Sterically-hindered Organosilicon Compounds Containing Cyclohexyl Groups. II[1]. *Hydrogenation of Phenylsilicon Compounds*

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Since Cusa and Kipping[2] studied the reaction of cyclohexylmagnesium chloride with phenyltrichlorosilane, much effort has been made to overcome the steric hindrance of a cyclohexyl group and prepare highly substituted organosilicon compounds with the cyclohexyl groups. Recently, reactions between fluorosilanes and organolithium compounds[3] were shown to be quite effective ways to obtain those compounds, and preparation of a series of tricyclohexylalkyl- and -aryl-silanes by this method was studied by the present author[1]. Steric hindrance of three cyclohexyl groups attached to one silicon atom does not allow the introduction of a *sec*-alkyl group as the fourth substituent even with this powerful combination of reagents.

The steric hindrance here implies merely that the formation of an intermediate complex is prevented, or simply, attack of the reagent on the silicon atom is obstructed. In these cases, dimensions of both reagents should be naturally considered, as well as their reactivities. It is also quite obvious that magnitude of steric hindrance varies with a type of reaction.

Cyclohexane derivatives are often prepared by hydrogenation of corresponding benzene derivatives, and the method can be applied to the preparation of organosilicon compounds

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[1] Part I: M. Takakusa, This Bulletin, 36, 31 (1963).

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

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

containing cyclohexyl groups[4,5]. As this reaction involves attack on the phenyl group surrounding silicon, not on the silicon atom, by the smallest hydrogen atom[6], the steric hindrance will be much less important. Kanazashi and Takakusa prepared tetracyclohexylsilane[5a], hexacyclohexyldisilane[5b], and some other related compounds in this way.

The present paper reports hydrogenation of several phenylsilicon compounds as a route to cyclohexylsilicon compounds, and the results are compared with those of organolithium compound route obtained in the preceding paper[1]. Attempts were made to prepare tricyclohexyl-isopropylsilane and -*t*-butylsilane through the interactions of triphenylfluorosilane with the corresponding alkyllithiums followed by hydrogenation of the products, since they are expected to be the most hopeful ways for the preparation of these compounds.

Experimental*

Triphenylbutylsilane.—*From Triphenylchlorosilane.* — Triphenylbutylsilane was prepared from the interaction of the chlorosilane with *n*-butyllithium in a yield of 55%. M. p. 87.8∼88.5°C (reported[7], 87.5∼88°C).

From Butyltrichlorosilane.—A mixture of 9.6 g. of butyltrichlorosilane and 17 g. of chlorobenzene was added dropwise to a mixture of 7 g. of sodium sand and 120 ml. of benzene, the whole mixture refluxed for 2 hr., and then treated with water. Evaporation of the solvent from the benzene layer yielded a crude solid from which 2 g. of triphenylbutylsilane, m. p. 87.5∼88°C, was separated. The mixed melting point measurement of both materials did not show any depression.

Triphenylisopropylsilane (Attempted). — Isopropyllithium was prepared in ethyl ether from 0.7 g. of lithium and 5.3 g. of isopropyl bromide in a 300 ml. three-necked round-bottomed flask equipped with a reflux condenser, protected with a calcium chloride tube, a mercury-sealed stirrer and a dropping funnel under nitrogen atmosphere. To the isopropyllithium solution was added 40 ml. of triphenylfluorosilane (6.5 g.) solution in ethyl ether, the mixture refluxed, the solvent replaced by petroleum ether (b. p. 70∼90°C), and then the mixture refluxed for 7 hr. From the reaction mixture, 0.2 g. of crude hexaphenyldisiloxane and 1.8 g. of triphenylfluorosilane were recovered.

