Anal. Calcd. for $C_{22}H_{34}Fe$ (tributyl-compound): C, 74.57; H, 9.67; Fe, 15.76. Found: C, 74.13; H, 9.38; Fe, 15.82. Calcd. for $C_{20}H_{30}Fe$ (di-/tributyl-compound): C, 73.61; H, 9.27; Fe, 17.12. Found: C, 73.02; H, 8.71; Fe, 17.70.

From the next-to-last cut, besides 0.7 g. of ferrocene crystallizing from the concentrate, 0.5 g. (4.35%) of crude VIII was separated as a reddish oil (*Anal.* Found: C, 69.15; H, 7.25; Fe, 23.41). The final fraction gave only ferrocene (0.5 g.).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN, MADISON 6, WISC.]

The Preparation and Characterization of the *cis*- and *trans*-Methylsilylcyclohexanes[1]

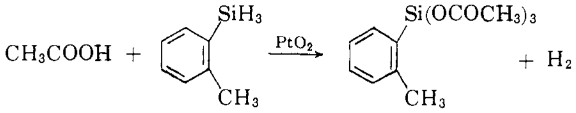
BY TERRY G. SELIN[2] AND ROBERT WEST

RECEIVED OCTOBER 19, 1961

The pure *cis* and *trans* isomers of 1-methyl-2-silylcyclohexane, 1-methyl-3-silylcyclohexane and 1-methyl-4-silylcyclohexane have been prepared and characterized. Hydrogenation of the various tolyltriethoxysilanes over Raney nickel followed by lithium aluminum hydride reduction to the free silanes produced principally the *cis* isomers. The coupling of the 3- and 4-methylcyclohexyl Grignard reagents with silicon tetrachloride again followed by reduction to the silane yielded predominantly the diequatorial isomers. The methylsilylcyclohexanes were resolved and purified by means of preparative gas chromatography. Configurational assignments were made using the modified von Auwers–Skita rule, and were consistent with predictions based on the mode of synthesis. The Grignard reagents from 1- and 2-methylcyclohexyl halides did not couple with silicon tetrachloride but instead reacted to form olefins and Si–H-containing products. 1-Methylcyclohexylmagnesium chloride also reacted abnormally with tetraethoxysilane.

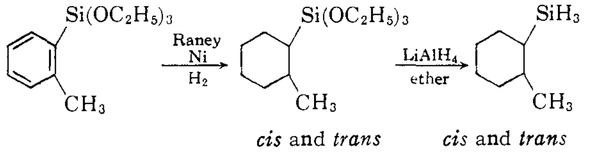
In the course of stereochemical studies concerning the addition of silanes to olefins it was necessary to prepare and identify the *cis* and *trans* isomers of 1,2-, 1,3- and 1,4-methylsilylcyclohexane (*i.e.*, 4-methylcyclohexylsilane). Normally, the syntheses would involve reactions known to be selective or stereospecific thus simplifying the configurational assignment. However, the relatively few methods by which silicon–carbon bonds can be formed limits the synthetic approach in the present case.

The heterogeneously catalyzed hydrogenation of olefins and substituted aromatic compounds frequently gives products corresponding to *cis* addition of hydrogen.[3,4] This is especially true for hydrogenation in the presence of platinum dioxide in acetic acid under mild conditions. Unfortunately, *o*-tolylsilane, triacetoxy-*o*-tolylsilane and triethoxy-*o*-tolylsilane could not be hydrogenated using platinum dioxide in acetic acid at moderate temperatures and pressures (*i.e.*, 30° and 60 p.s.i.g.). The addition of Adams catalyst to solutions of *o*-tolylsilane in acetic acid resulted in the rapid evolution of hydrogen and the formation of triacetoxy-*o*-tolylsilane



Similar reactions have recently been described utilizing chloroplatinic acid as a catalyst.[5]

Raney nickel in absolute ethanol at temperatures of 95–115° readily effected hydrogenation of triethoxy-*o*-tolylsilane. These conditions are similar to those used by Benkeser[6] in selectively hydrogenating trimethylsilylalkynes to the corresponding *cis*-olefins. The product, after reduction to the silane with lithium aluminum hydride, was resolved into two isomeric components by the use of vapor phase chromatography. The *m*-



and *p*-tolyltriethoxysilanes were hydrogenated in the same way with two isomers arising in each instance. Samples of the isomers were collected from the gas chromatograph and characterized by their refractive indices, infrared spectra and combustion analyses.

