up in the usual manner, *i.e.*, ether extraction, drying of extracts over sodium sulfate, filtration and distillation of the solvent, left 17.1 g. (100%) of a crude product (melting over the range 128–140°). This crude material was washed thoroughly with methanol (200 ml.) leaving 12.1 g. of white solid (melting at 138–146°). Multiple recrystallizations from ethanol, acetone and methanol–ethanol solvent pairs finally afforded 4.5 g. (26.3%) of product, m.p. 145–146°.

Anal. Calcd. for $C_{24}H_{26}Si$: Si, 8.20. Found: Si, 8.30, 8.26.

In three other similar experiments, near quantitative yields of crude product were obtained, but work-up finally left yields of 1% (m.p. 148–149°), 7.8% (m.p. 144–146°) and 25.6% (m.p. 146–148°). Infrared spectra of each of the products were identical.

B. From Trichlorocyclohexylsilane and Phenyllithium in Tetrahydrofuran.—In accordance with a recent procedure[16] phenyllithium (0.196 mole, 96%) was prepared in specially dried tetrahydrofuran. To the stirred solution of phenyllithium was added 7.35 g. (0.0388 mole) of trichlorocyclohexylsilane, keeping the flask at −70° by means of an external Dry Ice–acetone-bath. The resulting mixture was stirred at −70° overnight, at −30° for 12 hr., at room temperature (25–28°) for 12 hr. (Color Test I[15] was still positive), and finally at reflux for 12 hr. Color Test I was negative, so the mixture was hydrolyzed and worked up as in the previous experiment to yield 6.85 g. (59%) of slightly crude product, melting at 140–143°. Evaporation of the methanol washing yielded another 1.9 g. (17%) of very crude material, melting over the range 110–130°. Multiple recrystallizations finally afforded 4.5 g. (34.5%) of product, m.p. 145–146°. A mixture melting point with the authentic cyclohexyltriphenylsilane from the previous experiment was not depressed and an infrared spectrum was identical to that of the authentic material.

C. From Cyclohexyllithium and Chlorotriphenylsilane.—As noted previously, some difficulty was experienced in the preparation of cyclohexyllithium. The following experiment represents the best details available from the several experiments conducted.

To 50 ml. of *n*-pentane (99% pure) was added slightly more than 0.7 g. (0.1 g.-atom) of lithium wire (the surface of which was filed to increase its total area). The stirrer was started and 50 drops of a solution containing 5.9 g. (0.05 mole) of cyclohexyl chloride in 50 ml. of *n*-pentane was added. Refluxing the mixture gave no evidence of a spontaneous reaction, so more alkyl halide solution was added. After addition of *ca.* one-half of the halide solution with intermittent refluxing, the reaction commenced and the remaining alkyl halide solution was added slowly. After refluxing overnight, the solution was filtered. The RLi yield was 0.0143 mole (28.3%). This was added with stirring to 3.5 g. (0.012 mole) of chlorotriphenylsilane and then stirred for 48 hr., after which time Color Test I[15] was negative. Hydrolysis and work-up in the usual manner yielded 3.25 g. (79%) of product, melting at 135–146°. This was combined with material from another run of equal size which also yielded 3.25 g. (79%) of crude product. The combined material was recrystallized to give 1.6 g. (19.5% based on 0.024 mole of product) of cyclohexyltriphenylsilane, m.p. 145–147°, which was further crystallized to give 1.0 g., m.p. 146–148°. This material did not depress the melting point of an authentic specimen and had an infrared spectrum identical to that of the pure material.

D. From Cyclohexene and Triphenylsilane in the Presence of Benzoyl Peroxide (Attempted).—In a flask were combined 50 ml. of *n*-heptane, 8.4 g. (0.1 mole) of cyclohexene, 16.5 g. (0.063 mole) of triphenylsilane[17] and 0.3 g. of benzoyl peroxide. The mixture was refluxed at 75° for 72 hr. Cooling and work-up of the mixture left 16.5 g. (100%) of triphenylsilane (crystallized from cold methanol), m.p. 42–44°.

E. From Cyclohexene and Triphenylsilane in the Presence of Chloroplatinic Acid (Attempted).—Cyclohexene (10.6 g., 0.126 mole), 16.5 g. (0.063 mole) of triphenylsilane and 0.1 ml. of 0.1 *M* $H_2PtCl_6 \cdot 6H_2O$ in isopropyl alcohol were combined in a flask, and then stirred and refluxed for 96 hr. Attempts to crystallize the oily product failed, and the material was distilled. Some cyclohexene distilled first, followed by 12.0 g. (73%) of unreacted triphenylsilane, boiling at 130–140° (0.1 mm.), m.p. 42–44°. There also was obtained 1.4 g. of an oily solid, melting over the range 100–175°, and 0.12 g. of a solid, melting over the range 140–170°. Recrystallization of the latter two substances finally afforded 0.8 g. of a solid (melting at 200–220°) and 0.05 g. of very impure cyclohexyltriphenylsilane (melting at 145–160°). An infrared spectrum of the material melting at 200–220° indicated that some cyclohexyl groups might be present, but also indicated that the substance was mainly hexaphenyldisiloxane. The lower melting material has bands in the infrared spectrum which indicate that some hexaphenyldisiloxane also may be present in this sample.

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[14] All melting points are uncorrected. An inert nitrogen atmosphere was used in the reactions involving organometallic compounds.

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

[16] H. Gilman and B. J. Gaj, *J. Org. Chem.*, **22**, 1165 (1957).

[17] Kindly furnished by Dr. L. O. Moore, formerly of this Laboratory.