Triphenyl-*t*-butylsilane (Attempted).—To *t*-butyllithium solution prepared from 4.0 g. of lithium and 22.2 g. of *t*-butyl chloride in petroleum ether (b. p. 30∼50°C) was added 7.15 g. of triphenylfluorosilane. The mixture was refluxed with stirring, the solvent gradually replaced by higher boiling petroleum ether, the content of the flask kept refluxing for 16 hr. From the reaction mixture 84% of triphenylfluorosilane and 10% of hexaphenyldisiloxane were recovered. The repeated run using 10.1 g. of lithium and 54.3 g. of *t*-butyl chloride also failed to yield the desired product.

Tricyclohexylphenylsilane. — Prepared in a previous report[1]. M. p. 207∼208°C.

Triphenylphenoxysilane. — To sodium phenoxide prepared from 18.6 g. of phenol and 2.5 g. of sodium in benzene 26.7 g. of triphenylchlorosilane dissolved in benzene was added dropwise, and the mixture refluxed for 6 hr. The solvent was distilled off, and 9.2 g. (30%) of triphenylphenoxysilane, m. p. 101∼103°C, obtained. Recrystallization from petroleum ether gave 8.4 g. of th material melting at 103∼105°C (reported[8], 103∼104°C). Found: C, 81.04; H, 5.38. Calcd. for $C_{24}H_{20}OSi$: C, 81.77; H, 5.72%.

Raney Nickel Catalyst. — The catalyst, Adkins' "W-6"[9], was prepared in the same way as that in a previous paper[5a], and stored under absolute alcohol in a refrigerator. The alcohol was replaced by the reaction solvent before being used. Several attempts to obtain more active catalysts showed that lower temperature in development and digestion caused much loss of the catalyst during washing process, though the catalyst appeared to carry higher activity.

Hydrogenation Procedure. — Unless otherwise described, phenylsilanes were dissolved in 40∼50 ml. of cyclohexane, and hydrogenated over Raney nickel catalyst. A 100 ml. stainless steel autoclave equipped with a magnetic inner agitator was used, and about 100∼110 atm. of hydrogen was charged. Other conditions are listed in Table I.

Tricyclohexylbutylsilane.—(a) (Table I, No. 1) Evaporation of solvent from the hydrogenated mass yielded a crude material melting at about 100°C. Crystallization of the material from ethanol gave 0.35 g. of impure tricyclohexylbutylsilane melting at 149∼154°C, and, from its mother liquor, 0.1 g. of another material melting at 86∼100°C was obtained. The latter was subjected to chromatography on alumina and separated into two components, one melting at 92∼98°C and the other at 111∼122°C, but further purifications were not successful. Recrystallization of the impure tricyclohexylbutylsilane raised the melting point to 157∼158°C.

(b) From the hydrogenation of 1.6 g. of triphenylbutylsilane was obtained 0.7 g. of a crude material melting at 151∼156°C. Three recrystallizations from ethanol-benzene (3 : 1) yielded 0.4 g. of tricyclohexylbutylsilane, m. p. 159∼160°C (see the previous paper[1]). (Found: C, 78.87; H, 12.22. Calcd. for $C_{22}H_{42}Si$: C, 78.95; H, 12.65%).

From the mother liquor of the first recrystallization, 0.02 g. of a compound which melts at 97∼106°C was obtained, but further purification was not successful.

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[4] J. L. Speier, *J. Am. Chem. Soc.*, **74**, 1003 (1952).

[5] a) M. Kanazashi and M. Takakusa, This Bulletin, **27**, 441 (1954); b) M. Kanazashi and M. Takakusa, ibid., **35**, 1840 (1962).

[6] Physico-chemical aspects of catalytic action of Raney nickel catalyst are not considered here.

* All melting points reported here are uncorrected.

[7] H. Gilman, R. A. Benkeser and G. E. Dunn, *J. Am. Chem. Soc.*, **72**, 1689 (1950).

[8] H. Gilman and G. N. R. Smart, *J. Org. Chem.*, **19**, 441 (1954).

