*Syntheses of Tetracyclohexylsilane and Methylcyclohexylsilanes**

By Motonori KANAZASHI and Michio TAKAKUSA

(Received June 22, 1954)

Preparation of tetracyclohexyl-silane[1] and germane[2,3,4] were attempted by several workers with the lithium compound or the Grignard reagent unsuccessfully. Even tricyclohexylalkylsilanes[1,5] could not be obtained due to a large steric hindrance of the cyclohexyl group. The present authors succeeded in making syntheses of these compounds by hydrogenation of methylphenylsilanes and found that the steric hindrance in these molecules was conquerable, though it had a fairly large effect in the case of substitution reaction. In this work, trimethylcyclohexylsilane, dimethyldicyclohexylsilane, methyltricyclohexylsilane, and tetracyclohexylsilane were prepared.

Experimental**

Methylphenylsilanes.—These compounds were prepared from chlorobenzene and corresponding methylchlorosilane by the Wurtz-Fittig reaction in benzene solution.

Trimethylphenylsilane: b.p. 170–171°, n_D^{20} 1.4901, d_4^{20} 0.8687. MR_D: obsd. 50.03, calcd. 50.10.

Dimethyldiphenylsilane: b.p. 101–104° at 2.5 mm Hg., n_D^{20} 1.5593, d_4^{20} 0.9877MR_D: obsd. 69.45, calcd. 69.92.

Methyltriphenylsilane: m.p. 65–67°.

Tetraphenylsilane: m.p. 229–231°.

Raney Nickel Catalyst.—The catalyst was prepared from Raney nickel alloy, containing 38% of nickel, according to the direction of Adkins' so-called "W-6"[6], except that washing was done in hydrogen atmosphere under 300 mm. in water column instead of 1.5 atm.

Hydrogenation of Methylphenylsilanes.—Hydrogenation was carried out in a stainless-steel shaking type autoclave, 300 cc. in capacity under the condition shown in Table I. Methylcyclohexane was used as a solvent. The catalyst was supplied in two portions as the reaction did not proceed smoothly with an exception of trimethylphenylsilane.

TABLE I
HYDROGENATION OF METHYLPHENYLSILANES

Material	g. (mol.)	Catalyst g. (wt. %) (a)	Solvent g.	Pressure atm.	Temperature °C. (b)	Time hrs.	H_2 (c)	Product	Yield %
Me_3SiPh	30 (0.2)	4.5(15)	70	110–150	100–140(108)	2	2.98	I	67
Me_2SiPh_2	32.1(0.15)	5 (15)	70	80–100	85–170 (90)	7	5.9	II	62
$MeSiPh_3$	27.4(0.1)	5 (18)	70	60–100	80–170(100)	6	9.0	III	61
$SiPh_4$	51 (0.15)	10 (20)	80	50–100	80–150(100)	7	12.0	IV	63

(a) In the case of trimethylphenylsilane, "W-2" Raney nickel catalyst was used.
(b) The starting temperature of absorption was shown in brackets.
(c) Moles of hydrogen absorbed, to one mole of reactant.

Separation and Purification of Methylcyclohexylsilanes.

Trimethylcyclohexylsilane (I). Out of the hydrogenation mixture[a] a fraction boiling at 67–69° (25 mm.) was collected after removal of the reaction solvent by a fractionating distillation.

Dimethyldicyclohexylsilane (II). A fraction boiling at 94–103° (3–3.5 mm.) was collected.

Methyltricyclohexylsilane (III). A crystalline part was filtered out of the concentrated reaction mixture[a], washed with ethanol-methylcyclohexane mixture and recrystallized from methylcyclohexane[b].

Tetracyclohexylsilane (IV). An aimed product was extracted from the solid phase of the reaction mixture and recrystallized twice with decahydronaphthalene[c], washed with methylcyclohexane and dried in vacuum.

---

* Presented at the 7th. Annual Meeting of the Chemical Society of Japan held in Tokyo, April, 1954.

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

2) H. Bauer and K. Burschkies, *Ber.*, **65** 956 (1932).

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

4) O. H. Johnson and W. H. Nebergall, ibid., **71**, 1720 (1949).

