at the same composition, a situation similar to that in Figures 1 and 2. While we have no detailed explanation for this, it is interesting that the peak composition is about 80 mole % VI which at least allows for the possibility of a molecular bundle unit in the nematic mesophase similar to the one that we have proposed in which four molecules of VI are clustered around one of VII.

Several other features of our data merit comment. There has been disagreement as to whether nematic-isotropic transitions of binary systems occur sharply or over a temperature range.[21] The question is incidental to the main theme of this paper, but our results indicate a significant temperature range for such transitions so clearly in most cases that it must be mentioned here. The range becomes larger as the concentration of the nonmesomorphic component increases except at a maximum in the transition curve. The data also show that the smectic–nematic transitions are not sharp with the same exception. Other workers have obtained similar results.[20]

The nematic–isotropic transition curves in Figures 2 and 3 extrapolate nicely to the virtual transition temperatures for pure IIb and IIc provided by analogous data for mixtures of these anils with 4,4′-dimethoxyazoxybenzene (Ia) reported by Dave and Dewar.[3b]

In the system Ib–IIb (Figure 2), a second smectic phase was found for mixtures in the composition range 80.4–84.9 mole % Ib. The monotropic smectic–smectic transitions, which were observed on cooling the melts to 73–79°, are not included in the phase diagram because of the congestion of data points in this region.

Registry No.—Ib, 15450-65-4; IIa, 15450-66-5; IIb, 5455-87-8; IIc, 703-39-2; IV, 15440-98-9.

Acknowledgments.—This work was supported in part by a grant-in-aid from The University of North Carolina at Greensboro Research Council. The elemental analysis was performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

[21] See ref 1, p 127 ff.

The Preparation and Properties of Cyclic Six-Membered Silicon Compounds[1]

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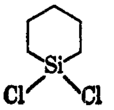
Received July 6, 1967

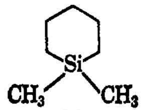
The reaction of 1,1-dichlorosilacyclohexane and 1,1-dimethylsilacyclohexane with sulfuryl chloride was studied. The chlorination of 1,1-dichlorosilacyclohexane caused little opening of the ring which was extensive during the chlorination of 1,1-dimethylsilacyclohexane. The distributions of isomers obtained from these cyclic silanes were compared with those obtained by chlorination of *n*-alkylchlorosilanes. Chlorine atoms on silicon disfavor free-radical chlorination on carbon atoms directly attached to such a silicon both in linear and cyclic silanes. Dehydrohalogenation was carried out on the monochlorinated 1,1-dichlorosilacyclohexanes with quinoline, ferric chloride, and pyrolysis.

In a continuation of our studies concerned with the preparation and properties of cyclic sila olefins,[2] the free-radical chlorination of 1,1-dichloro- and 1,1-dimethylsilacyclohexane was studied to obtain workable quantities of monochlorinated intermediates which would lend themselves to the formation of silacyclohexenes by dehydrohalogenation.

Our attention was first directed to the chlorination of 1,1-dichlorosilacyclohexane (I) since reports concerning the chlorination of 1,1-dimethylsilacyclohexane (II) had already appeared,[3] although the results were still somewhat unclear.

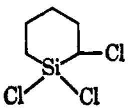


I

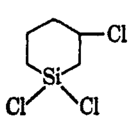


II

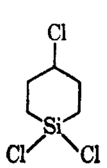
Treatment of I with sulfuryl chloride and benzoyl peroxide resulted in a good yield of monochlorinated product. Complete separation of the isomers by vpc was not achieved completely, despite the use of many different analytical columns[4] and conditions. It was possible by this analytical method, however, to estimate that the 2-chloro isomer[4] (III) comprised about 19% of the reaction product. This value was corroborated by the nmr spectrum[5] of a reaction mixture consisting of compounds III, IV, and V. By comparison of the relative peak areas of the methine hydrogens in these three compounds, a value of 22% for III was obtained. Indirect methods were devised to determine the relative percentages of IV and V.



III



IV



V

Direct titration of a redistilled sample of the monochlorinated isomers for hydrolyzable chlorine gave a value of 58% for compound IV. This value is based on the assumption that only the β isomer (IV) will provide 3 equiv[6] of hydrochloric acid, while III and V will pro-

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[1] Part V of a series on cyclic silicon compounds. Part IV: R. A. Benkeser and R. F. Cunico, *J. Org. Chem.*, **32**, 395 (1967).

[2] (a) R. A. Benkeser, Y. Nagai, J. L. Noe, R. F. Cunico, and P. H. Gund, *J. Am. Chem. Soc.*, **86**, 2446 (1964); (b) R. A. Benkeser, J. L. Noe, and Y. Nagai, *J. Org. Chem.*, **30**, 378 (1965); (c) R. A. Benkeser and R. F. Cunico, *J. Organometal. Chem.*, **4**, 284 (1965).

