The Preparation of Cyclic Siliconmethylene Compounds

WILLIAM A. KRINER[1]

The Rohm and Haas Company, Philadelphia, Pennsylvania

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A novel method has been found for the preparation of cyclic siliconmethylene compounds such as $[(CH_3)_2SiCH_2]_2$, $[(CH_3)_2SiCH_2]_3$, $[Cl(CH_3)SiCH_2]_2$, $[C_2H_5O(CH_3)SiCH_2]_2$, $[C_2H_5O(CH_3)SiCH_2]_3$, and others. The above cyclic compounds containing Cl^- or $C_2H_5O^-$ groups bonded to silicon were converted to various derivatives such as $[H(CH_3)SiCH_2]_2$, $[H(CH_3)SiCH_2]_3$, $[C_6H_5(CH_3)SiCH_2]_2$, $[C_6H_5(CH_3)SiCH_2]_3$, etc.

The common method for preparing compounds containing the Si–C–Si linkage utilizes the coupling reaction of halomethylsilanes with halo or alkoxy silanes by means of lithium, sodium, or magnesium. These reactions have been reviewed elsewhere.[2] Cyclic siliconmethylene compounds of the general formula $[(CH_3)_2SiCH_2]_n$ have been prepared in this manner, but in small yields.[2] A six-membered ring compound, $[Cl_2SiCH_2]_3$, has been isolated from the products of the reaction of CH_2Cl_2 with Si–Cu alloys. This has been converted to $[H_2SiCH_2]_3$ by reaction with lithium aluminum hydride, and to various alkyl derivatives.[2] Fritz and co-workers have shown that cyclic siliconmethylenes can be obtained in small quantities from the pyrolysis of $(CH_3)_4Si$, $(CH_3)_3SiCl$, $(CH_3)_2SiCl_2$, and $(CH_3)SiCl_3$.[2]

The smallest cyclic siliconmethylene ring, 1,3-disilacyclobutane, has been synthesized as the 1,1,3,3-tetramethyl derivative[3] by a multistep process culminating in the ring closure dehalogenation reaction as shown by the following equation.

$$F(CH_3)_2SiCH_2Si(CH_3)_2CH_2Cl + Mg \longrightarrow [(CH_3)_2SiCH_2]_2 + MgCl(F) \quad (1)$$

A similar preparation was carried out using $Cl(CH_3)_2SiCH_2Si(CH_3)_2CH_2Cl$ in the final step.[4] Recently, 1,1,3,3-tetramethyl-1,3-disilacyclobutane was identified as one of the products from the pyrolysis of $(CH_3)_4Si$.[5] The four-membered ring compound has also been isolated from the products of the reaction of chloromethyldimethylchlorosilane and magnesium in ether in yields around 4%.[6]

None of the above described methods provides a quick, versatile means for preparing cyclic siliconmethylene compounds in substantial yields. The purpose of this investigation was to perfect a method for preparing these compounds and particularly to introduce some silicon functionality into the rings. The method chosen was similar to that of Müller, *et al.*[6]

Results and Discussion

Direct Preparation of Cyclic Siliconmethylenes.—The interaction of chloromethyldimethylchlorosilane with magnesium in diethyl ether proceeded as in eq. 2. The yield of small ring compounds (n = 2, 3, and 4) was small, in agreement with Müller, *et al.*,[6] most of the product being a viscous residue. The reaction proceeded more readily in tetrahydrofuran; however, the yield of simple compounds was again small, the major product being a siliconmethylene polymer having an average molecular weight of 930 ± 10. A most successful procedure, resulting in yields up to 50% for 1,1,3,3-tetramethyl-1,3-disilacyclobutane (I) and around 19% for 1,1,3,3,5,5-hexamethyl-1,3,5-trisilacyclohexane (II) and 1,1,3,3,5,5,7,7-octamethyl-1,3,5,7-tetrasilacyclooctane (III) in small quantities, was perfected by utilizing the reverse addition of magnesium to the silane in tetrahydrofuran (reaction 1D in Experimental). High molecular weight cyclic silmethylenes and possibly some linear compounds probably linked with Si–O–Si bonds, due to hydrolysis of residual Si–Cl end groups, were also produced.

$$nClCH_2Si(CH_3)_2Cl + nMg \longrightarrow [(CH_3)_2SiCH_2]_n + nMgCl_2 \quad (2)$$
$$n = 2 \text{ and greater}$$

The most likely steps for this reaction are shown in Scheme I, eq. 3–10.

This reaction path involves multiple steps, which are consistent with the literature. However, it is oversimplified in that all the Grignard intermediates formed, such as shown in eq. 6 and 8, can react with any active Si–Cl available, not just starting material. It can be seen, according to Scheme I, that linear siliconmethylenes terminated by unreacted $\equiv SiCH_2Cl$ and $\equiv SiCl$ groups can also be produced in addition to cyclic compounds.

One can postulate that the reason for the success of the inverse addition process is that this procedure favors the production of $ClCH_2(CH_3)_2SiCH_2Si(CH_3)_2Cl$ according to eq. 4, since only small amounts of $ClMgCH_2Si(CH_3)_2Cl$ will be formed in an environment rich in $ClCH_2Si(CH_3)_2Cl$. This advantage holds until the concentration of $ClCH_2(CH_3)_2SiCH_2Si(CH_3)_2Cl$ becomes appreciable. The normal addition method, in contrast, will produce a relatively high concentration of $ClMgCH_2Si(CH_3)_2Cl$ resulting in a preponderance of chain lengthening reactions.