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

** All temperatures reported here were uncorrected.

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

a) The catalyst was removed by filtration prior to these treatments.

b) This compound was dissolved in hot methylcyclohexane easily, contrasting with the case of IV.

c) This compound was hardly soluble in various solvents:

The solvent recovered from the reaction mixture was fractionated through a 30 cm. distillation column packed with stainless-steel helices, but hardly any benzene or cyclohexane were found in all cases.

Infrared Absorption Spectra.—The spectra were measured using a Perkin-Elmer Model 12–C Spectrometer with a rock salt prism of Government Chemical Industrial Research Institute, Tokyo. Two samples, trimethylphenylsilane and dimethyldiphenylsilane, were run in a potassium bromide cell 0.0125 mm. thick, without using a solvent. The other samples were measured in carbon tetrachloride solution.

$MeSiPh_3$, in about 20% carbon tetrachloride solution, cell thickness 0.1 mm.

I–III, in about 10% 0.1 mm.

IV, in about 3% 0.2 mm. and 1 mm.

Results and Discussion

All these phenylsilanes absorbed the theoretical amount of hydrogen and hydrogenation products were formed. Their physical constants and analytical data are given in Table II.

TABLE II

PHYSICAL CONSTANTS AND ANALYSES OF METHYLCYCLOHEXYLSILANES

Compound	b.p.		n_D^{20}	d_4^{20}	Molar ref.		Analyses				
							C		H		
	°C.	mm.Hg.			Obsd.	Calcd.(a)	Found	Calcd.	Found	Calcd.	
I	67–9	25	1.4477	0.8163	51.24	51.30	(b)		(b)		(c)
II	101–3	3–3.5	1.4850	0.9136	71.50	72.32	74.01	74.91	12.61	12.57	(d)
	m.p.(°C.)										
III	73.0–73.2						78.21	77.99	12.39	12.40	
IV	279–281						79.97	79.91	12.40	12.30	(e)

(a) Calculated from bond refractivities reported by E. L. Warrick, *J. Am. Chem. Soc.*, **68**, 2455 (1946).

(b) Analyses of this compound were unsuccessful due to its explosibility in the combustion tube.

(c) Mass spectra. Parent peaks: mass 156, 157 and 158 (peak height 131, 20.2 and 6.0, respectively).

(d) Mass spectra. Parent peaks: mass 224, 225 and 226 (peak height 52.8, 11.0 and 2.8, respectively).

(e) Analysis. Si %: found 7.71, calcd. 7.79.

Mass-spectrometric data are available for identification of liquid products. The mass of trimethylcyclohexylsilane consisting of the most abundant isotopes of carbon, hydrogen, and silicon, i.e. $C_9{}^{12}H_{20}{}^{1}Si^{28}$, is 156 and this peak was found in the parent group of the spectra of I.[d] Besides, the relative heights of these three peaks (see Table II (c)) accord with those calculated for $C_9H_{20}Si$ based on the known isotopic abundance ratios[7] of involved elements. Other remarkable peaks are: "73, 74, 75" (corresponding to Me_3Si^+), "141, 142, 143" ($Me_2C_6H_{11}Si^+$), and "135, 136, 137" (Me_2PhSi^+). The presence of the last group (135–137), with absence in the intermediate region (p.e. from 152 to 155, or from 137 to 140), reveals contamination of unreacted trimethylphenylsilane, and at the same time shows that no incomplete hydrogenation products were formed (see Table III). The similar results were derived from mass spectra of II, but unreacted dimethyldiphenylsilane was not found.

TABLE III

POSSIBLE PRODUCTS IN HYDROGENATION OF TRIMETHYLPHENYLSILANE AND THEIR MASSES. (Some of fragments of these to be found in mass spectra are also listed)

$Me_3C_6H_{11}Si^+$	156	157	158
$Me_3C_6H_9Si^+$	154	155	156
$Me_3C_6H_7Si^+$	152	153	154
$Me_3C_6H_5Si^+$	150	151	152
$Me_2C_6H_{11}Si^+$	141	142	143
$Me_2C_6H_9Si^+$	139	140	141
$Me_2C_6H_7Si^+$	137	138	139
$Me_2C_6H_5Si^+$	135	136	137
Me_3Si^+	73	74	75