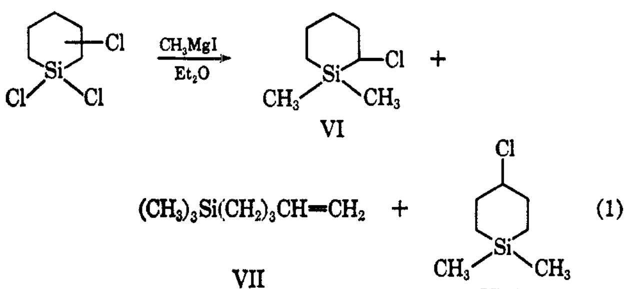
[3] R. Fessenden and F. J. Freenor, *J. Org. Chem.*, **26**, 2003 (1961); R. J. Fessenden and J. S. Fessenden, *ibid.*, **28**, 3490 (1963).

[4] Approximately 20 different columns were tried. The best separation which could be achieved resulted in two peaks. The first peak was pure 1,1,2-trichlorosilacyclohexane and the second was a mixture of 1,1,3- and 1,1,4-trichlorosilacyclohexanes.

[5] The methine hydrogen of III is quite characteristic at about τ 6.41 and lies upfield from the methine hydrogens of IV and V.

[6] L. H. Sommer and F. C. Whitmore, *J. Am. Chem. Soc.*, **68**, 485 (1946).

vide only 2 equiv of acid. Corroboration of this value of 58% was obtained by two other methods. In one case the isomer mixture was treated with methylmagnesium iodide in ether as shown in eq 1. Separation of VI, VII, and VIII was possible by vpc and values of 19% (VI), 55% (VII), and 26% (VIII) were obtained.



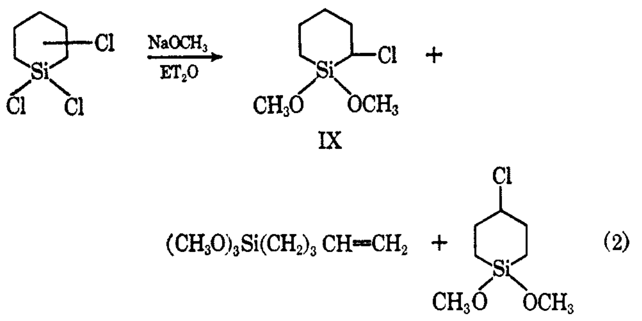
VI

VII

VIII

(1)

In another case, the isomer mixture was treated with sodium methoxide in anhydrous ether as shown in eq 2.



IX

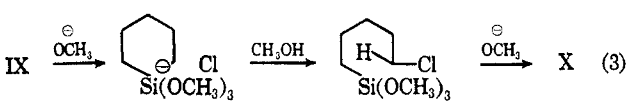
X

XI

(2)

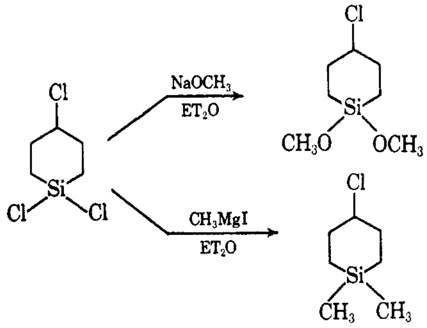
Again, IX, X, and XI were separable by vpc and values of 14% (IX), 61% (X), and 25% (XI) were obtained. When the reaction with sodium methoxide was carried out in anhydrous methanol rather than in ether, only a small amount of IX was obtained (4%) and a larger quantity of X (71%). While, at first sight, it would appear that compound IX is somehow suffering ring fission to form X, this conclusion is not justified with the data at hand. Only a 62% yield of products was realized in the methanol reaction and hence an equally plausible explanation is that compound IX suffers destruction under the conditions of the reaction[7] (hence causing a poor material balance).

One pathway whereby compound X might be arising from IX was investigated, however. It is conceivable that methoxide ion displacement on silicon in IX might occur, forming an intermediate carbanion which is instantly protonated by solvent to form 5-chloropentyltrimethoxysilane. The latter might then undergo dehydrohalogenation to form X (eq 3). That such a reaction sequence was not responsible for the formation of X was demonstrated by treating an authentic sample of 5-chloro-*n*-amyltrichlorosilane with sodium methoxide in methanol. The reaction conditions (*e.g.*, solvent and temperature) were the same as those used in the methoxide–methanol reaction with monochlorinated 1,1-dichlorosilacyclohexane. Only 0.5% of compound X was formed in this instance[8] compared with the 71% yield previously observed.