Each set of isomers must necessarily be *cis–trans* pairs since the purity of the triethoxytolylsilanes was demonstrated by lithium aluminum hydride reduction to the tolylsilane followed by gas chromatographic analysis. The chromatogram of each tolylsilane was shown to be characteristic and illustrated the absence of the other isomers except in trace amounts.

A second synthetic approach was also utilized in the preparation of the 1,3- and 1,4-methylsilylcyclohexanes. Coupling of the appropriate Grignard reagent with silicon tetrachloride provided a mixture of the *cis*- and *trans*-methylcyclohexyltrichlorosilanes. The methylsilylcyclohexanes were obtained by lithium aluminum hydride reduction and the isomers were separated by gas chromatography. These isomers were present in different ratios, but were otherwise identical in all respects to those obtained by the hydrogenation route. The Grignard reagent from 2-methylcyclohexyl bromide did not react with silicon tetrachloride or tetraethoxysilane in the expected manner

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(1) This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under Contract No. AF 49(638)-285. Reproduction in whole or part is permitted for any purpose of the United States Government.

(2) General Electric Co., Silicone Products Department, Waterford, N. Y.

(3) S. Siegel and M. Dunkel in "Advances in Catalysis," edited by A. Farkas, Vol. IX, Academic Press, Inc., New York, N. Y., 1957, p. 15.

(4) R. P. Linstead, W. E. Doering, S. B. Davis, P. Levine and R. R. Whetstone, *J. Am. Chem. Soc.*, **64**, 1985 (1942).

(5) G. H. Barnes, Jr., and G. W. Schweitzer, U. S. Patent 2,967,171 (1961).

(6) R. A. Benkeser and R. A. Hickner, *J. Am. Chem. Soc.*, **80**, 5298 (1958).

and thus did not provide an alternate path to *cis-* and *trans-*1-methyl-2-silylcyclohexane.

While the methods of synthesis suggest configurational assignments for the several *cis–trans* pairs, additional certainty was achieved by application of the von Auwers–Skita rule,[7–9] restated to the effect that the isomer having the greater number of axial substituents within a series will have the higher boiling point and refractive index and the greater density.[10] It is recognized that such an empirical rule is of limited reliability especially in complex systems. However, the application of the modified von Auwers–Skita rule to disubstituted cyclohexanes has proved very successful with a variety of compounds.[11] In Table I the assignment is given for the isomeric methylsilylcyclohexanes and their carbon analogs, the dimethylcyclohexanes. The various isomers could not be completely separated by fractional distillation so retention times are included instead of boiling points. Cason and Miller[13] have shown that compounds which differ only in subtle changes of structure give retention times on non-polar columns which are proportional to their boiling points.

Table I

Properties of Isomeric Dimethylcyclohexanes and Methylsilylcyclohexanes

Compound	Dimethylcyclohexanes[12] B.p., °C.	Dimethylcyclohexanes[12] $n^{25}\text{D}$	Retention time, min.[a]	Methylsilylcyclohexanes $n^{25}\text{D}$	Methylsilylcyclohexanes Anal.[b] Carbon	Methylsilylcyclohexanes Anal.[b] Hydrogen
1,4-*trans*	119.4	1.4185	47.68	1.4431	65.5, 65.3	12.3, 12.3
1,3-*cis*	120.1	1.4206	47.53	1.4450	65.7, 65.5	12.4, 12.4
1,2-*trans*	123.4	1.4247	56.33	1.4500	65.9	12.9
1,4-*cis*	124.3	1.4273	56.60	1.4510	65.7	12.7
1,3-*trans*	124.5	1.4284	56.40	1.4523	65.3	12.5
1,2-*cis*	129.7	1.4336	71.60	1.4592	65.7	12.6

[a] The retention times were determined at 100° utilizing a 25-foot column packed with Dow Corning 550 Silicone fluid on firebrick. The helium flow rate was 60 ml. per min. [b] Calcd. for $C_7H_{15}Si$: C, 65.53; H, 12.57.

