Sterically-hindered Organosilicon Compounds Containing Cyclohexyl Groups. III.[1,2] Notes on Petrov and Chernysheva's Tetracyclohexylsilane and Tricyclohexyl-n-butylsilane

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It occasionally happens that two or more melting point values are given to a single compound by separate workers in silico-organic chemistry[3].

The present author[10] obtained tetracyclohexylsilane, m. p. 279~281°C, by hydrogenation of tetraphenylsilane, while Petrov and Chernysheva[11] reported tetracyclohexylsilane melting at 198°C, which was obtained by the reaction of cyclohexyllithium with tetrafluorosilane or dicyclohexyldifluorosilane. The two tetracyclohexylsilanes have been generally

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

[2] Part II: M. Takakusa, ibid., **36**, 284 (1963).

[3] For example: 172°C by Gilman[4] and 185°C by Petrov[5] for 1-naphthyltriphenylsilane, 161°C by Petrov[6] and 193°C by Gilman[7] for tri-1-naphthylphenylsilane, and 148°C by Gilman[8] and 232°C by Nametkin[9] for triphenylcyclohexylsilane.

[4] H. Gilman and C. G. Brannen, *J. Am. Chem. Soc.*, **73**, 4640 (1951).

[5] A. D. Petrov and V. S. Chugunov, *Doklady Akad. Nauk S. S. S. R.*, **82**, 917 (1952).

[6] A. D. Petrov and V. S. Chugunov, ibid., **77**, 815 (1951).

[7] H. Gilman, C. G. Brannen and R. K. Ingham, *J. Am. Chem. Soc.*, **77**, 3916 (1955).

[8] H. Gilman and D. H. Miles, ibid., **80**, 611 (1958).

[9] N. S. Nametkin, A. V. Topchiev and T. I. Chernysheva, *Doklady Akad. Nauk S. S. S. R.*, **111**, 1260 (1956).

[10] M. Kanazashi and M. Takakusa, This Bulletin, **27**, 441 (1954).

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

thought to be stereoisomers due to steric hindrance[12]. Stereoisomerism in the silane would be possible in the case that free rotation around the Si-C_6H_{11} bond is hindered, but actual existence of isomers, which is the case in tetra-*o*-tolylsilane[13], seems to be less probable in tetracyclohexylsilane because of a squat shape of the cyclohexyl group. Moreover, if there exist some isomers of steric origin, the product of hydrogenation of tetraphenylsilane should be a mixture of the isomers. Our repeated studies on hydrogenation of tetraphenylsilane and phenyltricyclohexylsilane[2] were not successful in an attempt to isolate any other compound than the one melting at 281°C which was previously reported[10]. Interaction of tricyclohexylfluorosilane and cyclohexyllithium was reinvestigated by the present author[1], and the fourth cyclohexyl group could not be introduced under conditions similar to Petrov and Chernysheva's.

Eaborn[14] obtained tricyclohexylcyclohexoxysilane during the reaction of cyclohexylmagnesium bromide with dicyclohexyldifluorosilane at 70°C. A similar example has been reported by Cusa and Kipping[15] who obtained phenyldicyclohexylcyclohexoxysilane from the reaction of cyclohexylmagnesium bromide with phenyltrichlorosilane. The present author separated tricyclohexylcyclohexoxysilane, m. p. 201～203°C, from the reaction mixture of cyclohexyllithium with tetrachlorosilane. The result obtained here seems to be the first example of formation of such a type of compound during the reaction of organolithium compounds with halosilanes. The process seems to involve formation of $C_6H_{11}OLi$ in the reaction system and its successive interaction with tricyclohexylchlorosilane.

$$(C_6H_{11})_3SiCl + C_6H_{11}OLi \rightarrow (C_6H_{11})_3SiOC_6H_{11}$$

Though the cyclohexoxysilane was not obtained in the reaction[1] of tricyclohexylfluorosilane (2.5 g.) with an excess of cyclohexyllithium under a forced condition, about 2～5% (to tetrachlorosilane) of the compound was obtained in every larger scale reaction in which tetrachlorosilane or dicyclohexyldichlorosilane was used. Hence, the compound melting at 198°C, which Petrov and Chernysheva reported as tetracyclohexylsilane, might possibly be tricyclohexylcyclohexoxysilane[16], instead of a stereoisomer.

In addition to the case of tetracyclohexylsilane, tricyclohexylbutylsilane[2] obtained by hydrogenation of triphenylbutylsilane showed a different melting point, 159～160°C, from that of the compound, m. p. 133～135°C, obtained by Petrov and Chernysheva[11] through the substitution reaction with butyllithium. The existence of two isomeric tricyclohexylbutylsilanes can not be accounted for in terms of stereoisomerism due to steric hindrance.

A previous paper[1] reported that the reaction of butyllithium with tricyclohexylfluorosilane gives a compound (41%) identical with that obtained in hydrogenation study, m. p. 159～160°C, instead of Petrov and Chernysheva's tricyclohexylbutylsilane.

Tricyclohexylbutoxysilane was prepared by treating tricyclohexylchlorosilane with sodium butoxide. The butoxysilane was first reported here, but again, its melting point, 132～133°C, is close to that of Petrov and Chernysheva's tricyclohexylbutylsilane[17], 133～135°C; the fact suggests that their compound might be possibly tricyclohexylbutoxysilane.

The infrared spectra of the compounds obtained in our laboratory are shown in Fig. 1, being thought to be of some use for identification.

