*Preparation of Some Tricyclohexylsilyl Derivatives**

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Preparation of organosilicon compounds containing cyclohexyl groups has been studied by several workers[1-5] from a viewpoint of steric effect. Nebergall and Johnson[3] synthesized a wide variety of tricyclohexylsilyl compounds through the reaction of cyclohexyllithium with silicon tetrachloride. Lately it was reported by Eaborn[4] and Petrov[5] that the use of silicon tetrafluoride or fluorosilanes was more effective than that of silicon tetrachloride in the reaction. However, substitution or condensation reaction of a compound carrying two or three bulky cyclohexyl groups has an unavoidable difficulty in approaching of a reagent. We overcame the difficulty and prepared tetracyclohexylsilane and three cyclohexylmethylsilanes by hydrogenation of the corresponding phenyl-silicon compounds[1].

Hexacyclohexyldisilane was not obtained by the reaction of tricyclohexylchlorosilane with metallic sodium[3], whereas the corresponding digermane was obtained by a similar treatment[6]. It has been also reported by Nebergall and Johnson[3] that the hydrolysis product of chlorosilane was tricyclohexylsilanol, m. p. 177°C. The compound reported by Jenkins and Post[7] as "probably hexacyclohexyldisiloxane", m. p. 178°C, seems to be the same compound.

In the present paper hydrogenations of hexaphenyldisilane, hexaphenyldisiloxane and triphenylsilanol are reported.

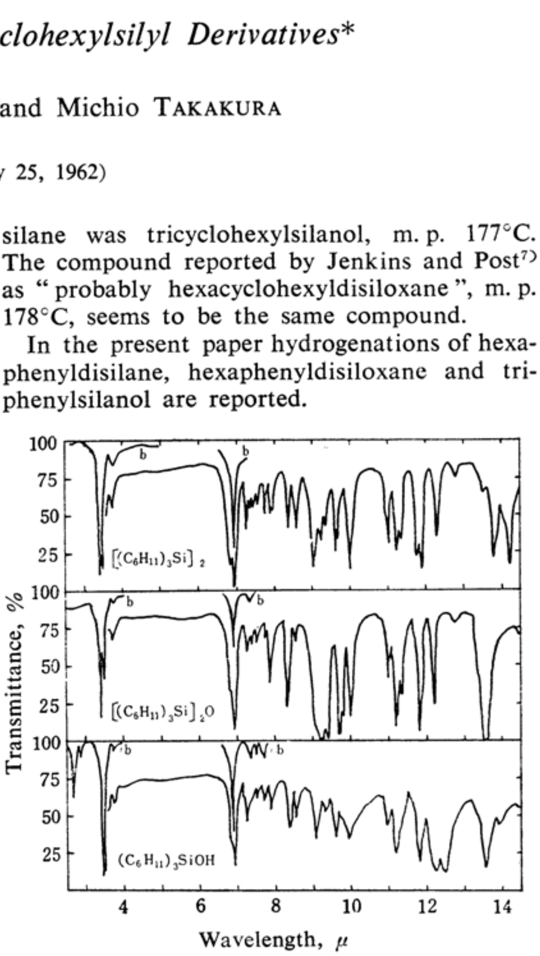

Fig. 1 (A). Infrared spectra of cyclohexyl-compounds.

(a) Absorption bands of Nujol appear at 3.4∼3.5, 6.80 and 7.23 μ.

(b) Parts of spectra obtained with CCl_4 solu- are shown by curve b.

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* This work was presented at the 9th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1956.

1) The first paper of this series. M. Kanazashi and M. Takakusa, This Bulletin, **27**, 441 (1954).

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

3) W. H. Nebergall and O. H. Johnson, *J. Am. Chem. Soc.*, **71**, 4022 (1949).

4) C. Eaborn, *J. Chem. Soc.*, **1952**, 2840.

5) A. D. Petrov and T. I. Chernysheva, *Zhur. Obshchei* Khim., **24**, 1189 (1954).

6) O. H. Johnson and W. H. Nebergall, *J. Am. Chem. Soc.*, **70**, 1706 (1948).

7) J. W. Jenkins and H. W. Post, *J. Org. Chem.*, **15**, 556 (1950).

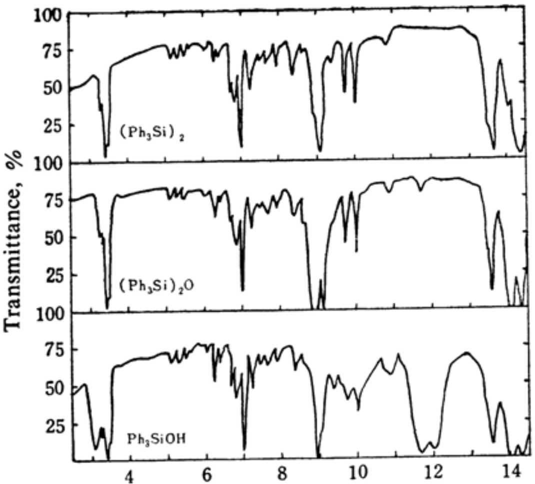

Fig. 1 (B). Infrared spectra of phenyl-silicon compounds measured in Nujol mull.

Each compound absorbed the calculated amount of hydrogen, and hexacyclohexyldisilane, m. p. 351°C, hexacyclohexyldisiloxane, m. p. 308°C, and tricyclohexylsilanol, m. p. 177°C, were obtained. As was expected, hydrogenation of triphenylsilanol proceeded more smoothly than those of tetraphenylsilane, hexaphenyldisilane and hexaphenyldisiloxane.