(3)

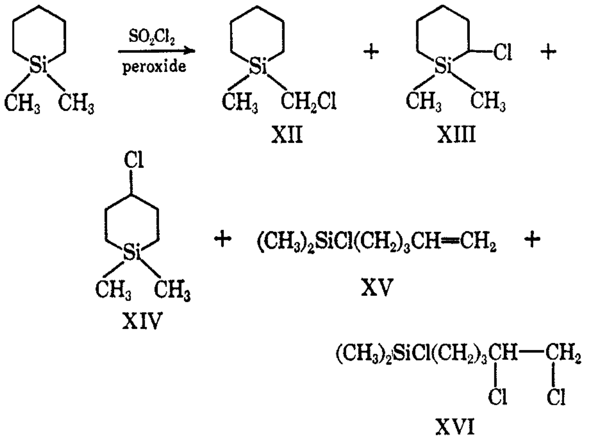
In order to show that compounds VII and X were not arising in some fashion from compound V, an authentic sample of the latter[9] was prepared and treated separately with the methyl Grignard and sodium methoxide in ether. In both cases very clean reactions occurred with only the chlorines attached to silicon being displaced. No ring opening was observed.



(4)

From the foregoing one can deduce that the percentage of 1,1,4-trichlorosilacyclohexane determined by treating the mixture of isomers with methyl Grignard and sodium methoxide in ether is reasonably accurate. Likewise the 19–22% determined directly from vpc and nmr data constitutes an accurate estimate for 1,1,2-trichlorosilacyclohexane. The remainder, or approximately 53–55%, must constitute the amount of 1,1,3-trichlorosilacyclohexane. This value compares favorably with the percentages found for the ring-opened products VII and X and by titration. Hence, the latter reflect rather well the amount of 1,1,3-trichlorosilacyclohexane in the original mixture.

In order to assess the effect of replacing the two chlorines in 1,1-dichlorosilacyclohexane by methyl groups, the chlorination of 1,1-dimethylsilacyclohexane with sulfuryl chloride was also carried out under essentially identical conditions.



XII

XIII

XIV

XV

XVI

(5)

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[7] On the supposition that IX might be dehydrohalogenated under the reaction conditions to form 1,1-dimethoxysila-2-cyclohexene, we subjected 1,1-dichlorosila-2-cyclohexene to sodium methoxide in methanol. Extensive decomposition of the olefin resulted following the usual work-up procedure. Hence, *if* the methanol promoted dehydrohalogenation, the 1,1-dimethoxysila-2-cyclohexene would not have survived, resulting in a poor material balance and a lowering of the percentage of the 2-chloro isomer.

[8] It is recognized that other mechanisms can be envisioned to account for the formation of X from IX. Since tests of such pathways were beyond the scope of the research, this aspect was not investigated further.

[9] This compound could be made conveniently by treating 1,1-dimethoxy-4-chlorosilacyclohexane with hydrogen chloride (see Experimental Section).

There were five identifiable products (XII–XVI) formed in this reaction as shown in eq 5. Compound XV was identified by matching its infrared spectrum with that of an authentic sample prepared by treating the Grignard reagent derived from 5-chloro-1-pentene with dimethyldichlorosilane. The major product (XVI) was identified from its nmr spectrum and by the fact that treatment of XVI with zinc dust produced compound XV. Authentic samples of XIII and XIV were already at hand (from reaction 1) and were identical in all respects with the 2- and 4-chloro isomers isolated from reaction 5. The identity of XII was easily established from its distinctive nmr spectrum.

Dehydrohalogenation of Monochlorinated 1,1-Dichlorosilacyclohexane.—Attempts were made to dehydrohalogenate the mixture obtained by chlorination of 1,1-dichlorosilacyclohexane. Quinoline, both in excess and in catalytic quantities, was used as well as ferric chloride and pyrolysis. The results of these attempts are set forth in Table I. Since a mixture of isomers was used in this study, the results have only qualitative significance. However, none of the dehydrohalogenation methods tried is particularly attractive as a route to the silacyclohexenes. In almost every case, isomeric mixtures result and ring opening is extensive.

TABLE I

PRODUCTS OBTAINED FROM DEHYDROHALOGENATION OF MONOCHLORINATED 1,1-DICHLOROSILACYCLOHEXANE[a,b]

Reaction	1,1-Dichloro-sila-2-cyclo-hexene, %	1,1-Dichloro-sila-3-cyclo-hexene, %	4-Pentenyl-trichloro-silane, %	Recovered starting material, %
(1) Quinoline (catalytic)	Trace	Trace	34	41
(2) Quinoline (excess)	6	15	36	. . .
(3) Ferric chloride	4	16	24	33
(4) Pyrolysis	11	19	29	23

[a] The percentages listed for each of the olefins represent an actual material balance based upon redistilled samples. The cyclic olefins reported in this table were characterized previously (see ref 2c). [b] The chlorinated mixture used here was estimated to contain 23% of the 2-chloro isomer, 57% of the 3-chloro isomer, and 20% of the 4-chloro isomer.

Nmr Spectra.—In Table II are listed the nmr spectra of the compounds whose structures were determined, either wholly or in part, by this physical method.

Chlorination Results.—In Table III are listed the ratios of isomers obtained by other workers in the chlorination and ethyl- and propylchlorosilanes. These are contrasted with the ratios obtained by us in the chlorination of 1,1-dichlorosilacyclopentane and 1,1-dichlorosilacyclohexane. In all of these compounds it is apparent that chlorination at the α position is disfavored relative to the β and probably to the γ. The best explanation seems to be the electron-withdrawing inductive effect of a dichloro- or trichlorosilyl group.