One of the major objects of this research was to produce cyclic siliconmethylenes having silicon functionality, *i.e.*, compounds containing Si–halogen, Si–H, and Si–alkoxy bonds. The direct preparation of 1,3-dichloro-1,3-dimethyl-1,3-disilacyclobutane (IV), according to eq. 11, gave low yields as a result of the many side reactions which can occur as evidenced by the large yield of the isotropic mixture, $C_6H_{15}Cl_3Si_3$. This mixture could be separated into two components: a liquid, $Cl_2(CH_3)SiCH_2\underline{Si(CH_3)CH_2Si(CH_3)(Cl)CH_2}$ (V), and a solid, $[Cl(CH_3)SiCH_2]_3$ (VI), the major portion being V. According to the reaction path proposed, the possible expected intermediate, $Cl_2(CH_3)SiCH_2Si(CH_3)(Cl)CH_2Si(CH_3)(Cl)CH_2MgCl$, could couple with itself

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[1] University of Pennsylvania, Philadelphia, Pa.

[2] R. K. Ingham and H. Gilman, "Inorganic Polymers," F. G. A. Stone and W. A. G. Graham, Ed., Academic Press, New York, N. Y., 1962, p. 321.

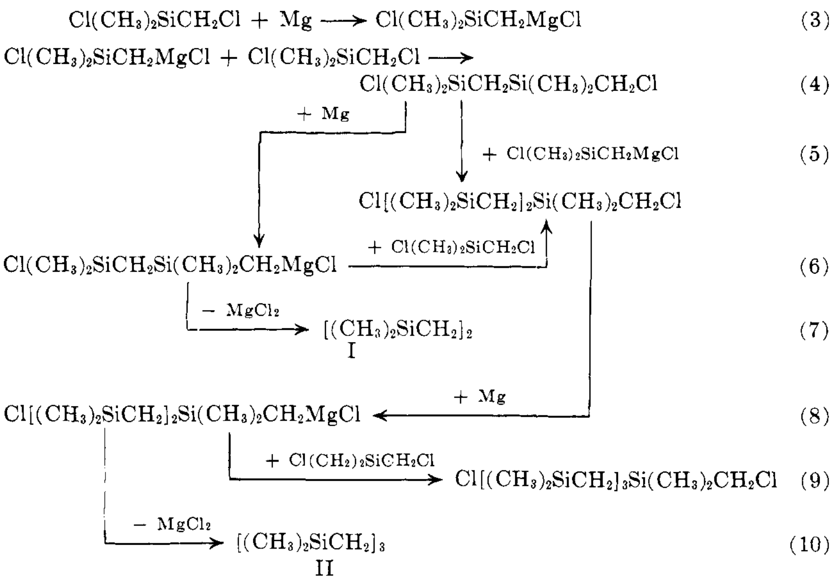
[3] W. H. Knoth, Jr. and R. V. Lindsey, Jr., *J. Org. Chem.*, **23**, 1392 (1958); W. H. Knoth, Jr., U. S. Patent 2,850,514 (1958).

[4] G. Greber and G. Degler, *Makromol. Chem.*, **52**, 174 (1962).

[5] G. Fritz and J. Grobe, *Z. anorg. allgem. Chem.*, **315**, 157 (1962); G. Fritz, W. Kemmerling, G. Sonntag, H. J. Becker, E. H. V. Ebsworth, and J. Grobe, *ibid.*, **321**, 10 (1963). The latter paper includes a correction of a previous work [G. Fritz and J. Grobe, *ibid.*, **311**, 325 (1961)] in which the structure $(CH_3)_2Si{=}CHSi(CH_3)_3$ was assigned to $Si_2C_6H_{16}$.

[6] R. Müller, R. Köhne, and H. Beyer, *Ber.*, **95**, 3030 (1962).

SCHEME I



$$2ClCH_2Si(CH_3)Cl_2 + 2Mg \longrightarrow [Cl(CH_3)SiCH_2]_2 + 2MgCl_2 \quad (11)$$

by interaction of the Grignard end with the silicon halogen bond in either the 4- or the 6-position leading to V or VI, respectively. An alternate course to V would be the reaction of the intermediate, $Cl_2(CH_3)SiCH_2MgCl$ with IV. Proof of the structures IV, V, and VI is discussed later.

To eliminate the side reactions discussed above the starting silane was modified by substituting the less active ethoxy group for one of the chlorines on silicon, *i.e.*, $ClCH_2Si(CH_3)(OC_2H_5)Cl$. This resulted in a moderate (35.3%) yield of 1,3-diethoxy-1,3-dimethyl-1,3-disilacyclobutane (VII), along with a small quantity of 1,3,5-triethoxy-1,3,5-trimethyl-1,3,5-trisilacyclohexane (VIII). When the starting silane had both active chlorines replaced by ethoxy groups, *i.e.*, $ClCH_2Si(CH_3)(OC_2H_5)_2$, the reaction with magnesium gave 12.4% VII and a moderate (40.4%) yield of VIII. These results are consistent with the proposed scheme in that the intermediate $Cl(C_2H_5O)(CH_3)SiCH_2Si(CH_3)(OC_2H_5)CH_2MgCl$ would be more likely to undergo a ring closure reaction than the intermediate of the second case, $(C_2H_5O)_2(CH_3)SiCH_2Si(CH_3)(OC_2H_5)CH_2MgCl$, due to the steric hindrance of the ethoxy groups. The latter would more readily proceed similarly to eq. 5, resulting eventually in the formation of $(C_2H_5O)_2(CH_3)SiCH_2Si(CH_3)(OC_2H_5)CH_2Si(CH_3)(OC_2H_5)CH_2MgCl$ which can undergo a less hindered ring closure reaction to give the six-membered ring, VIII.