Infrared spectra of the four products and the three materials are given in Fig. 1. The quite identical spectra were obtained for the three methylcyclohexylsilanes. They also accord with spectrum of dicyclohexylsilane reported by West and Rochow[8], except absence of the absorption bands of Si—H[8], in 4.7–4.8 μ and 10.6–10.7 μ, and presence in 7.11 μ and 8.0 μ. Absorption bands in 7.11 μ and 8.0 μ are assigned to methyl group bonded to silicon as reported by Young et. al.[9] The

---

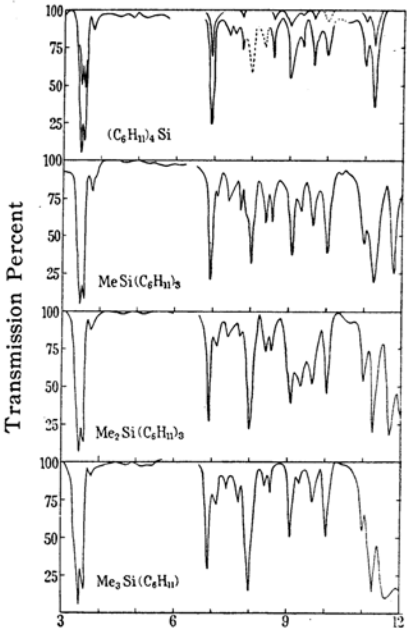
ether, ethanol, carbon tetrachloride, benzene, cyclohexane, and methylcyclohexane. This compelled us to choose a high-boiling solvent for extraction and recrystallization.

[d] It is impossible to calculate the ordinary molecular weight from the masses and the relative heights of the parent peaks strictly, unless numbers of included atoms are postulated.

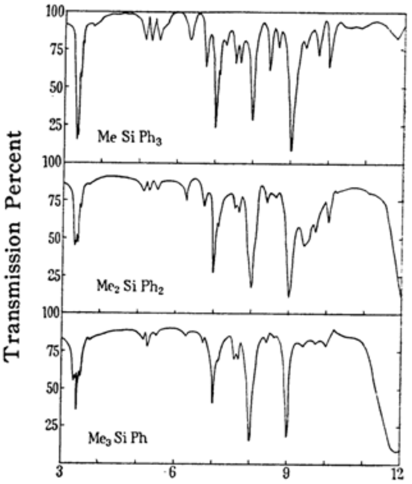
[7] G. T. Seaborg and I. Perlman, *Revs. Modern Phys.*, **20**, 585 (1948).

[8] R. West and E. G. Rochow, *J. Org. Chem.*, **18**, 303 (1953).

[9] C. Young, P. C. Servais, C. C. Currie and M. J. Hunter, *J. Am. Chem. Soc.*, **70**, 3758 (1948).



Wave Length in Microns
Fig. 1 (A).
Infrared spectra of cyclohexylsilanes.



Wave Length in Microns
Fig. 1 (B).
Infrared spectra of methylphenylsilanes.

spectrum of tetracyclohexylsilane is identical with that of dicyclohexylsilane except the absorption bands of Si—H. In these spectra, the absorption assigned to alkene or phenyl group was not found, 3.2–3.4 μ, 7.0 μ and 9.7–9.8 μ. Further discussions, p. e. on the characteristic bands of cyclohexyl bonded to silicon or on the inverted isomerism, could not be made for the lack of data to which to refer.

All these results give a sufficient support to the identification of the prepared substances.

Steric hindrance of cyclohexyl group in organosilicon compounds was first discussed by Kipping and Cusa.⁵⁾ Their attempt to introduce one phenyl and three cyclohexyl groups to one silicon atom with Grignard reagent resulted in formation of phenyldicyclohexylcyclohexoxysilane. The reaction involving cyclohexyllithium and silicon tetrachloride¹⁾ was studied by Nebergall and Johnson, and only tricyclohexylchlorosilane was obtained. Concerning it, the following reactions were also reported;

$$(C_6H_{11})_3SiCl + LiAlH_4 \longrightarrow (C_6H_{11})_3SiH$$
$$(C_6H_{11})_3SiH + X_2 \longrightarrow (C_6H_{11})_3SiX$$
where X is Br or I,
$$(C_6H_{11})_3SiCl + KOH \longrightarrow (C_6H_{11})_3SiOH$$
$$(C_6H_{11})_3SiOH + Ac_2O \longrightarrow (C_6H_{11})_3SiOAc$$

but the halogen atom was not substituted for by any alkyl groups. These facts should be attributed to the steric hindrance of the cyclohexyl group. The steric hindrance in organosilicon compounds is small, compared with carbon compounds because of the larger size of silicon and the longer distance in which silicon is bonded to carbon or other atoms.

