SILICON HETEROCYCLIC COMPOUNDS

I. RING SIZE EFFECT IN RING CLOSURE BY HYDROSILATION

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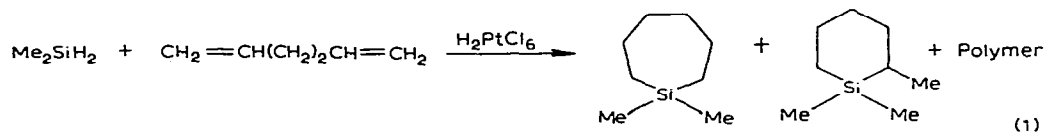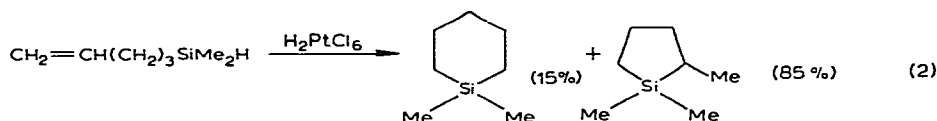
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Summary

The hydrosilation reaction has been utilized for the synthesis of silicon heterocyclic compounds. The effect of n upon the ease of ring formation from compounds of the formula $CH_2=CH(CH_2)_n SiMe_2 H$ (n = 0—6) has been investigated with chloroplatinic acid as a catalyst. No ring closure occurred when silacyclopropane and silacyclobutane were the expected products (n = 0 and 1). When n = 2, only 1,1-dimethyl-1-silacyclopentane (46.3%) was obtained. With n = 3, two isomers, 1,1,2-trimethyl-1-silacyclopentane and 1,1-dimethyl-1-silacyclohexane were found (58.1%) in a 9/1 ratio. When n = 4, 1,1-dimethyl-1-silacycloheptane and its isomer, 1,1,2-trimethyl-1-silacyclohexane were obtained (69.8%) in about a 1/1 ratio. When n = 5, 1,1-dimethyl-1-silacyclooctane and its isomer 1,1,2-trimethyl-1-silacycloheptane were also observed (16.4%) in about a 1/1 ratio but the yield was only one fourth that of the previous one. With n = 6, only 1,1,2-trimethyl-1-silacyclooctane (2.4%) was obtained. A mechanism explaining the findings is discussed.

Introduction

Several hydrosilation ring closure reactions have been reported recently. Kobrakov and co-workers [1] reported that the addition of dimethylsilane to 1,5-hexadiene in the presence of chloroplatinic acid catalyst gave 1,1-dimethyl-1-silacycloheptane and 1,1,2-trimethyl-1-silacyclohexane (eqn. 1). Other dialkylsilanes were also added to 1,5-hexadiene. Later they found two isomers, 1,1-dimethyl-1-silacyclohexane and 1,1,2-trimethyl-1-silacyclopentane, in a 9/1 ratio from ring closure of 5-dimethylsilyl-1-pentene [2] (eqn. 2).

$$Me_2SiH_2 \ + \ CH_2=CH(CH_2)_2CH=CH_2 \ \xrightarrow{H_2PtCl_6} \quad \text{(structures)} \ + \ \text{(structure)} \ + \ Polymer$$

(1)

$$CH_2 = CH(CH_2)_3 SiMe_2H \xrightarrow{H_2PtCl_6}$$


(15%) + (85%) (2)

Recently, Fessenden and Kray [3] reported that the treatment of 5-dimethylsilyl-1-hexene with chloroplatinic acid catalyst in pentane gave a mixture of *cis*- and *trans*-1,1,2,5-tetramethyl-1-silacyclopentane and a trace of 1,1,2-trimethyl-1-silacyclohexane. Because of the potential importance of ring closure for the preparation of silacycloalkanes, we investigated the overall yields and isomer distributions for the ring closures of ω-dimethylsilyl-1-alkenes [CH_2=CH-$(CH_2)_n SiMe_2H$, n = 0—6] with chloroplatinic acid catalyst.

Results and discussions

Syntheses of the appropriate starting materials were carried out by Grignard or hydrosilation procedures. Spectral properties of the ω-dimethylsilyl-1-alkenes are presented in Table 2 and physical properties are given in the Experimental section.
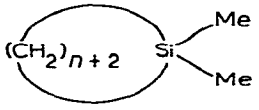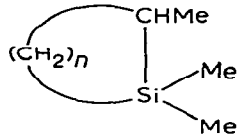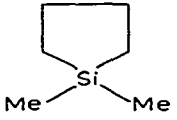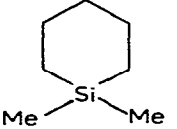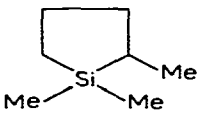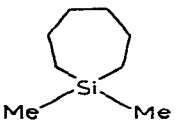
ω-Dimethylsilyl-1-alkenes with chloroplatinic acid catalyst in pentane or cyclohexane gave 1,1-dimethyl-1-silacycloalkanes and 1,1,2-trimethyl-1-silacycloalkane isomers. The reactions were followed by noting the disappearance of the Si—H heptet and the disappearance of the olefinic hydrogens in the NMR spectra. The general route for these reactions is shown in eqn. 3. Table 1 lists typical results for such intramolecular hydrosilations of ω-dimethylsilyl-1-alkenes.

