Sterically-hindered Organosilicon Compounds Containing Cyclohexyl Groups. I. Reactions of Organolithium Compounds with Tricyclohexylfluorosilane

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(Received August 29, 1962)

Since organolithium compounds were reported to be very effective in obtaining highly-substituted organosilicon compounds[1], most studies on steric hindrance have been done with the reactions between silicon tetrachloride and alkyl- or aryl-lithiums. By these reactions tetra(*o*-phenoxyphenyl)silane[2], tetra-*o*-anisylsilane[3] and tetra-*o*-tolylsilane[3,4] were successfully obtained, while, with 1-naphthyl[5],

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[1] For example, H. Gilman and R. N. Clark, *J. Am. Chem. Soc.*, **68**, 1675 (1946).

[2] K. Oita and H. Gilman, *J. Org. Chem.*, **21**, 1009 (1956).

[3] H. Gilman and G. N. R. Smart, ibid., **15**, 720 (1950).

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

[5] H. Gilman and C. G. Brannen, ibid., **73**, 4640 (1951).

2-biphenylyl[6], cyclohexyl[7] and isopropyl[8] groups, only a trisubstituted silane was obtained even when an excess of the lithium compound was used.

$$R_3SiCl + RLi \not\longrightarrow R_4Si$$

$$R\,;\ 1\text{-}C_{10}H_7,\ o\text{-}Ph\text{-}C_6H_4,\ C_6H_{11}\ \text{or}\ iso\text{-}Pr$$

An attempt to introduce a third *t*-butyl group was unsuccessful in the reaction of di-*t*-butyldichlorosilane with the lithium compound[9].

These results provide some rough idea about the steric nature of those groups, but more detailed knowledge on the steric hindrance can be obtained by comparing difficulties with which various types of groups are introduced into a fixed radical (for example, R_3Si-).

Advantage of using fluorosilanes in preparation of sterically-hindered organosilicon compounds was shown by Eaborn[10] who paid attention to the smaller atomic size of fluorine. Thus, Grignard reactions with fluorosilanes gave many compounds that had not been obtained through interaction of Grignard reagents and chlorosilanes.

$$(C_6H_{11})_2SiF_2 + C_6H_{11}MgX \rightarrow (C_6H_{11})_3SiF$$

It was proved by Petrov and Chernysheva[11] that the feature was the case also in reactions of organolithium compounds. They reported that the combination of fluorosilanes and the alkyl- or aryl-lithium gave three tetraorganosubstituted silanes, tetra-1-naphthylsilane, tetraisopropylsilane and tetracyclohexylsilane, which had not been obtained by the reactions with chlorosilanes.

At the present stage, an interaction of alkyllithium with alkylfluorosilanes under drastic conditions is thought to be the most effective way of obtaining a highly-substituted organosilicon compound with some bulky groups, and hence, reactions of some organolithium compounds with tricyclohexylfluorosilane were studied in the present work.

$$(C_6H_{11})_3SiF + RLi \rightarrow$$

$$R\,;\ n\text{-}Bu,\ iso\text{-}Pr,\ C_6H_{11}\ \text{or Ph}$$

Prolonged treatment of tricyclohexylfluorosilane with an excess of butyllithium in boiling petroleum ether (90~110°C)[12] yielded 41% of tricyclohexylbutylsilane which melts at 160°C. This compound was identical with tricyclohexylbutylsilane[13] obtained from hydrogenation of triphenylbutylsilane, but not the same as the tricyclohexylbutylsilane[11] that Petrov and Chernysheva obtained from a similar butyllithium reaction[14]. Tricyclohexylphenylsilane was obtained in a pretty high yield from the reaction after 12 hrs' refluxing in petroleum ether. Tricyclohexylfluorosilane did not react with an excess of isopropyllithium nor an excess of cyclohexyllithium even at an elevated temperature. The results obtained here show that the presence of three cyclohexyl groups on a silicon atom allows introduction of only a less bulky group such as *n*-alkyl or phenyl but not that of the *sec*-alkyl group, though[14] tetracyclohexylsilane has been reported by Petrov and Chernysheva[11] to be obtained through a similar route. No evidence was obtained that would indicate any difference in the reactivity between isopropyl and cyclohexyl groups.

Experimental*

Tricyclohexylfluorosilane. — A typical example was shown here. A mixture of 5.2 g. of tricyclohexylsilanol, 350 ml. of ethanol and 50 ml. of 58% hydrofluoric acid solution was kept at about 70~75°C for 2.5 hr., and then poured onto 1 l. of cold water. The product was extracted with petroleum ether (50~70°C), and the extract dried over Drierite. On concentration of the extract, 2.3 g. of tricyclohexylfluorosilane melting at 44.5~46°C was obtained. Recrystallization from ethanol gave 2.1 g. of the fluorosilane, m. p. 45.8~46.5°C (reported[15], 45~46°C).

Isopropyl Bromide. — Reagent grade isopropyl bromide was dried over Drierite and distilled. B. p. 59.2~59.4°C.

Cyclohexyl Bromide.—The bromide was prepared by introducing hydrogen bromide to cyclohexanol. A fraction boiling at 74~76°C/33 mmHg was collected. n_D^{20} 1.4866. A commercial material was also used after distillation.