Steric effects of *tert*-butyl¹⁰⁾, isopropyl¹¹⁾, cyclohexyl¹²⁾, *o*-tolyl¹³⁾, and 1-naphthyl¹⁴⁾ have been discussed in previous literatures in silico-organic chemistry. The *t*-butyl has the largest effect of them and the results lead to the natural conclusion that the extent of the group in the surrounding space of silicon atom is a sole factor. From this point of view, cyclohexyl and isopropyl or other secondary alkyl groups have almost equal effects, as far as cyclohexyl is combined with

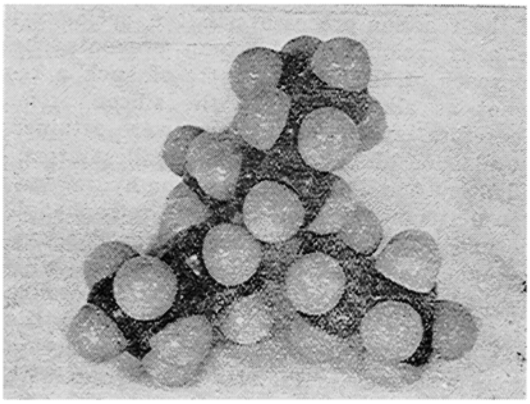


Fig. 2.
Stuart model of tetracyclohexylsilane.

---

10) L. J. Tyler, L. H. Sommer and F. C. Whitmore, *J. Am. Chem. Soc.*, **69**, 981 (1947); **70**, 2876 (1948); L. H. Sommer and L. J. Tyler, ibid., **76**, 1030 (1954).

11) H. Gilman and R. N. Clark, *J. Am. Chem. Soc.*, **69**, 1499 (1947); C. Eaborn, *J. Chem. Soc.*, **1952**, 2840.

12) Loc. cit.

13) H. Gilman and G. N. R. Smart, *J. Org. Chem.*, **15**, 720 (1950); **16**, 424 (1951).

14) H. Gilman and C. G. Brannen, *J. Am. Chem. Soc.*, 4640 (1951); A. D. Petrov and V. S. Chugunov, ***Doklady Akad. Nauk, S. S. S. R.***, **77**, 815 (1951); P. S. Sanin and A. D. Petrov, ***Zhur. Obschei Khim.***, **22**, 1124 (1952).

silicon in *e*-bond. And free rotation around C—C bond in it is somewhat prevented because of its ring-form structure.

The stuart model of tetracyclohexylsilane is constructed without much jostling, but the free rotation around the Si—C bond and the inverted isomerism of the cyclohexane ring is prevented entirely as shown in Fig. 2. The inversion is possible with difficulty in models of the other three compounds. The difficulty is diminished with the number of cyclohexyl groups, but these inverted isomers involving *p*-bond seemed to be more unstable than the original isomers involving no *p*-bond. (See Fig. 3.) It is of much theoretical interest to determine whether the inverted isomer is present or not in the real substance, but this fact is not known from the infrared spectra of these compounds.