Derivatives and Conversions.—Compounds I through XVI and some of their physical properties are summarized in Table I. The ethoxy derivatives VII and VIII were converted to the corresponding chloro derivatives IV and VI, respectively, by conventional means. The latter chloro derivatives gave high yields of the hydride derivatives IX and X with lithium aluminum hydride. Complete methylation of IV, VI, VII, and VIII with methyl Grignard gave the known methyl derivatives I and II. Partial methylation of IV and VII gave the monofunctional derivatives XI and XII, respectively. Compound V was methylated to give XIII. An alternate preparation of XIII was accomplished by the reaction of XI with $(CH_3)_3SiCH_2Li$. Compounds IV and VI were readily converted to phenyl derivatives using phenyl Grignard. The novel siloxane XVI resulted from the hydrolysis of XII.

Some of the derivatives (IV–X, XIV, and XV) of 1,3-disilacyclobutane and 1,3,5-trisilacyclohexane obviously can have isomeric forms. However, none as yet have been resolved into one form or the other and must be assumed to be mixtures.

Spectroscopic Data.—The infrared spectra of compounds I through XVI were recorded on a Perkin-Elmer Model 21 spectrophotometer equipped with sodium chloride optics. Their absorption frequencies are recorded in Table II. Assignments were made wherever possible. All compounds, except VI (which was dissolved in carbon tetrachloride), were examined as thin films between sodium chloride plates. Of particular interest in these spectra is the position of the Si–CH₂–Si band which in linear siliconmethylenes is found in the 1050-cm.⁻¹ region.[7] This band is usually much narrower than the broad Si–O–Si absorption frequency also found around 1050 cm.⁻¹. The 1,3,5-trisilacyclohexane derivatives gave an absorption band in the 1040–1065-cm.⁻¹ region, but the 1,3-disilacyclobutane derivatives absorbed between 935–955 cm.⁻¹. This shift may be attributed to the strained ring structure of the latter compounds and may be compared to the similar shifts of the Si–O–Si frequency which occur in several cyclic siloxanes as the ring size is decreased.[8,9] In the compounds $Cl_2(CH_3)SiCH_2\underline{Si(CH_3)CH_2Si(CH_3)(Cl)CH_2}$ and $(CH_3)_3SiCH_2\underline{Si(CH_3)CH_2Si(CH_3)_2CH_2}$ which contain both a linear and cyclic Si–CH₂–Si structure, two bands are indeed found, one in the 1050-cm.⁻¹ region and one in the 950-cm.⁻¹ region.

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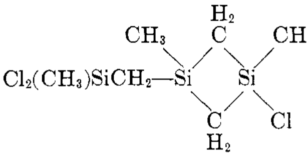
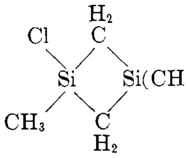
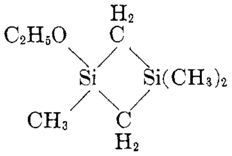
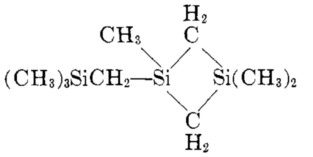
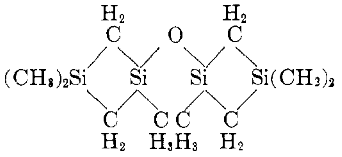
[7] H. Kriegsmann, *Z. Electrochem.*, **61**, 1088 (1957).

[8] W. A. Piccoli, G. G. Haberland, and R. L. Merker, *J. Am. Chem. Soc.*, **82**, 1883 (1960).

[9] A. W. P. Jarvie, H. J. S. Winkler, and H. Gilman, *J. Org. Chem.*, **27**, 614 (1962).

TABLE I

PHYSICAL PROPERTIES OF CYCLIC SILICONMETHYLENES

	Compound	B.p., °C. (mm.) [m.p., °C.]	$n^{25}D$
I	$[(CH_3)_2SiCH_2]_2$	119.5 60 (100) [−9 to −8.5]	1.4401
II	$[(CH_3)_2SiCH_2]_3$	112 (50)	1.4601
III	$[(CH_3)_2SiCH_2]_4$	104 (2) [79–80.5]	
IIV	$[Cl(CH_3)SiCH_2]_2$	59 (20) [−7 to −6.5]	1.4725
V		131 (20)	1.4901
VI	$[Cl(CH_3)SiCH_2]_3$	117–118 (5) 93–94 (2) [59]	
VII	$[(C_2H_5O)(CH_3)SiCH_2]_2$	78–79 (16)	1.4336
VIII	$[(C_2H_5O)(CH_3)SiCH_2]_3$	68–69 (0.20–0.25) 97 (1.7)	1.4478
IX	$[H(CH_3)SiCH_2]_2$	96	1.4546
X	$[H(CH_3)SiCH_2]_3$	68–71 (19)	1.4705
XI		67.5–68 (59)	1.4568
XII		71 (40)	1.4364
XIII		112.5–113 (50) 75 (10)	1.4556
XIV	$[C_6H_5(CH_3)SiCH_2]_2$	99 (1.1)	1.5727
XV	$[C_6H_5(CH_3)SiCH_2]_3$		1.5873
XVI			1.4525

Experimental

Materials.—Anhydrous ether was used without further treatment. Tetrahydrofuran was distilled as needed from lithium aluminum hydride. Magnesium turnings were ground to 2-mm. mesh and stored under nitrogen. Grignard reagents were standardized commercial products unless otherwise indicated. Commercially available chloromethyldimethylchlorosilane and chloromethylmethyldichlorosilane were redistilled on a 36-in. spinning band column. Ethoxy derivatives of the latter were prepared as described below.