Table II

Preparation of Isomeric Methylsilylcyclohexanes

Compound	Hydrogenation, % *cis*	Hydrogenation, % *trans*	Grignard coupling, % *cis*	Grignard coupling, % *trans*
1,2	85	15	..	..
1,3	57	43[a]	72	28
1,4	82	18	30	70

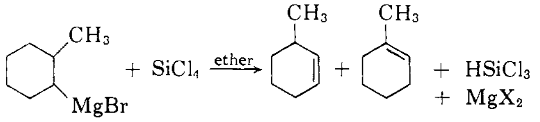
[a] Somewhat higher temperatures were required to hydrogenate triethoxy-*m*-tolylsilane, and this may serve to explain the comparatively lower *cis/trans* ratio.

It can be seen in Table I that the retention times of the methylsilylcyclohexanes fall into three groups as do the boiling points of the corresponding dimethylcyclohexanes. Each group is characterized by the number of skew interactions which are present in the molecule in addition to those of the cyclohexyl ring itself. The first group consists of the 1,3-*cis* and 1,4-*trans* isomers containing no additional skew interactions in the more stable conformation. The second group includes the 1,2-*trans*, 1,3-*trans* and 1,4-*cis* isomers having either one or two additional interactions. The 1,2-*cis* isomer constitutes the third group having three additional skew interactions. Comparison of the refractive indices of the methylsilylcyclohexanes and the dimethylcyclohexanes shows that the order is the same for each series. In fact, the difference in refractive index of each *cis–trans* pair is approximately the same in each series. It is important to note that the infrared spectrum of each of the six purified methylsilylcyclohexanes is unique.

The above configurational assignment is consistent with the mode of synthesis since hydrogenation over Raney nickel resulted in preferential formation of the *cis* isomers. The Grignard route produced a preponderance of the diequatorial isomer in both instances. These data are summarized in Table II.

Surprisingly few reactions of substituted cyclohexyl Grignard reagents have been studied with regard to stereochemistry of the products.[13] The few examples which exist support the present work in that a majority of the more thermodynamically stable isomer[14] is found. For example, Corey and Sneen[15] have shown that carbonation of cholestanyl and cholesteryl Grignard reagents results in a *β*-oriented carboxyl group (*i.e.*, equatorial). Similarly, Goering and McCarron[16] obtained primarily the *cis* isomer from carbonation of the Grignard reagent of either *cis-* or *trans-*3-methylcyclohexyl chloride.

The Grignard reagents prepared from 1-methylcyclohexyl chloride and 2-methylcyclohexyl bromide reacted with silicon tetrachloride to yield olefinic products and silicon hydrides. Although the nature of the silicon hydrides was not established, the over-all reaction is probably well represented as



When 2-methylcyclohexyl Grignard reagent was prepared using ether as a solvent, the majority of the olefin produced was 3-methylcyclohexene. However, the use of tetrahydrofuran as a solvent resulted in almost exclusive formation of 1-methylcyclohexene. Reduction of chlorosilanes with Grignard reagents has been reported by a number of workers.[17–19] However, in previous work the

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(7) K. von Auwers, *Ann.*, **420**, 84 (1920).

(8) A. Skita, *Ber.*, **53**, 1792 (1920).

(9) A. Skita and W. Faust, *ibid.*, **64**, 2878 (1931).

(10) W. G. Dauben and K. S. Pitzer in "Steric Effects in Organic Chemistry," edited by M. S. Newman, John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 1.

(11) R. B. Kelly, *Can. J. Chemistry*, **35**, 149 (1957).

(12) "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," American Petroleum Institute Research Project 44, Carnegie Press, 1953.

(13) M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, Inc., New York, N. Y., 1954.

(14) The more thermodynamically stable isomer as used in this discussion refers to the *cis–trans* isomer which contains the smaller number of skew interactions in excess of those in the cyclohexyl ring itself. Of course, the more stable conformation is assumed. In simple disubstituted cyclohexanes, it refers to the isomer having the fewer number of axial substituents, neglecting electrostatic interactions and other similar effects.

(15) E. J. Corey and R. A. Sneen, *J. Am. Chem. Soc.*, **75**, 6234 (1953).

(16) H. L. Goering and F. H. McCarron, *ibid.*, **80**, 2287 (1958).

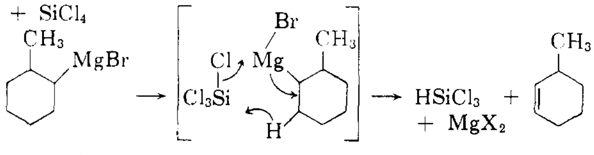
(17) A. G. Brook and S. Wolfe, *ibid.*, **79**, 1437 (1957).