Of some interest are the results with 1,1-dimethylsilacyclohexane. Because of the complexity of the reaction products, the isomer ratios obtained in this case (Table III) can be viewed only qualitatively. It appears, however, that the presence of two methyl groups on silicon enhances chlorination at the α position which would again be predicted purely from an inductive-effect argument. Perhaps more significant, however, was almost the complete absence of β isomer in the case of 1,1-dimethylsilacyclohexane.[10] The major product in this reaction was, in fact, dimethyl(4,5-dichloropentyl)chlorosilane arising probably from extensive ring opening of the β-chloro isomer to form first dimethyl-4-pentenylchlorosilane followed by the addition of chlorine.[11] It is of interest that a similar behavior was noted when we attempted chlorination of 1,1-dimethylsilacyclopentane.[12]

Experimental Section

1,1-Dichlorosilacyclohexane[13] was prepared in 68% yield from 230 g (1.0 mole) of 1,5-dibromopentane, 48.6 g (2.0 g-atoms) of magnesium turnings, and 170 g (1.0 mole) of silicon tetrachloride. The product (114 g) boiled at 169–171° (lit.[13] bp 169–71°). Analysis by vpc (10-ft silicone oil column, 110°) indicated that the product was always contaminated with small amounts of *n*-pentyltrichlorosilane[14] (~8%) and 4-pentenyltrichlorosilane (~2%).

4-Pentenyltrichlorosilane, prepared in 60% yield from the Grignard reagent, was obtained by treating 10 g (0.067 mole) of 5-bromo-1-pentene (K & K Laboratories) with 2.4 g (0.10 g-atom) of magnesium in anhydrous ether. The product (8 g) boiled at 162–163° and was 95% pure. An analytical sample was isolated by vpc (Autoprep 20 ft × 3/8 in., QF-1 column, 135°).

Anal. Calcd for $C_5H_9SiCl_3$: C, 29.50; H, 4.46; Cl, 52.25. Found: C, 29.77; H, 4.60; Cl, 52.04.

Chlorination of 1,1-Dichlorosilacyclohexane.—A solution of 169.2 g (1.0 mole) of 1,1-dichlorosilacyclohexane, 67.5 g (0.5 mole) of sulfuryl chloride, and 0.8 g of benzoyl peroxide was heated in a 500-ml flask equipped with a magnetic stirrer. When the vigorous exothermic reaction had subsided, the mixture was stirred at 65–80° for 5 hr. An additional 0.8 g of benzoyl peroxide and 67.5 g (0.5 mole) of sulfuryl chloride were added and the heating was continued for 2.5 hr at 63°. This was followed by the addition of another 0.8 g of benzoyl peroxide and further heating at 65° for 10 hr. Distillation through a Todd column afforded 36.9 g (22%) of starting material and 104.3 g (51%) of monochlorinated product boiling at 85–87° (12 mm).

Analysis of the monochlorinated product by vpc (8-ft QF-1 column, 90°) showed two peaks of which the first represented 19% of the mixture. Analytical samples of each of the two peaks were obtained by vpc (20 ft × 3/8 in. QF-1 column, 125°). The first peak (19%) was found by its nmr spectrum (Table II) to be due to 1,1,2-trichlorosilacyclohexane.

Anal. Calcd for $C_5H_9SiCl_3$: C, 29.50; H, 4.48; Cl, 52.25. Found (1,1,2-trichlorosilacyclohexane): C, 29.76; H, 4.75; Cl, 52.40.

Anal. Found (peak 2—1,1,3- and 1,1,4-trichlorosilacyclohexane): C, 29.88; H, 4.67; Cl, 52.45.

A comparison of the areas of the methine hydrogens in the nmr spectrum of the isomer mixture showed the 1,1,2-trichlorosilacyclohexane to be present in approximately 22% quantity.

The monochlorinated product was always contaminated with a small amount (~4%) of 4-chloropentyltrichlorosilane which could be largely removed by careful redistillation through a Todd column. A vpc collected sample (20 ft × 3/8 in. QF-1 column, 125°) gave the same nmr spectrum as an authentic sample.[15]

Quantitative Determination of 1,1,3-Trichlorosilacyclohexane.—Titration of a redistilled sample of the monochlorinated isomer mixture for hydrolyzable chlorine[6] with standard sodium

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(10) This result seems at a variance with the published[9] results on this chlorination.

(11) A reaction commonly observed with olefins in the presence of sulfuryl chloride; see M. S. Kharasch and H. C. Brown, *J. Am. Chem. Soc.*, **61**, 3432 (1939).

(12) Dr. Y. Nagai, unpublished studies from this laboratory.

(13) A. Bygden, *Ber.*, **48**, 1236 (1915); R. West, *J. Am. Chem. Soc.*, **76**, 6012 (1954).