[9] H. Adkins and H. R. Billica, *J. Am. Chem. Soc.*, **70**, 695 (1948).

Tetracyclohexylsilane.—*From Tricyclohexylphenylsilane (Table I, No. 2).* — The solvent was distilled off, and 2.2 g. of a solid melting at 271∼275°C was obtained. Recrystallization from benzene gave 1.8 g. of tetracyclohexylsilane, m. p. 276∼278°C. Mixed melting point with an authentic sample[5a] did not show depression.

From Tetraphenylsilane (Table I, No. 3). — In a similar way, tetracyclohexylsilane was obtained. The concentrated mother liquor was chromatographed on alumina, but no solid but tetracyclohexylsilane was obtained.

Tricyclohexylphenylsilane. — (Table I, No. 4). Products of partial hydrogenation were separated by chromatography on alumina with petroleum ether as an eluent, and 0.4 g. of a solid melting at 200∼230°C, 0.2 g. of a solid melting at about 200°C and 0.3 g. of material melting at 120∼140°C were obtained. The middle fraction, melting at 200°C, was recrystallized from ethanol and ethanol-benzene to give pure tricyclohexylphenylsilane, m. p. 204∼206.5°C. (Found: C, 81.80; H, 10.77. Calcd. for $C_{24}H_{38}Si$: C, 81.28; H, 10.80%.)

Mixed melting point with an authentic sample[1] did not show any depression.

Hydrogenation of Triphenylsilanol at Higher Temperature. — The reaction mixture of the Run No. 8 of Table I was a very sticky viscous liquid, from which neither tricyclohexylsilanol nor hexacyclohexyldisiloxane was separated. Its infrared spectrum does not show an absorption near 4.7 μ of Si-H bond. From another run carried out at about 150°C, a sticky liquid was obtained, from which only a low yield of tricyclohexylsilanol was separated.

Tricyclohexylcyclohexoxysilane (Attempted). — (Table I, No. 10). Hydrogenation of triphenylphenoxysilane gave a material melting at 168∼171°C, but not tricyclohexylcyclohexoxysilane. The product was recrystallized twice from petroleum ether to give a compound melting at 175∼176.5°C, which was identified as tricyclohexylsilanol by mixed melting point measurement. Cyclohexanol seemed to be also formed.

Results and Discussion

Isopropyltriphenylsilane or *t*-butyltriphenylsilane has not been reported yet in the literature. Incidentally, attempts to prepare them by treating triphenylfluorosilane with the corresponding alkyllithiums were also unsuccessful probably due to steric hindrance, and hence, only tricyclohexylbutylsilane and tetracyclohexylsilane were prepared by hydrogenation as members of a tricyclohexylalkylsilane series. Tricyclohexylphenylsilane was prepared by partial hydrogenation of tetraphenylsilane.

Hydrogenation of hexaphenyldisilane and hexaphenyldisiloxane, which was the subject of a previous paper[5b], was also carried out under similar conditions for comparison. The reaction conditions are shown in Table I. Apparent difference in reaction conditions does not lead to any significant conclusion, since the activity of the catalyst used could not be uniform throughout the series of experiments, and all starting materials were finally converted into the desired products. The greatest difficulty was encountered with hexaphenyldisilane, where the product should have the largest steric requirement among the compounds studied here. With this compound, hydrogen absorption occasionally ceased, but every addition of some fresh catalysts to the system started the reaction again until the calculated amount of hydrogen was completely absorbed. One possible explanation is not steric hindrance but simply low solubility of the product. As the hydrogenated disilane is hardly soluble in the solvent, it probably covered the surface of nickel catalyst, reducing its activity temporarily. It was actually observed that a pretty strong activity had still remained in the used catalyst after completion of the reaction. Furthermore, the difficulty was reduced when a diluted sample was hydrogenated.