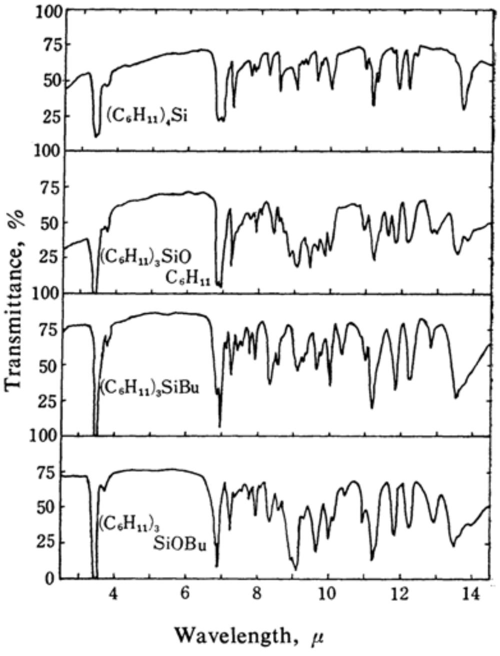

Fig. 1. Infrared spectra.

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12) a) H. Gilman and D. H. Miles, *J. Am. Chem. Soc.*, **80**, 611 (1958); b) M. Kumada, A lecture given at Symposium on Organosilicon and Organometallic Compounds, Osaka, October 1958.

13) G. N. R. Smart, H. Gilman and H. W. Otto, *J. Am. Chem. Soc.*, **77**, 5193 (1955).

14) T. Eaborn, *J. Chem. Soc.*, **1952**, 2840.

15) N. W. Cusa and F. S. Kipping, ibid., **1933**, 1040.

16) Calcd. for $C_{24}H_{44}OSi$: C, 76.52; H, 11.77; Si, 7.46. Calcd. for $C_{24}H_{44}Si$ (tetracyclohexylsilane): C, 79.92; H, 12.30; Si, 7.46%. Petrov and Chernysheva reported for their compound: Si, 7.47, 7.87%.

17) No analytical data are shown in their report.

Experimental*

Formation of Tricyclohexylcyclohexoxysilane.— A dry 1 l. three-necked flask equipped with a mercury-sealed stirrer, a reflux condenser and a dropping funnel was flashed with nitrogen, and 400 ml. of petroleum ether was placed in it. Fourteen grams of lithium shots were transfered to the flask under nitrogen atmosphere, and then nitrogen was bubbled through petroleum ether. A long calcium chloride tube connected to a washing bottle containing alkaline pyrogallol solution was attached to the top of the reflux condenser for protection against moisture and oxygen. Ten milliliters of cyclohexyl chloride was added, and the reaction mixture warmed to start the reaction. Over a period of 2 hr., 103 g. of cyclohexyl chloride was added dropwise, and the mixture was kept warm with stirring for an additional 3 hr. Then, 17.6 g. (0.104 mol.) of silicon tetrachloride in 50 ml. of petroleum ether was added slowly, and the mixture refluxed for 5 hr. The reaction mixture was filtered. To the precipitates was added about 400 ml. of petroleum ether, and the mixture treated with diluted hydrochloric acid and fractionated. A fraction boiling at 160～175°C under 6 mmHg gave 3.2 g. (10 %) of tricyclohexylchlorosilane and 4.3 g. (14%) of tricyclohexylsilanol. The distillation residue was subjected to chromatography on alumina, and 1.8 g. of a white solid melting at 192～195°C was obtained. Recrystallization from carbon tetrachloride-ethanol and then from petroleum ether-ethanol raised the melting point to 201～203.5°C.

Found: C, 76.67; H, 11.91. Calcd. for $C_{24}H_{44}OSi$: C, 76.52; H, 11.77%. A mixed melting point measurement with an authentic sample[18] indicated that this compound is tricyclohexylcyclohexoxysilane. Two additional runs also gave about 2～5% of tricyclohexylcyclohexoxysilane, but one case did not give the compound, where treatment with hydrochloric acid solution was so vigorous that cyclohexanol was liberated.

Preparation of Tricyclohexylbutoxysilane.— Sodium butoxide was prepared by dissolving about 0.6 g. of sodium in 50 ml. of dry freshly-distilled *n*-butyl alcohol. The mixture of the solution and 1.7 g. (0.0058 mol.) of tricyclohexylchlorosilane was refluxed for 5 hr. After being cooled, 100 ml. of petroleum ether was added to it, and the solution poured onto cold water. The organic layer was washed and dried over sodium sulfate. The solvent was driven off, and 1.0 g. of crude material obtained, m. p. 117～127°C. Recrystallization twice from ethanol gave pure tricyclohexylbutoxysilane, m. p. 132～133.4°C.

Found: C, 75.31; H, 12.00. Calcd. for $C_{22}H_{42}OSi$: C, 75.35; H, 12.05%.

Summary

Discrepancies among reported melting ponints for tetracyclohexylsilane and tricyclohexylbutylsilane were discussed. Tricyclohexylcyclohexoxysilane was obtained in 2～5% yield in addition to tricyclohexylchlorosilane from the reaction of cyclohexyllithium with silicon tetrachloride. Petrov's compound melting at 198°C is most likely to be tricyclohexylcyclohexoxysilane and not a stereoisomeric tetracyclohexylsilane. Tricyclohexylbutoxysilane, m. p. 133°C, was prepared by treating sodium butoxide with tricyclohexylchlorosilane, and it was pointed out that Petrov's "tricyclohexylbutylsilane" is probably tricyclohexylbutoxysilane.

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* All melting points reported here are uncorrected.

[18] The pure sample was kindly granted by Dr. C. Eaborn.