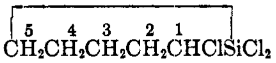
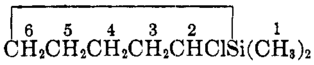
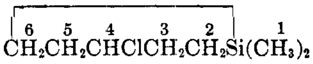
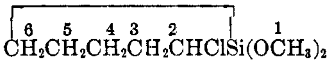
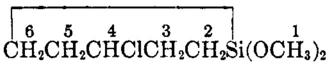
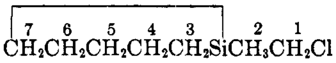
(14) An authentic sample of this material was at hand prepared by the method of F. C. Whitmore, *et al.*, *ibid.*, **68**, 475 (1946).

(15) This was prepared by the aluminum chloride catalyzed addition of hydrogen chloride to 4-pentenyltrichlorosilane. The product boiled at 52–55° (0.7 mm).

Anal. Calcd for $C_5H_{10}SiCl_4$: C, 25.02; H, 4.20; Cl, 59.08. Found: C, 25.15; H, 4.20; Cl, 59.10.

TABLE II

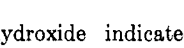
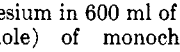
NMR SPECTRA OF VARIOUS SILANES[a,b]

Silane	τ values
(1)  $\overset{5}{C}H_2\overset{4}{C}H_2\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}HClSiCl_2$	6.48 (H^1 multiplet), 7.58–9.15 (H^2, H^3, H^4, H^5 complex pattern)
(2)  $\overset{5}{C}H_2\overset{4}{C}H_2\overset{3}{C}HCl\overset{2}{C}H_2\overset{1}{C}H_2SiCl_2$	5.77 (H^3 quintet), 7.76 (H^2 and H^4 multiplet), 8.57 (H^1 and H^5 complex pattern)
(3)  $\overset{6}{C}H_2\overset{5}{C}H_2\overset{4}{C}H_2\overset{3}{C}H_2\overset{2}{C}HClSi(\overset{1}{C}H_3)_2$	6.84 (H^2 quartet), 7.77–9.02 (H^3, H^4, H^5 complex pattern), 9.13–9.75 (H^6 complex pattern), 9.92 (H^1 singlet)
(4)  $\overset{6}{C}H_2\overset{5}{C}H_2\overset{4}{C}HCl\overset{3}{C}H_2\overset{2}{C}H_2Si(\overset{1}{C}H_3)_2$	5.99 (H^4 septet), 7.90 (H^3 and H^5 multiplet), 8.71–9.70 (H^2 and H^6 complex pattern), 9.86 and 9.91 (H^1 two singlets)
(5)  $\overset{6}{C}H_2\overset{5}{C}H_2\overset{4}{C}H_2\overset{3}{C}H_2\overset{2}{C}HClSi(O\overset{1}{C}H_3)_2$	6.47 (H^1 and H^2 multiplet with spikes at 6.45 and 6.52), 7.78–8.78 (H^3, H^4, H^5 complex pattern), 9.25 (H^6 multiplet)
(6)  $\overset{6}{C}H_2\overset{5}{C}H_2\overset{4}{C}HCl\overset{3}{C}H_2\overset{2}{C}H_2Si(O\overset{1}{C}H_3)_2$	5.90 (H^4 quintet), 6.49 and 6.53 (H^1 two singlets), 7.87 (H^3 and H^5 multiplet), 9.21 (H^2 and H^6 complex pattern)
(7) $\overset{6}{C}H_2{=}\overset{5}{C}H\overset{4}{C}H_2\overset{3}{C}H_2\overset{2}{C}H_2Si(\overset{1}{C}H_3)_3$	4.30 (H^5 multiplet), 5.14 (H^6 multiplet), 8.01 (H^4 quartet), 8.63 (H^3 multiplet), 9.57 (H^2 multiplet), 10.00 (H^1 singlet)
(8) $\overset{6}{C}H_2{=}\overset{5}{C}H\overset{4}{C}H_2\overset{3}{C}H_2\overset{2}{C}H_2Si(O\overset{1}{C}H_3)_3$	4.20 (H^5 multiplet), 4.98 (H^6 multiplet), 6.45 (H^1 singlet), 7.89 (H^4 multiplet), 8.47 (H^3 multiplet), 9.43 (H^2 multiplet)
(9)  $\overset{7}{C}H_2\overset{6}{C}H_2\overset{5}{C}H_2\overset{4}{C}H_2\overset{3}{C}H_2Si\overset{2}{C}H_3\overset{1}{C}H_2Cl$	7.23 (H^1 singlet), 8.40 (H^4, H^5, H^6 multiplet), 9.29 (H^3 and H^7 multiplet), 9.87 (H^2 singlet)
(10) $\overset{6}{C}H_2Cl\overset{5}{C}HCl\overset{4}{C}H_2\overset{3}{C}H_2\overset{2}{C}H_2Si(\overset{1}{C}H_3)_2Cl$	5.88–6.58 (H^5 and H^6 complex pattern), 7.90–8.71 (H^3 and H^4 complex pattern), 9.17 (H^2 multiplet), 9.59 (H^1 singlet).