Chloromethylmethylethoxychlorosilane was prepared by the partial ethanolysis of $(CH_3)(CH_2Cl)SiCl_2$. To a vigorously stirred solution of 655.0 g. (4.005 moles) of $(CH_3)(CH_2Cl)SiCl_2$ and 316.4 g. (4.000 moles) of pyridine in 500 ml. of benzene was slowly added 184.2 g. (3.998 moles) of ethanol over a period of 4 hr. After an additional 16 hr. of stirring, the pyridine hydrochloride was filtered off and washed with benzene. The benzene was removed from the filtrate by distillation. Fractional distillation of the residue gave 435.7 g. (2.517 moles, 62.9% yield) of $(CH_3)(CH_2Cl)Si(OC_2H_5)Cl$, b.p. 64° (40 mm.), $n^{25}D$ 1.4256.

Anal. Calcd. for $C_4H_{10}Cl_2OSi$: C, 27.75; H, 5.82; Cl, 40.96; mol. wt., 173. Found: C, 28.07; H, 5.83; Cl, 41.13; mol. wt., 175. All molecular weights were determined cryoscopically in benzene unless otherwise indicated.

Chloromethylmethyldiethoxysilane was prepared in a similar manner. $(CH_3)(CH_2Cl)SiCl_2$ (327 g., 2.00 moles) reacted with excess ethanol (240 ml., 4.09 moles) in the presence of pyridine (320 ml., 3.97 moles) in 300 ml. of benzene. Distillation yielded 239 g. (1.43 moles, 71.5% yield) of $(CH_3)(CH_2Cl)Si(OC_2H_5)_2$, b.p. 67° (20 mm.), lit.[10] b.p. 162–165°, $n^{25}D$ 1.4120, lit.[10] $n^{20}D$ 1.4145.

Reaction Procedure.—The reactions were carried out under nitrogen in conventional standard tapered glassware unless otherwise indicated. A conventional vacuum line was used for the manipulation of small quantities.

Reaction 1. Chloromethyldimethylchlorosilane and Magnesium. A. No Solvent.—No reaction occurred when 2.62 g. (0.0183 mole) of $(CH_3)_2(CH_2Cl)SiCl$ and 0.50 g. (0.021 g.-atom) of magnesium were heated to reflux in a sealed evacuated Carius tube.

B. In Diethyl Ether.—To a mixture of 6.1 g. (0.25 g.-atom) of magnesium in 100 ml. of ether, plus a few iodine crystals to activate the magnesium, was slowly added, over a period of 3.5 hr., a 50% solution of 35.5 g. (0.248 mole) of $(CH_3)_2(CH_2Cl)SiCl$ in ether while heating to reflux. The reaction mixture became cloudy and upon an additional 16 hr. of stirring a thick white sludge was produced. The product was hydrolyzed, extracted with ether, and distilled to give 1.79 g. (0.0124 mole, 10.0% yield) of 1,1,3,3-tetramethyl-1,3-disilacyclobutane (I); mol. wt. found, 145 (vapor density), and calcd., 144; b.p. 119.5°, lit.[3] b.p. 117–119°. A viscous yellow clear residue was the major product.

C. In Tetrahydrofuran.—To a mixture of 20 g. (0.82 g.-atom) of magnesium in 50 ml. of tetrahydrofuran was added a small amount of iodine and 4 drops of methyl iodide. To this stirred mixture was slowly added over a period of 2.5 hr., 71 g. (0.50 mole) of $(CH_3)_2(CH_2Cl)SiCl$ in sufficient tetrahydrofuran to make a 33% solution. The exothermic reaction was cooled occasionally. After the reduction had subsided, the viscous slurry, due to the large amount of magnesium chloride formed, was heated to reflux for 2 hr. and then cooled. A slow addition of 250 ml. of water produced two layers which were separated. The water layer was extracted with ether and the extract was added to the organic layer and distilled to give 2.4 g. (0.017 mole, 6.7% yield) of I, b.p. 60° (100 mm.), identified also by infrared; 0.50 g. (0.0023 mole, 1.4% yield) of 1,1,3,3,5,5-hexamethyl-1,3,5-trisilacyclohexane (II), b.p. 120° (50 mm.); and 21 g. (58% yield based on $[(CH_3)_2SiCH_2]_n$) of a viscous opaque residue, mol. wt. 930 ± 10, the infrared spectrum of which indicated a siliconmethylene polymer.