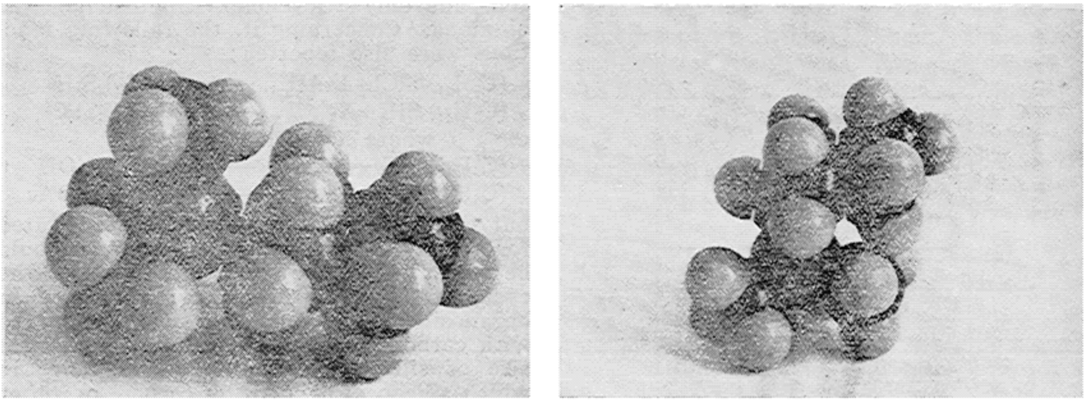


Fig. 3 (1). Fig. 3 (2).

Fig. 3. The two forms of stuart models of cyclohexyltrimethylsilane.
Left: Cyclohexyl bonds to silicon in *e*-bond and Si-cyclohexyl rotation is free.
Right: Cyclohexyl bonds to silicon in *p*-bond and the rotation is prevented.

Now it is clear that the steric hindrance in them is not essential, or, not a subject of the structures themselves but a subject of the reaction processes; that is, cyclohexyl in a tricyclohexylsilyl group prevents the approach of the active centre of such a reagent as alkyllithium to the silicon atom. Therefore, syntheses of them were attained by addition of hydrogen, the smallest atom.

Ipatiev and Dolgov reported on hydrogenation of triphenylcarbinol[15] and tetraphenylmethane[16]. In both cases, tricyclohexylmethane was produced. Consideration with the Stuart model shows that it is impossible to introduce the fourth cyclohexyl to the central carbon atom in tricyclohexylmethyl group as shown in Fig. 4. This agrees with the results of Ipatiev and Dolgov. The difference in these and our results is explained by differences of atomic sizes and bond lengths. Ipatiev and Dolgov also studied analogous reaction of tetraphenylsilane under high pressure at high temperature without a catalyst[17]. In this experiment, hydrogenation did not take place, and the cleavage of Si—Ph bond with liberation of benzene was observed.

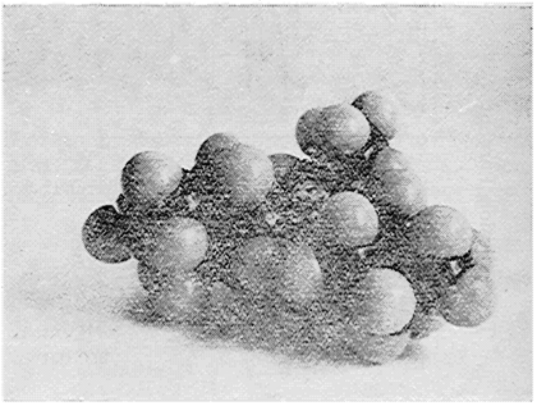


Fig. 4.
Stuart model of tricyclohexylmethyl.

Studies on the steric hindrance of cyclohexyl group in organosilicon compounds are continued and syntheses of hexacyclohexyldisilane, hexacyclohexyldisiloxane and *t*-butyltricyclohexylsilane are under investigation now in this laboratory.

Summary

For new organosilicon compounds containing cyclohexyl group were prepared by hydrogenation of corresponding phenylsilanes. They are: trimethylcyclohexylsilane, dimethyldicyclohexylsilane, methyltricyclohexylsilane, and tetracyclohexylsilane. Physical

---

[15] V. N. Ipatiev and B. N. Dolgov, *Compt. rend.*, **183**, 304 (1926).

[16] V. N. Ipatiev and B. N. Dolgov, ibid., **185**, 210 (1627).

[17] V. N. Ipatiev and B. N. Dolgov, *Ber.*, **62**, 1220 (1929).

constants and infrared absorption spectra of these compounds were measured and discussions on the steric hindrance were done with Stuart models.

The authors are indebted to Mr. S. Saeki and Mr. T. Yoshimoto for the infrared spectra and Mr. H. Sakai for the mass spectra reported in this paper. They are also grateful to Dr. O. Simamura and Dr. T. Yamada for their helpful advice and encouragement during this work.

Electrotechnical Laboratory, Agency
of Industrial Science & Technology
Nagata-cho, Chiyoda-ku, Tokyo