[a] Unless otherwise stated, these spectra were determined in carbon tetrachloride solution with tetramethylsilane as an internal standard. A Varian A-60 nmr spectrometer was employed. Chemical shifts are measured to the estimated center of a singlet or multiplet. Benzene was used as an internal standard for entry 4. [b] In the case of each of the spectra listed in this table, the peak areas were consistent with the proton assignments made.

TABLE III

CHLORINATION OF VARIOUS SILANES WITH SULFURYL CHLORIDE[a]

Silane	Ratio of products			Ref
	α	β	γ	
$(CH_3CH_2)_2SiCl_2$	1	1.7	...	b
$CH_3CH_2CH_2SiCl_3$	1	3.5	3.1	c
 $CH_2(CH_2)_3SiCl_2$	1	4	...	2a
 $CH_2(CH_2)_4SiCl_2$	1	2.6	1.1	This work
 $CH_2(CH_2)_4Si(CH_3)_2$	3.2	...	1	This work

[a] In all cases listed, a sulfuryl chloride–benzoyl peroxide combination was employed for chlorination. [b] L. H. Sommer, *et al.*, *J. Am. Chem. Soc.*, **76**, 1613 (1954). [c] L. H. Sommer, *et al.*, *ibid.*, **68**, 488 (1946).

hydroxide indicated that 1,1,3-trichlorosilacyclohexane constituted 58% of the isomer mixture.

Monochlorinated 1,1-Dichlorosilacyclohexane with Methylmagnesium Iodide.—Methylmagnesium iodide, prepared from 142 g (1.0 mole) of methyl iodide and 24.3 g (1.0 g-atom) of magnesium in 600 ml of anhydrous ether, was added to 54.4 g (0.267 mole) of monochlorinated 1,1-dichlorosilacyclohexane with stirring. After refluxing for 12 hr, the mixture was hydrolyzed with saturated ammonium chloride solution and worked up in the customary way. Analysis by vpc (8-ft QF-1 column, 90°) of a concentrated ethereal solution of the product showed the following composition: 19% 1,1-dimethyl-2-chlorosilacyclohexane, 55% 4-pentenyltrimethylsilane, and 26% 1,1-dimethyl-4-chlorosilacyclohexane. Distillation afforded two fractions, bp 49–54° (29 mm) and 42–44° (2 mm), but analysis by vpc indicated that neither fraction was pure. The total yield was 30.9 g (69%). Elemental analyses and nmr spectra of vpc collected samples (8-ft QF-1 column, 75°, and 26-ft QF-1 column, 100°) established the identity of the three products.

Anal. Calcd for $C_7H_{15}SiCl$ (1,1-dimethyl-2-chlorosilacyclohexane): C, 51.67; H, 9.29; Cl, 21.79. Found: C, 52.00; H, 9.47; Cl, 21.50. Calcd for $C_8H_{18}Si$ (4-pentenyltrimethylsilane): C, 67.52; H, 12.75. Found: C, 67.71; H, 12.98. Calcd for $C_7H_{15}SiCl$ (1,1-dimethyl-4-chlorosilacyclohexane): C, 51.67; H, 9.29; Cl, 21.79. Found: C, 51.95; H, 9.54; Cl, 21.68.

1,1,4-Trichlorosilacyclohexane with Methylmagnesium Iodide.—Methylmagnesium iodide, prepared from 11.7 g (0.0827 mole) of methyl iodide and 2.0 g (0.0824 g-atom) of magnesium, was added to an ethereal solution of 4.53 g (0.022 mole) of 1,1,4-trichlorosilacyclohexane (see below). The mixture was refluxed for 16 hr, hydrolyzed, and worked up in the usual manner. Removal of solvent followed by distillation afforded 2.68 g (74%) of 1,1-dimethyl-4-chlorosilacyclohexane boiling at 38–42° (2 mm). Analysis by vpc (7.5-ft QF-1 column, 90°) indicated a purity greater than 97% and the absence of 4-pentenyltrimethylsilane. The product had vpc retention time and infrared spectrum identical with those of a previously confirmed sample (see above).

Monochlorinated, 1,1-Dichlorosilacyclohexane with Sodium Methoxide. A. In Methanol.—Sodium methoxide, prepared from 1.88 g (0.082 g-atom) of sodium and 42.2 g (1.32 moles) of methanol was added dropwise with stirring to 6.53 g (0.032 mole) of monochlorinated 1,1-dichlorosilacyclohexane in 35 ml of anhydrous ethyl ether at 0°. The mixture was stirred for 1 hr at room temperature and filtered, and then the solvent was removed. Distillation afforded 0.98 g, bp 59° (5 mm), and two indistinct cuts comprised of 1.45 and 1.35 g boiling at 46–58° (2 mm). Analysis by vpc (8-ft QF-1 column at 110 and 150° and 4-ft silicone rubber, 120°) indicated that all fractions were mixtures of 4-pentenyltrimethoxysilane (71%), 1,1-dimethoxy-2-chlorosilacyclohexane (4%), and 1,1-dimethoxy-4-chlorosilacyclohexane (25%) in a total yield of 62%. Elemental analysis and infrared and nmr spectra of samples collected by vpc (8-ft QF-1 column at 110° and 10-ft QF-1 at 140°) established the identity of the three products.