D. Reverse Addition in Tetrahydrofuran.—To a small mixture of magnesium turnings covered by tetrahydrofuran was added 4 drops of methyl iodide followed by the addition of a small portion of 284 g. (1.98 moles) of $(CH_3)_2(CH_2Cl)SiCl$ to start the reaction which was evidenced by a sharp exotherm. The remainder of the silane, in sufficient tetrahydrofuran to bring the final silane concentration to 33%, was added rapidly with continuous stirring. The remainder of 80 g. (3.3 g.-atoms) of magnesium turnings was slowly added to maintain a reaction temperature of 30–50° over a period of 2 hr. Occasional cooling was necessary. After an additional 1.5 hr. of stirring with heating to 50°, the reaction was cooled and 500 ml. of water was added slowly. The organic layer was separated, washed with water, and distilled to give 71.3 g. (0.494 mole, 49.9% yield) of I, m.p. −9 to −8.5° (by magnetic plunger technique[11]), b.p. 60.5–61.0° (100 mm.), $n^{25}D$ 1.4401, lit.[3] $n^{27}D$ 1.4380, d_{25} 0.793.

Anal. Calcd. for $C_6H_{16}Si_2$: C, 49.91; H, 11.17; mol. wt., 144. Found: C, 50.03; H, 11.37; mol. wt., 145 (vapor density).

In addition there was obtained 26.7 g. (0.123 mole, 18.6% yield) of II, b.p. 112° (50 mm.), lit.[12] b.p. 96–97° (26 mm.), $n^{25}D$ 1.4601, lit.[13] $n^{25}D$ 1.4606.

Anal. Calcd. for $C_9H_{24}Si_3$: C, 49.91; H, 11.17; mol. wt., 217. Found: C, 49.94; H, 11.00; mol. wt., 215.

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(10) K. A. Andrianov and L. M. Volkova, *Zh. Obshch. Khim.*, **30**, 2393 (1960).

(11) A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933, p. 184.

(12) N. S. Nametkin, A. V. Topchiev, and V. I. Zetkin, *Dokl. Akad. Nauk SSSR*, **93**, 1045 (1953).

(13) J. T. Goodwin, U. S. Patent 2,607,791 (1952).

TABLE II

INFRARED ABSORPTION FREQUENCIES OF CYCLIC SILICONMETHYLENES[a]

Compound																
I	II	III	IV	V	VI[b]	VII	VIII	IX	X	XI	XII	XIII	XIV	XV	XVI	Assignments
													3090 ms	3070 m		C–H stretch (C_6H_5Si)
													3040 ms	3020 m		
2995 s	2960 m	2970 ms	2980 m	3009 m	2970 m	2985 s	2975 ms	2975 ms	2960 s	2970 ms	2970 s	2960 s	2975 ms	2960 m	2965 s	C–H stretch
2930 m	2910 m	2910 ms	2920 w	2970 w	2920 w	2900 m	2890 m	2920 w	2915 m	2910 m	2905 m	2910 ms	2920 ms	2910 m	2910 ms	(CH_3Si) and/or (C_2H_5—O—Si)
							2750vw	2140 vs	2120 vs		2735 vw					Si–H stretch
													1965 w	1955 w		
													1885 w	1875 w		
													1815 w	1810 w		
													1765 w			
													1645 vw			
													1590 w	1593 m		C═C stretch (C_6H_5Si)
													1490 ms	1488 m		
						1485 w	1485 w				1482 w					CH_2 deformation (C_2H_5OSi)
						1447 w	1447 w				1445 w					CH_3–C deformation (C_2H_5OSi)
													1434 vs	1430 vs		C═C stretch (C_6H_5Si)
1410 w	1410 w	1420 w	1405 m	1415 ms	1405 m	1393 m	1395 m	1415 w	1415 w	1402 m	1393 m	1405 m	1407 w	1407 vw	1403 m	CH_2 deformation (antisym.)
		1398 w														
1365 m	1355 w	1374 m	1345 s	1352 s	1350 m	1342 m	1353 m	1357 m	1360 m	1350 s	1350 m	1355 ms	1345 m	1355 m	1342 s	CH_2 deformation ($SiCH_2Si$)
1340 m																
													1302 w	1298 w		C–H deformation (C_6H_5Si)
						1293 w	1295 w				1290 w					C_2H_5OSi characteristic
1255 vs	1250 vs	1255 vs	1256 vs	1262 s	1258 s	1253 s	1256 s	1258 ms	1252 vs	1250 vs	1251 vs	1250 vs	1251 vs	1253 s	1252 vs	CH_3–Si sym. deformation
	1184 vw															
													1190 w	1190 w		
						1165 ms	1166 ms				1165 m					C_2H_5OSi rocking
													1157 w	1153 w		C_6H_5–Si
													1115 vs	1108 vs		
						1105 vs	1110 vs				1107 vs					Si–O–C stretch
						1075 vs	1083 vs				1080 vs					
													1090 w			
													1067 w			
	1045 vs	1048 vs		1065 vs	1050 vs		1040 vs		1040 vs			1045 vs		1040 vs		CH_2 wag ($SiCH_2Si$)
															1050 vs	Si–O–Si
														1025 vs	1025 vs	
													1010 m			
													1000 m	996 w		
													987 w			