The series of studies on hydrogenation of phenylsilicon compounds showed that steric hindrance is not important in hydrogenation process of those compounds and allows the formation of several cyclohexylsilicon compounds that can not be obtained by other

TABLE I. HYDROGENATION CONDITIONS

No.	Material	g.	Ni g.	Temp. °C	Time hr.	Hydrogen, l.		Product	%
						Absorbed	Calcd.		
1	$BuSiPh_3$	1.0	1.4	110∼120	2	0.7	0.64	$BuSi(C_6H_{11})_3$	20
2	$(C_6H_{11})_3SiPh$	2.2	1.6	100∼140	2.5	0.5	0.42	$(C_6H_{11})_4Si$	80
3	Ph_4Si	1.68	2.0	120∼170	2.5	1.4	1.34	$(C_6H_{11})_4Si$	—
4	Ph_4Si	2.1	1.4	90∼100	2	1.4	1.26[a]	$(C_6H_{11})_3SiPh$	8
5	$(Ph_3Si)_2$[b]	2.1	4.0	110∼160	5	2.1	1.63	$(C_6H_{11})_6Si_2$	
6	$(Ph_3Si)_2O$[b]	2.1	1.6	100∼160	1.5	1.6	1.59	$(C_6H_{11})_6Si_2O$	
7	Ph_3SiOH	5.8	1.6	100∼120	2	4.2	4.24	$(C_6H_{11})_3SiOH$	85
8	Ph_3SiOH	13.9	4	100∼170	—	10.3	10.1	None	
9	Ph_3SiOPh	1.2	1.4	100∼120	1.5	1.0	0.91	$(C_6H_{11})_3SiOH$	
10	Ph_3SiOPh	7.04	6	110∼160	—	6.0	5.4	$(C_6H_{11})_3SiOH$	

a) Partial hydrogenation b) Methylcyclohexane was used as a solvent.

conventional methods. The steric effects of the residual or pre-existing groups are also small, and limitation of this method for preparation of cyclohexane derivatives in silico-organic chemistry does not lie in steric hindrance.

Si–C and Si–Si bonds are stable enough in the hydrogenation process, and many sterically-hindered cyclohexylsilanes were prepared by hydrogenation without any cleavage of those bonds. The siloxane bond is also stable to hydrogenation, but hydrogenation of triphenylsilanol at higher temperature often yielded a very sticky liquid. The optimum temperature for obtaining tricyclohexylsilanol seems to be 100～120°C, and at a higher temperature a yield of tricyclohexylsilanol was largely reduced. Stability of triphenylsilanol under hydrogen at higher temperature was studied by Dolgov et al.¹⁰⁾, and it was shown that the silanol was converted into hexaphenyldisiloxane at 280°C. Under the present conditions, however, no solid product but tricyclohexylsilanol was obtained, nor any compound with Si–H bond was detected by infrared measurement. An attempt to obtain tricyclohexylcyclohexoxysilane by hydrogenating triphenylphenoxysilane was unsuccessful, and only tricyclohexylsilanol was obtained, probably as a result of hydrolysis.

Summary

Tricyclohexylbutylsilane, tetracyclohexylsilane and tricyclohexylphenylsilane were prepared by hydrogenation of triphenylbutylsilane and phenyltricyclohexylsilane and partial hydrogenation of tetraphenylsilane, respectively. Preparation of tricyclohexylisopropylsilane and tricyclohexyl-*t*-butylsilane was unsuccessful due to failure of obtaining corresponding triphenyl derivatives. An attempt to obtain tricyclohexylcyclohexoxysilane by hydrogenating triphenylphenoxysilane was also unsuccessful. In preparation of highly-substituted cyclohexylsilicon compounds, the steric factor is of less importance in the hydrogenation process, while it is very much enhanced in reactions with organolithium compounds.

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10) B. N. Dolgov and Yu. N. Volnov, *Zhur. Obshchei Khim., Ser. 1*, 91 (1931); *Chem. Abstr.*, 25, 4535 (1931).