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

(19) M. C. Harvey, W. H. Nebergall and J. S. Peake, *J. Am. Chem. Soc.*, **79**, 2762 (1957).

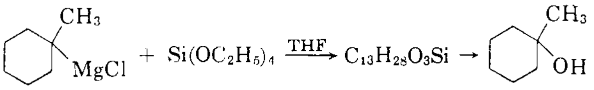
trialkyl stage was necessarily reached before reduction occurred.

These reactions may be analogous to reductions of ketones by hindered Grignard reagents, which are thought to occur by a cyclic mechanism involving nucleophilic attack of a β-hydrogen atom of the Grignard reagent with simultaneous formation of an olefin.[20] An analogous path has been suggested for the reduction of trialkylchlorosilanes with Grignard reagents.[19] Thus, the ease of approach of a β-hydrogen atom from 2-methylcyclohexyl Grignard reagent may preclude the normal coupling

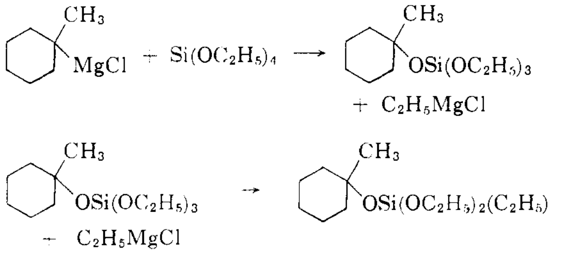


The lithium reagent from 1-methylcyclohexyl chloride also reacted with silicon tetrachloride to produce a silicon hydride and 1-methylcyclohexene. This behavior is somewhat surprising because *t*-butyltrichlorosilane can be prepared in good yield from *t*-butyllithium and silicon tetrachloride.[21]

An even more interesting result was obtained from the reaction of tetraethoxysilane and 1-methylcyclohexyl Grignard reagent. The reaction appeared to proceed normally giving a 19% yield of a product having the proper boiling range and analysis. However, reduction of this product with lithium aluminum hydride yielded only 1-methylcyclohexanol in 70% yield.



The structure of the intermediate has not yet been determined, but it seems probable that oxygenation of the ring must occur during the Grignard reaction. It is difficult to rationalize the results, but one possible explanation is that an alkyl exchange took place between tetraethoxysilane and the Grignard reagent, followed by a reaction with the resulting ethyl Grignard reagent



If these unprecedented reactions took place, the product diethoxy-(1-methylcyclohexoxy)ethylsilane would give the proper analysis and yield 1-methylcyclohexanol upon reduction and hydrolysis.

Experimental

Vapor Phase Chromatography.—Complete resolution of the various *cis–trans* pairs was accomplished on a 25-ft. copper column (0.25" o.d.) packed with 30% DC-550 Silicone oil on 30 mesh firebrick. Retention times were determined isothermally at 100° at a flow rate of 60 ml. of helium per minute. Samples of each of the isomers were obtained by preparative vapor phase chromatography. Isomers separated in this manner always contained small amounts of impurities, probably siloxanes from the liquid phase. To eliminate these impurities, each component was further purified by passing it through a 5-foot column at 80°. This procedure led to reproducible spectra and refractive indices for each component. Although such preparative gas chromatography is tedious, the quality of the results is unmatched by other procedures.

Since the peaks obtained from the chromatograph were nearly Gaussian in shape, the area under each was obtained by multiplying the height of the curve by the half-width. These areas were used as an indication of the percentage of each component in the mixture. In comparisons with mixtures of silanes with known compositions, this method was found to be accurate within 2%.

Materials.—The *o*-, *m*- and *p*-tolyl bromides were purchased from Eastman Kodak Co., and the 2-, 3- and 4-methylcyclohexyl bromides were obtained from Matheson, Coleman and Bell. The 1-methylcyclohexyl chloride was prepared from 1-methylcyclohexanol and anhydrous hydrogen chloride[22] in 75% yield. All halides were redistilled immediately before use. Silicon tetrachloride was purchased from Matheson Coleman and Bell and used without further purification. Tetraethoxysilane was purchased from the Dow Corning Corp. and redistilled, b.p. 161–163 (atm.).