Anal. Calcd for $C_8H_{18}SiO_3$ (4-pentenyltrimethoxysilane): C, 50.49; H, 9.53. Found: C, 50.26; H, 9.70.

Anal. Calcd for $C_7H_{15}SiClO_2$ (1,1-dimethoxy-2-chlorosilacyclohexane): C, 43.18; H, 7.76; Cl, 18.21. Found: C, 43.19; H, 7.62; Cl, 18.00. Found (1,1-dimethoxy-4-chlorosilacyclohexane): C, 43.16; H, 8.03; Cl, 18.04.

Similar results were obtained in a large-scale run employing 118.1 g (0.58 mole) of monochlorinated 1,1-dichlorosilacyclohexane. From this run, a sample of 1,1-dimethoxy-4-chlorosilacyclohexane adjudged to be 96% pure by vpc was obtained by two distillations of an impure sample, bp 85–88° (8.3 mm), through a Nester–Faust Annular Teflon spinning-band column.

B. In Ethyl Ether.—Sodium methoxide[16] (13.24 g, 0.245 mole) was added slowly with stirring to 19.51 g (0.095 mole) of monochlorinated 1,1-dichlorosilacyclohexane in 110 ml of anhydrous ethyl ether at 0°. The mixture was stirred at 0° for 1.5 hr and then at room temperature for 10 hr. The usual work-up produced 15.04 g (82%) of product which contained 14% 1,1-dimethoxy-2-chlorosilacyclohexane, 61% 4-pentenyltrimethoxysilane, and 25% 1,1-dimethoxy-4-chlorosilacyclohexane.

1,1,4-Trichlorosilacyclohexane with Sodium Methoxide.—Sodium methoxide (1.79 g, 0.033 mole) was added slowly with stirring to 3.37 g (0.0166 mole) of 1,1,4-trichlorosilacyclohexane (see below) in 26 ml of anhydrous ethyl ether at 0°. The mixture was stirred at this temperature for 1 hr and then at room temperature for 11 hr. Distillation, following the usual work-up, afforded about 2 g (61%) of 1,1-dimethoxy-4-chlorosilacyclohexane boiling at 52–65° (~2 mm). Analysis by vpc (8-ft DEGS column, 120°) indicated the product was 98% pure and had retention time and nmr spectrum identical with a previously confirmed sample (see above).

1,1,4-Trichlorosilacyclohexane.—Dry hydrogen chloride was bubbled through 17.8 g (0.087 mole) of neat 1,1-dimethoxy-4-chlorosilacyclohexane for 4.5 hr at −15°. During this period an upper layer consisting largely of methanol formed and was periodically removed. The product was distilled through a Nester Faust spinning-band column and four cuts were taken all of approximately the same boiling point, 70° (2.8 mm). The first of these (0.89 g), without further purification, gave the proper elemental analysis and infrared and nmr spectra for 1,1,4-trichlorosilacyclohexane. Analysis of the second cut (3.86 g) by vpc indicated that it was entirely 1,1,4-trichlorosilacyclohexane, while the third cut (3.51 g) was 93% pure and the fourth (5.24 g) was 78% pure. The total yield (12.1 g) was 68%.

Anal. Calcd for $C_5H_9SiCl_3$: C, 29.50; H, 4.46; Cl, 52.25. Found: C, 29.88; H, 4.46; Cl, 51.84.

5-Chloropentyltrichlorosilane was prepared from 4.07 g (0.167 g-atom) of magnesium turnings and 31.7 g (0.171 mole) of 1-bromo-5-chloropentane in 420 ml of anhydrous ethyl ether. The mixture was stirred at 0° for 4 hr and then at room temperature for 11 hr. This Grignard solution was then added slowly with stirring to 60.8 g (0.358 mole) of silicon tetrachloride in 500 ml of ether. The resulting mixture was stirred for 1 hr at room temperature and then for 18 hr at reflux. Distillation, following the customary work-up, afforded 6.83 g (17%) of 5-chloropentyltrichlorosilane boiling at 61–62° (0.6 mm).

Anal. Calcd for $C_5H_{10}SiCl_4$: C, 25.02; H, 4.02; Cl, 59.08; Si, 11.70. Found: C, 25.22; H, 4.17; Cl, 59.12; Si, 11.86.

5-Chloropentyltrimethoxysilane.—Sodium methoxide, prepared from 1.22 g (0.0529 g-atom) of sodium in 18 ml of absolute methanol, was added dropwise with stirring to 4.25 g (0.0177 mole) of 5-chloropentyltrichlorosilane in 7 ml of anhydrous ether at 0°. The mixture was stirred for 1 hr at 0° and then at room temperature for 16 hr. Distillation, following the usual work-up, afforded 2.01 g (50%)[17] of 5-chloropentyltrimethoxysilane boiling at 62–69° (0.65 mm).