Petroleum Ether.—High boiling petroleum ether was shaken with concentrated sulfuric acid until it did not give a yellow color, washed with alkali and water repeatedly, dried over calcium chloride and then over sodium, and distilled again. A fraction boiling at about 90~110°C was collected and dried over sodium.

Tricyclohexylbutylsilane.—Butyllithium was prepared from 1.2 g. of lithium and 10.2 g. of butyl

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[6] H. Gilman and K. Oita, *J. Org. Chem.*, **20**, 862 (1955).

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

[8] H. Gilman and R. N. Clark, ibid., **69**, 1499 (1947).

[9] L. J. Tyler, L. H. Sommer and F. C. Whitmore, ibid., 70, 2876 (1948).

[10] C. Eaborn, *J. Chem. Soc.*, **1952**, 2840.

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

[12] Throughout this study, petroleum ether boiling at 90~110°C was used as a reaction solvent.

[13] M. Takakusa, This Bulletin, in press. The preparation and physical properties of this compound were reported orally by T. Yoshimoto and M. Takakusa at Autumn Meeting of the Chemical Societies of Japan, Tokyo, Sept., 1956.

[14] Discussions on this discrepance will be done in a subsequent paper. M. Takakusa, This Bulletin, in press.

* All melting points reported here are uncorrected.

[15] C. Eaborn, *J. Chem. Soc.*, **1952**, 2846.

bromide in the usual method[16]. To the butyllithium solution in ethyl ether, 4.1 g. of tricyclohexylfluorosilane in 30 ml. of ethyl ether was added with stirring, the mixture warmed to reflux for 8 hr., ether distilled off, 40 ml. of petroleum ether added, and the content of the flask heated to reflux (oil bath, 120∼130°C) for 7 hr. After cooling, some petroleum ether was added, and the mixture was shaken with about 150 ml. of water. The organic layer was washed with water, and dried over anhydrous sodium sulfate. Concentration of the liquid gave 1.5 g. of tricyclohexylbutylsilane melting at 156∼159°C. From the mother liquor, on chromatography, was obtained 0.4 g. of crude material with a combined yield of 41%. Duplicated recrystallization from benzene-ethanol gave pure material melting at 159.2∼160.0°C. Further recrystallization did not raise the melting point. (Found: C, 78.90; H, 12.08. Calcd. for $C_{22}H_{42}Si$: C, 78.95; H, 12.65%.) The infrared spectrum of this compound was completely identical to that of tricyclohexylbutylsilane obtained by hydrogenation of triphenylbutylsilane, the mixed melting point with the authentic sample did not show any depression.

Tricyclohexylisopropylsilane (Attempted).—Isopropyllithium was prepared in ethyl ether from 0.9 g. of lithium shots and about 10 g. of isopropyl bromide. Preparation in petroleum ether was not successful. To the isopropyllithium solution was added 1.8 g. of tricyclohexylfluorosilane dissolved in 20 ml. of ethyl ether, the mixture was refluxed for 4 hr., the ether was substituted by petroleum ether, and refluxed for 10 hr. The reaction mixture was worked up in the same way as above, but only crude tricyclohexylfluorosilane, m. p. 43∼46°C, was recovered.

Tetracyclohexylsilane (Attempted).—Cyclohexyllithium solution was prepared from 17 g. of lithium and 162.3 g. of cyclohexyl bromide in petroleum ether, and 2.5 g. of tricyclohexylfluorosilane dissolved in 20 ml. of petroleum ether was added to it. The mixture was refluxed (oil bath, 150∼160°C) for 12 hr., and worked up in the usual way. Tricyclohexylfluorosilane was recovered.

Tricyclohexylphenylsilane. — Phenyllithium was prepared in the usual way[16] from 1.8 g. of lithium and 16.8 g. of phenyl bromide in 140 ml. of ethyl ether. To the stirred phenyllithium solution 3.7 g. of tricyclohexylfluorosilane dissolved in 20 ml. of ethyl ether was added, the mixture refluxed for 3 hr., the solvent substituted by petroleum ether, and then refluxed (oil bath, 100°C) for 12 hr. The reaction mixture was worked up in the usual way, and 4.1 g. of crude material melting at 202∼207°C was obtained. Recrystallization from petroleum ether-ethanol gave 3.2 g. (72%) of tricyclohexylphenylsilane melting at 206.8∼208.2°C. Further recrystallizations from petroleum ether-ethanol did not change the melting point. Infrared spectrum offered a structural support.

Found: C, 81.21; H, 10.80. Calcd. for $C_{24}H_{38}\cdot Si$: C, 81.28; H, 10.80%.

Summary

The reactions of tricyclohexylflurosilane with *n*-butyl-, phenyl-, isopropyl- and cyclohexyllithiums in boiling petroleum ether (90∼110°C) were studied, and tricyclohexylbutylsilane and tricyclohexylphenylsilane were prepared (41 and 72%, respectively) for the first time. A secondary alkyl group can not be bonded to the silicon of tricyclohexylsilyl group even under these drastic conditions.

The author expresses his hearty thanks to Dr. Motonori Kanazashi for his kind advice during this work.

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[16] R. G. Jones and H. Gilman, "Organic Reactions", Vol. VI, R. Adams ed., John Wiley and Sons, Inc., New York (1951), p. 339.