															975 s	
	955 w															
940 vs			955 vs	950 vs		945 vs	945 s	950 vs	942 m	942 vs	940 vs	937 vs	939 vs		938 vs	CH_2 wag ($SiCH_2Si$) and/or
			920 ms	925 s						925 s	918 s				910 m	C_2H_5OSi characteristic
														906 m		
								890 (b) vs	890 (b) vs							Si–H bending
870 vs	850 vs		863 vs	865				870 vs	870 vs	860 vs	860 vs		865 ms			
825 vs	815 vs	825 (b) vs	842 vs		830 vs	835 vs	823 vs	810 s		820 vs	825 vs	835 (b)vs	818 vs	810 vs	835 vs	
	785 mw	785 s	800 vs			790 s	787 s		795 vs	783 vs	780 vs	785 vs	782 vs	772 vs	801 vs	
	738 s	750 s	765 vs	· (b) vs		760 s	760 ms		738 vs			757 s	767 s		780 vs	$Si–CH_3$ rocking,
										732 m					758 s	Si–C stretch,
		730 m	710 ms							708 s	740 m				737 m	and Si–O stretch
690 s	680 m	686 ms	687 ms	700		690 m	690 m	715 s	693 ms	682 s	692 s	685 s			680 s	
	662 w	671 ms	650 ms	665 m						640 m			640 m			
													728 vs	730 vs		$Si–C_6H_5$
													699 vs	694 vs		

[a] Values are in cm.$^{-1}$; s = strong, m = medium, w = weak, v = very, (b) = broad (relative to the strongest peak). [b] In carbon tetrachloride.

Also obtained was 2.0 g. (0.0066 mole, 1.3% yield) of 1,1,3,3,5,5,7,7-octamethyl-1,3,5,7-tetrasilacyclooctane (III), m.p. 79–80.5°, lit.[14] m.p. 80.5–81°, b.p. 104° (2 mm.).

Anal. Calcd. for $C_{12}H_{32}Si_4$: C, 49.91; H, 11.17; mol. wt., 289. Found: C, 49.86; H, 11.19; mol. wt., 287.

The last product obtained was 18.8 g. (0.260 mole, 13.1% yield based on $[(CH_3)_2SiCH_2]_n$) of a viscous residue presumably containing higher cyclics and linear dimethylsilmethylene compounds. Molecular distillation of this residue gave four cuts having the molecular weights of 608, 803, 820, and 1460 ± 10 corresponding to n values in the above formula of 8.5, 11.1, 11.4, and 20.2.

Reaction 2. Chloromethylmethyldichlorosilane and Magnesium.—The procedure of reaction 1D was followed except for the work-up of product which was extracted from the slurry with hexane and distilled. To 305.9 g. (1.871 moles) of $(CH_3)(CH_2Cl)SiCl_2$ were added 80 g. (3.3 g.-atoms) of magnesium to give 22.8 g. (0.123 mole, 13.1% yield) of 1,3-dichloro-1,3-dimethyl-1,3-disilacyclobutane (IV), m.p. −7 to −6.5° (by magnetic plunger technique[11]), b.p. 59° (20 mm.), $n^{25}\text{D}$ 1.4725.

Anal. Calcd. for $C_4H_{10}Cl_2Si_2$: C, 25.94; H, 5.44; Cl, 38.29; neut. equiv., 185. Found: C, 25.75; H, 5.44; Cl, 38.05; neut. equiv., 193.

In addition, there was obtained 63.6 g. (0.229 mole, 36.7% yield) of an isotropic mixture of formula $C_6H_{15}Cl_3Si_3$, b.p. 108–109° (5 mm.).

Anal. Calcd. for $C_6H_{15}Cl_3Si_3$: C, 25.94; H, 5.44; Cl, 38.29; neut. equiv., 278. Found: C, 26.05; H, 5.36; Cl, 37.50; neut. equiv., 281.

This product was further fractionated to give mostly a liquid, assigned the structure $Cl_2(CH_3)SiCH_2Si(CH_3)CH_2Si(CH_3)(Cl)CH_2$ (V), b.p. 131° (20 mm.), $n^{25}\text{D}$ 1.4901; and a small quantity of a solid, 1,3,5-trichloro-1,3,5-trimethyl-1,3,5-trisilacyclohexane (VI), b.p. 117–118° (5 mm.).

A yellow brown residue probably containing higher molecular weight cyclic and linear compounds remained.

Reaction 3. Chloromethylmethylethoxychlorosilane and Magnesium.—Following the procedure of reaction 2, 66.7 g. (0.385 mole) of $(CH_3)(CH_2Cl)Si(OC_2H_5)Cl$ in sufficient tetrahydrofuran to bring the final silane concentration to 30% was treated with 15.0 g. (0.617 g.-atom) of magnesium to give on distillation 13.9 g. (0.0680 mole, 35.3% yield) of 1,3-diethoxy-1,3-dimethyl-1,3-disilacyclobutane (VII), b.p. 78–79° (16 mm.), $n^{25}\text{D}$ 1.4336, d_{25} 0.912.

Anal. Calcd. for $C_8H_{20}O_2Si_2$: C, 47.00; H, 9.86; mol. wt., 204. Found: C, 46.88; H, 9.69; mol. wt., 202.

In addition, there was obtained 2.1 g. (0.0069 mole, 5.3% yield) of 1,3,5-triethoxy-1,3,5-trimethyl-1,3,5-trisilacyclohexane (VIII), b.p. 68–69° (0.20–0.25 mm.), $n^{25}\text{D}$ 1.4478; and 14.6 g. (0.143 mole, 37.1% yield based on $[(CH_3)(C_2H_5O)SiCH_2]_n$) of a viscous residue containing higher cyclic and linear methylethoxysilmethylene compounds.