***o*-Tolyltriethoxysilane.**—A Grignard reagent was prepared from 103 g. (0.6 mole) of *o*-tolyl bromide and 18.6 g. (0.72 g. atom) of magnesium turnings. The preparation was initiated with 150 ml. of tetrahydrofuran and then completed using 300 ml. of diethyl ether as solvent. This reagent was transferred under nitrogen to a dropping funnel and added dropwise to a mixture of 250 g. (1.2 moles) of tetraethoxysilane in 1 liter of anhydrous ether. Although a large heat effect was not observed, the precipitation of magnesium salts was immediate. After the addition was complete, the mixture was stirred at reflux for an additional 16 hours. The magnesium salts were allowed to settle and the clear yellow solution decanted into a distillation pot. Attempts to filter such mixtures failed because the gelatinous salts consistently clogged the filters. After removal of the ether by distillation, the liquid residue was taken up in 300 ml. of petroleum ether (b.p. 60–68°) to precipitate further any dissolved salts. Again the clear solution was decanted and distilled to remove solvent. Two fractional distillations of the residue provided 105 g. (69% yield) of *o*-tolyltriethoxysilane, b.p. 106–109° at 2.4 mm., $n^{25}\text{D}$ 1.4660.

Anal. Calcd. for $C_{13}H_{22}O_3Si$: C, 61.37; H, 8.72. Found: C, 61.29; H, 8.84.

***m*-Tolyltriethoxysilane.**—A Grignard reagent was prepared from 103 g. (0.6 mole) of *m*-bromotoluene using diethyl ether as solvent. This Grignard reagent was added slowly to a stirred solution of tetraethoxysilane in ether and the mixture refluxed for a total of 36 hours. The reaction mixture was worked up in the manner described for the *o*-isomer. Fractional distillation yielded 44 g. (29% yield) of *m*-tolyltriethoxysilane, b.p. 70–73° at 0.1 mm., $n^{25}\text{D}$ 1.4622.

Anal. Calcd. for $C_{13}H_{22}O_3Si$: C, 61.37; H, 8.72. Found: C, 61.25; H, 8.84.

***p*-Tolyltriethoxysilane** was prepared in 48% yield from *p*-tolyl Grignard reagent and tetraethoxysilane using the method developed for the *m*-isomer. The final product distilled at 104–106° at 1.8 mm. and had $n^{25}\text{D}$ 1.4626.

Anal. Calcd. for $C_{13}H_{22}O_3Si$: C, 61.37; H, 8.72. Found: C, 61.29; H, 8.62.

***o*-Tolylsilane.**—Lithium aluminum hydride (2.5 g., 0.07 mole) was dissolved in 40 ml. of anhydrous ether. While stirring the mixture, a solution of 12.7 g. (0.05 mole) of *o*-tolyltriethoxysilane in 40 ml. of ether was added at a rate to maintain steady reflux. Upon completion of the addition, the mixture was stirred at reflux for an additional 16 hours. Utilizing a 30-cm. Widmer column, ether was removed by distillation to a pot temperature of 45°. The

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[20] H. S. Mosher and E. La Combe, *J. Am. Chem. Soc.*, **72**, 3994 (1950).

[21] L. H. Sommer and L. J. Tyler, *ibid.*, **76**, 1030 (1954).

[22] H. L. Goering, P. I. Abell and B. F. Aycock, *ibid.*, **74**, 3588 (1952).

receiving flask was replaced by a Dry Ice trap and the system connected to a water aspirator. The remainder of the liquid products was removed at reduced pressure over the temperature range 25–45°. Fractional distillation of the collected mixture gave 2.8 g. (46% yield) of *o*-tolylsilane boiling at 148–149°, $n^{25}\text{D}$ 1.5182. Gas chromatographic analysis indicated no impurities.

Anal. Calcd. for $C_7H_{10}Si$: C, 68.77; H, 8.25. Found: C, 68.28, 68.48; H, 8.44, 8.39.

***m*-Tolylsilane.**—By means of the method developed for the preparation of the *o*-isomer, *m*-tolylsilane was prepared in 87% yield by the lithium aluminum hydride reduction of *m*-tolyltriethoxysilane. The liquid product distilled at 145–145.5°, $n^{25}\text{D}$ 1.5111. Gas chromatographic analysis indicated that the product was contaminated by less than 1% *o*- and *p*-isomers.