Anal. Calcd for $C_8H_{19}SiO_3Cl$: C, 42.37; H, 8.45; Si, 12.38; Cl, 15.63. Found: C, 42.13; H, 8.61; Si, 12.22; Cl, 15.72.

Only 0.5% of 4-pentenyltrimethoxysilane had formed under these reaction conditions.

Chlorination of 1,1-Dimethylsilacyclohexane.[18]—The procedure here was similar to that described above for 1,1-dichlorosilacyclohexane except that 85.8 g (0.67 mole) of 1,1-dimethylsilacyclohexane, 45.2 g (0.335 mole) of sulfuryl chloride, and 0.8 g of benzoyl peroxide were used initially. Distillation afforded 14.2 g (17%) of starting material and essentially two cuts: 24.8 g, bp 83–115° (22 mm), and 24.09 g, bp 98° (4 mm). Analysis by vpc (8-ft QF-1 column at 100 and 150°) indicated the first fraction was a mixture of dimethyl-4-pentenylchlorosilane[18] (XV), 2- and 4-chloro-1,1-dimethylsilacyclohexane[19] (XIII and XIV), 1-methyl-1-chloromethylsilacyclohexane (XII), and dimethyl-(4,5-dichloropentyl)chlorosilane (XVI). The identity of XII and XVI were indicated by their elemental analyses and nmr spectra.

Anal. Calcd for $C_7H_{15}SiCl$ (XII): C, 51.67; H, 9.29; Cl, 21.79. Found: C, 51.97; H, 9.31; Cl, 21.50.

Anal. Calcd for $C_7H_{15}SiCl_3$ (XVI): C, 35.99; H, 6.47; Cl, 45.52. Found: C, 35.49; H, 6.83; Cl, 45.18.

Further proof of the structure of XVI was obtained by dechlorinating it with zinc dust. The product was identical with an authentic sample of compound XV. It was estimated that the yield of identifiable products was 32%, consisting approximately of 8% XV, 32% XIII, 10% XIV, 3% XII, and 47% XVI.

Dehydrohalogenation of Monochlorinated 1,1-Dichlorosilacyclohexane. A. Quinoline (Catalytic).—A flask containing 8 g (0.04 mole) of monochlorinated 1,1-dichlorosilacyclohexane and 0.2 g of quinoline was equipped with a micro-Vigreux distilling column and heated to 240° in an oil bath. Over a 1.5-hr period, 6 g of distilled material was collected from 160 to 190°. Analysis of this material by vpc (10-ft QF-1 column at 110°) gave results shown in Table I.

B. Quinoline (Excess).—Essentially the same reaction as described above was repeated using 6.5 g (0.032 mole) of monochlorinated 1,1-dichlorosilacyclohexane and 25 ml of quinoline. The results are shown in Table I.

C. Ferric Chloride.—Monochlorinated 1,1-dichlorosilacyclohexane (5.9 g, 0.029 mole) and 0.1 g of anhydrous ferric chloride were heated at 235° for 1.5 hr in a 10-ml flask fitted with a reflux condenser and protected from the atmosphere with a mercury bubbler. Distillation of the reaction mixture through a micro-Vigreux distilling column gave 2.6 g (43%) of olefins (see Table I) boiling at 160–163°. There was a 33% recovery of starting material.

D. Pyrolysis.—Monochlorinated 1,1-dichlorosilacyclohexane (5.2 g, 0.026 mole) was pyrolyzed in an apparatus described previously.[2b] The temperature of the furnace varied between 540 and 590°. The crude pyrolysate contained 77% olefins and 23% starting material. Distillation yielded 2.7 g (58%) of an olefin fraction (see Table I).

Registry No.—I, 2406-34-0; II, 4040-74-8; III, 15303-30-7; V, 15303-31-8; VI, 15303-32-9; VIII, 15303-33-0; IX, 15303-34-1; X, 15303-35-2; XI, 15303-36-3; XII, 15303-37-4; XVI, 15303-38-5; 4-pentenyltrichlorosilane, 2504-62-3; 4-pentenyltrimethylsilane, 763-21-3; 5-chloropentyltrichlorosilane, 15303-41-0; 5-chloropentyltrimethoxysilane, 15303-42-1.

Acknowledgment.—The authors are grateful to the National Science Foundation whose financial assistance made this work possible.

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[16] This material was prepared by adding clean sodium to absolute methanol. After removal of solvent, the product was heated at 175° under high vacuum for 2 hr. All transfers were carried out in a nitrogen-filled drybox.

[17] In a larger run employing 10.70 g (0.0446 mole) of 5-chloropentyltrichlorosilane, a 70% yield of product was realized.

[18] Identified by the superimposability of its infrared spectrum with that of an authentic sample: see D. G. Stoffey, Ph.D. Thesis, Purdue University, 1959.

[19] These compounds were identified by their nmr spectra with previously prepared samples (*vide supra*).