Reaction 4. Chloromethylmethyldiethoxysilane and Magnesium.—The procedure of reaction 2 was utilized. A 236-g. sample (1.431 moles) of $(CH_3)(CH_2Cl)Si(OC_2H_5)_2$ was treated with 45 g. (1.9 g.-atom) of magnesium to give 16.5 g. (0.0807 mole, 11.3% yield) of VII, b.p. 70° (10 mm.), $n^{25}\text{D}$ 1.4328, confirmed by infrared spectrum; and 44.5 g. (0.145 mole, 30.4% yield) of VIII, b.p. 97° (1.7 mm.), $n^{25}\text{D}$ 1.4483.

Anal. Calcd. for $C_{12}H_{30}O_3Si_3$: C, 46.88; H, 9.69; mol. wt., 307. Found: C, 47.26; H, 9.73; mol. wt., 304.

In addition there was obtained a viscous residue of higher molecular weight methylethoxysilmethylene compounds.

Reaction 5. 1,3-Diethoxy-1,3-dimethyl-1,3-disilacyclobutane and Benzoyl Chloride.—A 14.5-g. (0.0708 mole) sample of VII was treated with 20.5 g. (0.146 mole) of benzoyl chloride at 115° for 20 hr. in the presence of a trace of ferric chloride. A 76.9% yield (10.1 g., 0.0545 mole) of IV was obtained on distillation; b.p. 59° (20 mm.); $n^{25}\text{D}$ 1.4725; mol. wt. found, 183, and calcd., 185; confirmed by infrared.

Reaction 6. 1,3,5-Triethoxy-1,3,5-trimethyl-1,3,5-trisilacyclohexane and Phosphorus Trichloride.—A 17.6-g. (0.0574 mole) sample of VIII was treated with 23.7 g. (0.173 mole) of PCl_3 at reflux for 9 hr. with a noted rise in the temperature from 75° to 108°. Distillation gave 13.0 g. (0.0468 mole, 81.5% yield) of VI, m.p. 59°, b.p. 93–94° (2 mm.).

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Anal. Calcd. for $C_6H_{15}Cl_3Si_3$: C, 25.94; H, 5.44; Cl, 38.29; mol. wt., 278. Found: C, 26.02; H, 5.61; Cl, 38.13; mol. wt., 277.

Reaction 7. 1,3-Dichloro-1,3-dimethyl-1,3-disilacyclobutane and Lithium Aluminum Hydride.—To a stirred slurry of 1.20 g. (0.0316 mole) of lithium aluminum hydride in 50 ml. of diethylene glycol dimethyl ether was slowly added 10.19 g. (0.0550 mole) of IV over a period of 30 min. After stirring for an additional 30 min., the product was fractionated in the vacuum line by trap to trap distillation to give 6.11 g. (0.0525 mole, 95.5% yield) of 1,3-dimethyl-1,3-disilacyclobutane (IX), b.p. 96°, n^{25}D 1.4546.

Anal. Calcd. for $C_4H_{12}Si_2$: C, 41.30; H, 10.40; mol. wt., 116. Found: C, 41.20; H, 10.34; mol. wt., 114 (vapor density).

Reaction 8. 1,3,5-Trichloro-1,3,5-trimethyl-1,3,5-trisilacyclohexane and Lithium Aluminum Hydride.—Utilizing the procedure of reaction 7, 6.70 g. (0.0241 mole) of VI dissolved in 25 ml. of ether and 2.0 g. (0.053 mole) of lithium aluminum hydride in 25 ml. of ether were treated to give on distillation 3.26 g. (0.0187 mole, 77.6% yield) of 1,3,5-trimethyl-1,3,5-trisilacyclohexane (X), b.p. 68–71° (19 mm.), n^{25}D 1.4705.

Anal. Calcd. for $C_6H_{18}Si_3$: C, 41.30; H, 10.40; mol. wt., 174. Found: C, 41.75; H, 10.32; mol. wt., 173.

Reaction 9. 1,3-Dichloro-1,3-dimethyl-1,3-disilacyclobutane and Methylmagnesium Iodide in Excess.—To 0.0347 mole of freshly prepared $(CH_3)MgI$ in 25 ml. of diethyl ether was slowly added 3.15 g. (0.0170 mole) of IV over a period of 30 min. followed by an additional 30 min. of stirring. The product was filtered and distilled to give 2.08 g. (0.0144 mole, 84.7% yield) of I; mol. wt. found, 145 (vapor density), and calcd., 144; confirmed by infrared spectrum.

Reaction 10. 1,3-Diethoxy-1,3-dimethyl-1,3-disilacyclobutane and Methylmagnesium Bromide in Excess.—A 1.94-g. (0.00949 mole) sample of VII was added to a solution of 0.024 mole of $(CH_3)MgBr$ in ether, heated to reflux for 6 hr., and stirred for 16 hr. The product was fractionated to give 1.17 g. (0.00810 mole, 85.4% yield) of I, confirmed by infrared spectrum.

Reaction 11. 1,3,5-Trichloro-1,3,5-trimethyl-1,3,5-trisilacyclohexane and Methylmagnesium Bromide in Excess.—A 3.91-g. (0.0141 mole) sample of VI was treated with 0.045 mole of $(CH_3)MgBr$ in the manner described in reaction 10. Fractionation gave 2.92 g. (0.0135 mole, 95.7% yield) of II, n^{25}D 1.4605, confirmed by infrared spectrum.