The infrared spectra of the hydrogenation products show none of the absorption bands associated with the phenyl group or phenyl-silicon bond but, instead, clearly show the strong bands characteristic to the cyclohexyl group at 10.0, 11.2 and 11.8 μ[8].

Experimental

All melting points and boiling points are uncorrected.

Hexaphenyldisilane. — Triphenylchlorosilane was treated with sodium in xylene solution at reflux temperature. The precipitate was washed with benzene, treated with methanol, and then washed with hot water and methanol, to give hexaphenyldisilane, m. p. 342∼350°C.

Hexaphenyldisiloxane. — Triphenylchlorosilane was hydrolyzed in aqueous ethanol by refluxing for thirty hours with a small amount of hydrochloric acid. The precipitate of hexaphenyldisiloxane was washed with benzene repeatedly and recrystallized. M. p. 221∼222.5°C.

Triphenylsilanol.—Hydrolysis of triphenylchlorosilane was carried out in neutral acetone solution. Recrystallization from petroleum ether (50∼70°) of triphenylsilanol thus obtained gave white crystals melting at 152°C.

Methylcyclohexane. — Methylcyclohexane was dried over calcium chloride and fractionated through a 30 cm. column packed with single turn helices. B. p. 98∼98.5°C.

Raney Nickel Catalyst.—The catalyst was prepared from Raney nickel alloy (Ni content, 42%) in the same way as reported in a previous paper[1]. It was kept under absolute alcohol in a refrigerator, and the alcohol was substituted by methylcyclohexane before use.

Hydrogenation. — A sample in about 50 cc. of methylcyclohexane was hydrogenated in a stainless steel autoclave (capacity, 100 cc.) equipped with a magnetic inner agitator. The initial hydrogen pressure was 100∼110 atm., and the conditions are listed in Table I.

Separation of Products. Disilane (Table I, No. 1).—A solid part was separated from the reaction mixture, and the solid was extracted with about 500 cc. of cyclohexane. Recrystallization of a white material, 1.7 g., obtained from the extract gave 0.8 g. of hexacyclohexyldisilane, m. p. 339∼343°C. The melting point of hexacyclohexyldisilane was raised to 349∼351.5°C by recrystallization from cyclohexane-petroleum ether (9 : 1).

Found: C, 78.04, 78.09; H, 11.86, 11.75; mol. wt. (Rast), 539∼559. Calcd. for $C_{36}H_{66}Si_2$: C, 77.90; H, 11.99%; mol. wt., 555.

From the liquid part of the reaction mixture an additional 2.4 g. of hexacyclohexyldisilane was obtained. The solvent recovered was carefully fractionated, but cyclohexane was not detected; the fact shows that silicon-carbon cleavage did not occur during the course of hydrogenation. Another run carried out under forced conditions gave also hexacyclohexyldisilane as a sole product.

TABLE I. HYDROGENATION CONDITIONS

Exp. No.	Material	g.	Catalyst[a] g.	Reaction temp. °C	Hydrogen[c] absorbed l.	Hydrogen[c] calcd. l.
1	Ph_6Si_2	9.35	12∼15	110∼200	7.7	7.3
2	Ph_6Si_2O	8.0	4	110∼160	6.0	6.1
3	Ph_3SiOH	6.9	5	100∼130[b]	4.9	5.0

a) The catalyst was added in 3∼5 portions.
b) The reaction started at 70∼80°C.
c) The initial pressure of hydrogen was 100∼110 atm.

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[8] A study on the infrared spectra of organosilicon compounds containing cyclohexyl groups was presented at the Fall Meeting of the Chemical Society of Japan in 1956 by T. Yoshimoto and M. Takakusa; the paper will be published shortly.

Disiloxane (Table I, No. 2). — From the solid part of the reaction mixture, there was obtained 3.1 g. of crude material melting at 300~308°C. Recrystallizations from cyclohexane-ethanol and from petroleum ether gave 0.95 g. of hexacyclohexyldisiloxane, m. p. 305~308°C. Further recrystallization from petroleum ether, carbon tetrachloride or benzene did not raise the melting point.

Found: C, 76.22, 76.41, 76.44; H, 11.65, 11.75, 11.69; mol. wt. (Rast), 558~592, 575. Calcd. for $C_{36}H_{66}OSi_2$: C, 75.71; H, 11.65%; mol. wt., 571.

From the liquid part, 1.6 g. of hexacyclohexyldisiloxane was separated. Cyclohexane was not detected in the recovered reaction solvent.

Silanol (Table I, No. 3). — By a similar treatment, 6.2 g. of tricyclohexylsilanol was obtained from the reaction mixture. M. p. 174~176°C. Duplicated recrystallization from petroleum ether raised the melting point to 176~177°C (Reported[3], 177°C).

Found: C, 73.50, 73.57; H, 11.81, 11.78. Calcd. for $C_{18}H_{34}OSi$: C, 73.40; H, 11.64%.

Infrared Spectra.—The absorption spectra were measured in Nujol mull and in carbon tetrachloride solution with a Shimadzu AR-275-I infrared spectrophotometer equipped with a sodium chloride prism. Solubility in carbon tetrachloride of hexacyclohexyldisilane (less than 1%) or hexacyclohexyldisiloxane (ca. 2%) was not sufficient to give good spectra.

Summary

Hydrogenations of hexaphenyldisilane, hexaphenyldisiloxane and triphenylsilanol were carried out in the presence of Raney nickel catalyst (W-6), and hexacyclohexyldisilane**, hexacyclohexyldisiloxane** and tricyclohexylsilanol were obtained (41, 56, 84%, respectively). Infrared spectra of the products and the starting materials were measured.

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** New compounds.