Anal. Calcd. for $C_7H_{10}Si$: C, 68.77; H, 8.25. Found: C, 69.39; H, 8.74.

***p*-Tolylsilane.**—The lithium aluminum hydride reduction of *p*-tolyltriethoxysilane by the above method yielded 87% *p*-tolylsilane, b.p. 147–147.5° (m.p. −6°), $n^{25}\text{D}$ 1.5100. Gas chromatography indicated that approximately 1% *o*-tolylsilane was present as an impurity.

Anal. Calcd. for $C_7H_{10}Si$: C, 68.77; H, 8.25. Found: C, 68.57; H, 8.30.

Catalytic Hydrogenation of Tolyltriethoxysilanes.—In a typical run a stainless steel high pressure hydrogenation bomb was changed with 25.4 g. (0.1 mole) of the tolyltriethoxysilane, 2.5 g. of Raney nickel and 45 ml. of absolute ethanol. Hydrogenation was carried out at 1000 p.s.i. and 95–105° for 16 hours. The reaction mixture was filtered and distilled under reduced pressure. The mixture of isomeric methyl-(triethoxysilyl)-cyclohexanes and unreacted tolyltriethoxysilane was reduced by refluxing with lithium aluminum hydride in ether for 36 hours. The reaction mixture was poured onto ice and water and the ether layer was separated, washed with water and dried. Distillation gave a mixture of the *cis*- and *trans*-methylcyclohexylsilane, together with some tolylsilane (0–25%). The composition of the mixtures were determined by gas chromatography, and pure samples of the *cis* and *trans* isomers were obtained by preparative gas chromatography. Over-all yields of methylcyclohexylsilane (*cis* and *trans* isomers) were about 50%. The proportions of *cis* and *trans* isomers resulting from the hydrogenations are given in Table II.

Attempted Preparation of *cis*- and *trans*-1-Methyl-2-silylcyclohexane by the Grignard Method.—A Grignard reagent was prepared under nitrogen from 18 g. (0.1 mole) of 2-methylcyclohexyl bromide in 250 ml. of diethyl ether. The Grignard reagent was transferred to a dropping funnel which in turn was fitted to a 1-liter flask containing 34 g. (0.1 mole) of silicon tetrachloride and 200 ml. of ether. The Grignard reagent was added slowly to the silicon tetrachloride solution with stirring. No immediate reaction was evident and the mixture was heated at reflux for 16 hours. During this time, the dark color associated with the Grignard reagent disappeared with simultaneous formation of magnesium salts. The clear yellow solution was isolated by decantation and the volatile materials removed by distillation (32–60°). These volatile components were tested for the presence of Si–H by adding a few milliliters of the mixture to a dilute alcoholic KOH solution. The rapid evolution of hydrogen indicated the presence of the Si–H linkage. Distillation of the higher boiling components yielded 4.2 g. of material boiling at 104–108°. Gas chromatography identified this material as 79% 3-methylcyclohexene, 10% 1-methylcyclohexene and 2% methylcyclohexane.

The use of tetrahydrofuran as a solvent in this preparation also failed to provide any of the desired product. However, the olefin mixture which was isolated proved to be 1-methylcyclohexene with only a trace of 3-methylcyclohexene present. Similarly, the desired product was not obtained when tetraethoxysilane was used in place of silicon tetrachloride.

Grignard Preparation of *cis*- and *trans*-1-Methyl-3-silylcyclohexane.—A mixture of *cis*- and *trans*-1-methyl-3-(trichlorosilyl)-cyclohexane was prepared in 17% yield from the reaction of 3-methylcyclohexyl Grignard reagent with excess silicon tetrachloride in ether solvent. The reaction of the Grignard reagent with silicon tetrachloride was slow, requiring 18 hours for completion. The product was isolated by decantation from the magnesium salts followed by distillation (b.p. 80–100° at 12.5 mm.). Consistently low yields from this reaction were found to originate with the preparation of the Grignard reagent which was only 35–40% complete.

Anal. Calcd. for $C_7H_{13}SiCl_3$: active Cl, 46.0. Found: active Cl, 45.3, 45.7.