Reaction 12. 1,3-Dichloro-1,3-dimethyl-1,3-disilacyclobutane and Methylmagnesium Bromide in Equimolar Quantities.—To an ether solution of 7.70 g. (0.0416 mole) of IV was slowly added 0.042 mole of $(CH_3)MgBr$ over a period of 30 min. The reaction was stirred 16 hr., filtered, and distilled to give 0.20 g. of I and 3.40 g. (0.0206 mole, 49.5% yield) of 1-chloro-1,3,3-trimethyl-1,3-disilacyclobutane (XI), b.p. 67.5–68° (59 mm.), n^{25}D 1.4568.

Anal. Calcd. for $C_5H_{13}ClSi_2$: C, 36.44; H, 7.95; Cl, 21.52. Found: C, 37.24; H, 8.21; Cl, 19.84.

Reaction 13. 1,3-Diethoxy-1,3-dimethyl-1,3-disilacyclobutane and Methylmagnesium Bromide in Equimolar Quantities.—A 15.9-g. (0.0778 mole) sample of VII and 0.078 mole of $(CH_3)MgBr$ were treated as described in reaction 12. Distillation of the product gave 4.40 g. (0.0252 mole, 32.4% yield) of 1-ethoxy-1,3,3-trimethyl-1,3-disilacyclobutane (XII), b.p. 71° (40 mm.), n^{24}D 1.4364.

Anal. Calcd. for $C_7H_{18}OSi_2$: C, 48.21; H, 10.40; mol. wt., 174. Found: C, 48.31; H, 10.30; mol. wt., 175.

Reaction 14. 1-Methyldichlorosiliconmethylene-3-chloro-1,3-dimethyl-1,3-disilacyclobutane and Methylmagnesium Iodide.—To 0.0555 mole of freshly prepared $(CH_3)MgI$ was slowly added 5.00 g. (0.0180 mole) of V over a 30-min. period. The product was hydrolyzed, extracted with ether, and distilled to give 2.90 g. (0.0134 mole, 74.5% yield) of 1-trimethylsilmethyl-1,3,3-trimethyl-1,3-disilacyclobutane (XIII), b.p. 112.5–113° (50 mm.), n^{25}D 1.4578.

Reaction 15. 1-Chloro-1,3,3-trimethyl-1,3-disilacyclobutane and Trimethylsiliconmethylene Lithium.—A 4.50-g. (0.0273 mole) sample of XI was added to $(CH_3)_3SiCH_2Li$ prepared from 5.49 g. (0.0447 mole) of $(CH_3)_3SiCH_2Cl$ and excess lithium dispersion (0.26 mole) in hexane. The reaction was heated to reflux for 40 hr., cooled and filtered, and fractionated *in vacuo* to give 4.20 g. (0.0194 mole, 71.0% yield) of XIII, b.p. 75° (10 mm.), n^{25}D 1.4556. The infrared spectrum was identical with XIII prepared in reaction 14.

Anal. Calcd. for $C_9H_{24}Si_3$: C, 49.91; H, 11.17; mol. wt., 217. Found: C, 51.64; H, 11.19; mol. wt., 219.

Reaction 16. 1,3-Dichloro-1,3-dimethyl-1,3-disilacyclobutane and Phenylmagnesium Bromide in Excess.—To a solution of 0.0699 mole of $(C_6H_5)MgBr$ in 35 ml. of ether was slowly added 5.93 g. (0.0320 mole) of IV over a period of 30 min. The reaction was refluxed for 6 hr., stirred for 16 hr. more, and hydrolyzed; and the product was extracted with ether. Upon evaporation of all high volatiles, 8.00 g. (0.0298 mole, 93.1% yield) of crude 1,3-dimethyl-1,3-diphenyl-1,3-disilacyclobutane (XIV) was obtained. The product was difficult to distil conventionally and was best purified by molecular distillation. The physical properties were b.p. 99° (1.1 mm.), n^{25}D 1.5727.

Anal. Calcd. for $C_{16}H_{20}Si_2$: C, 71.57; H, 7.51; mol. wt., 269. Found: C, 71.89; H, 7.41; mol. wt., 263.

Reaction 17. 1,3,5-Trichloro-1,3,5-trimethyl-1,3,5-trisilacyclohexane and Phenylmagnesium Bromide in Excess.—Following the procedure of reaction 16, the interaction of 0.054 mole of $(C_6H_5)MgBr$ and 4.19 g. (0.0151 mole) of VI gave on work-up 4.01 g. (0.00996 mole, 66.0% yield) of crude 1,3,5-trimethyl-1,3,5-triphenyl-1,3,5-trisilacyclohexane (XV). Biphenyl which was formed as a by-product was sublimed *in vacuo*, and the residue was purified by molecular distillation. The purified XI was a slightly yellow viscous liquid, n^{25}D 1.5873.

Anal. Calcd. for $C_{24}H_{30}Si_3$: C, 71.57; H, 7.51; mol. wt., 403. Found: C, 69.85; H, 7.44; mol. wt., 402.

Reaction 18. Hydrolysis of 1-Ethoxy-1,3,3-trimethyl-1,3-disilacyclobutane.—A 8.10-g. (0.0464 mole) sample of XII was combined with 10.0 g. (0.555 mole) of water in 10 ml. of ethanol and refluxed for 16 hr. Ether extraction of the resulting mixture gave 5.20 g. (0.0189 mole, 81.8% yield) of bis(1,3,3-trimethyl-1,3-disilacyclobutyl)-1-siloxane (XVI), n^{25}D 1.4525.

Anal. Calcd. for $C_{10}H_{26}OSi_4$: C, 43.73; H, 9.54; mol. wt., 275. Found: C, 43.49; H, 9.54; mol. wt., 272.