Reduction of the *cis*- and *trans*-1-methyl-3-(trichlorosilyl)-cyclohexane mixture with lithium aluminum hydride provided a 32% yield of the desired silanes. The reaction mixture was worked up by hydrolysis in crushed ice followed by isolation and distillation of the ether phase. The mixture of silanes boiling at 145–146° was analyzed by gas chromatography and found to consist of 72% *cis*-1-methyl-3-silylcyclohexane, $n^{25}\text{D}$ 1.4450, and 28% *trans*-1-methyl-3-silylcyclohexane, $n^{25}\text{D}$ 1.4523. The infrared spectra and retention times of these isomers were identical with those obtained from the products of the hydrogenation route.

***cis*- and *trans*-1-Methyl-4-silylcyclohexane.**—Using the same procedure as in the preparation of the 1-methyl-3-(trichlorosilyl)cyclohexanes, a mixture of *cis*- and *trans*-1-methyl-4-(trichlorosilyl)-cyclohexane was obtained in 25% yield. The mixture boiled at 93–97° at 15 mm.

Anal. Calcd. for $C_7H_{13}SiCl_3$: active Cl, 46.0. Found: active Cl, 45.0, 45.7.

Lithium aluminum hydride reduction of the 1-methyl-4-(trichlorosilyl)-cyclohexane mixture yielded a mixture of *cis*- and *trans*-1-methyl-4-silylcyclohexane boiling at 132–134°. The composition of this mixture was 70% *trans*-1-methyl-4-silylcyclohexane, $n^{25}\text{D}$ 1.4431, and 30% *cis*-1-methyl-4-silylcyclohexane, $n^{25}\text{D}$ 1.4508. Again, the retention times and infrared spectra of these isomers were identical with those obtained from the hydrogenation procedure.

1-Methyl-1-silylcyclohexane (Attempted). A. Grignard Coupling with Silicon Tetrachloride.—A Grignard reagent was prepared in ether from 66 g. (0.5 mole) of 1-methylcyclohexyl chloride and added to 170 g. (1.0 mole) of silicon tetrachloride in ether. After 18 hours at reflux, the magnesium salts were removed by filtration under nitrogen and the clear yellow solution distilled to remove ether. The mixture of higher boiling products was reduced with lithium aluminum hydride without further purification. After hydrolysis of the reaction mixture, the organic phase was isolated and distilled to yield methylcyclohexane and 1-methylcyclohexane as the only volatile products of the reaction.

B. Organolithium Coupling with Silicon Tetrachloride.—Essentially the procedure employed by Kamienski and Esmay[23] in the preparation of *t*-butyllithium was used. In a dry-box, 3.5 g. (0.5 g. atom) of lithium dispersion (containing 2% sodium) and 200 ml. of purified pentane was placed in a 500-ml. three-necked flask. By means of a dropping funnel, 26.4 g. (0.2 mole) of 1-methylcyclohexyl chloride in 100 ml. of pentane was added to the dispersion at a rate to maintain reflux. The entire reaction was carried out under argon. This lithium reagent was added dropwise to 68 g. (0.4 mole) of silicon tetrachloride in 500 ml. of pentane. No reaction was evident, so the mixture was heated at reflux for 36 hours. The resulting solution was decanted from the salts and fractionally distilled to yield 17 g. (90%) of 1-methylcyclohexene and methylcyclohexane. No distillable higher boiling products were observed.

C. Grignard Coupling with Tetraethoxysilane.—A Grignard reagent was prepared as in part A except that tetrahydrofuran was used as solvent. The resulting Grignard reagent was added to excess tetraethoxysilane in ether and the mixture was refluxed for 20 hours. Magnesium salts were removed by filtration and the resulting solution was fractionally distilled. A 19% yield of a product having the proper analysis was obtained at 88–89° at 1.3 mm. with $n^{25}\text{D}$ 1.4205.

Anal. Calcd. for $C_{13}H_{28}O_3Si$: C, 59.95; H, 10.84. Found: C, 59.60; H, 10.66.

Lithium aluminum hydride reduction of the above product followed by hydrolysis and fractional distillation yielded 71% 1-methylcyclohexanol boiling at 153–155°, $n^{25}\text{D}$ 1.4588. A known sample of 1-methylcyclohexanol boiled at 154–155° and had $n4\text{D}$ 1.4588. The infrared spectrum was superimposable with that obtained from a known sample.

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(23) C. W. Kamienski and D. L. Esmay, *J. Org. Chem.*, **25**, 1807 (1960).