$$CH_2 = CH(CH_2)_n SiMe_2H \xrightarrow[\text{Solvent}]{H_2PtCl_6}$$

(3)
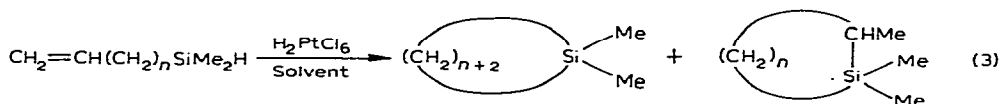
The probable mechanism for these reactions according to the mechanism for hydrosilation generally agreed on by Chalk [4], Sommer [5], and Hartley [6], indicates that chloroplatinic acid is initially reduced to the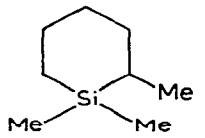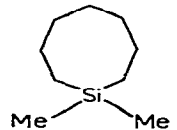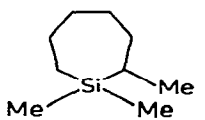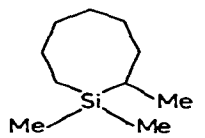 Pt^{II} state. The Pt^{II} species then reacts with the olefin to give a Pt^{II}—olefin complex I. Complex I then forms a Pt^{IV} complex II by incorporation of the silyl group into the complex. Complex II can now react by adding H^- to the double-bonded carbons in two competitive ways to give complexes III and IV from which the respective 1,1-dimethyl-1-silacycloalkane V and its isomer, 1,1,2-trimethyl-1-silacycloalkane VI are obtained by formation of a carbon—silicon bond and catalyst displacement (Scheme 1).

It is possible to explain the product distribution in Table 1 using this mechanism. Two competitive complexes III and IV can be formed, when n = 2, a six-membered ring complex III and a five-membered ring complex IV. These complexes should differ little in their rates of formation and k_2/k_{-2} vs. k^1_{-2} should not be a large factor. However, in the product formation step, the five-membered ring complex would lead to a four-membered ring product whereas the six-membered ring complex would be required as the key intermediate in the formation of a five-membered ring. As expected, the production of a four-membered ring is considerably more difficult than a five-membered ring. Therefore,

TABLE 1

CYCLIC HYDROSILATION PRODUCTS

n^a	Product ratio (area %)[b]				Yield (%)
	$(CH_2)_{n+2}$—Si(Me)(Me)		$(CH_2)_n$—CHMe—Si(Me)(Me)		
2^c		(100)	None		46.3
3^d		(10)		(90)	58.1
4^d		(47.5)		(52.5)	69.8
5^d		(45.8)		(54.2)	16.4
6^d	None			(100)	2.4

[a] With $n = 0$ and 1, the expected silacyclobutane and silacyclopropane were not observed. Only polymeric materials were obtained. [b] Percentage by respective GLPC area. [c] Pentane as the solvent. [d] Cyclohexane as the solvent.

no 1,1,2-trimethyl-1-silacyclobutane was found and only 1,1-dimethyl-1-sila-cyclopentane was observed. From these results, it seems likely that k_3 and k'_3 are the governing factors in the product formation from a small ring complex with $k_3 \ggg k'_3$.

TABLE 2

NMR SPECTRAL DATA OF REACTION PRODUCTS[a]

Compounds	τ value
$\overset{5}{C}H_2=\overset{6}{C}H\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{S}i(CH_3)_2\overset{4}{H}$	9.98 (d, J 4 Hz, H^1), 9.15-9.47 (m, H^2), 7.90 (q, J 6 Hz, H^3), 6.07 (h, J 3.5 Hz, H^4), 4.85-5.25 (m, H^5), 3.80-4.50 (m, H^6)
$\overset{6}{C}H_2=\overset{7}{C}H\overset{4}{C}H_2\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{S}i(CH_3)_2\overset{5}{H}$	9.98 (d, J 4 Hz, H^1), 9.20-9.59 (m, H^2), 8.52 (p, J 6.5 Hz, H^3), 7.92 (q, J 6 Hz, H^4), 6.05 (h, J 3.5 Hz, H^5), 4.83-5.25 (m, H^6), 3.88-4.55 (m, H^7)
$\overset{6}{C}H_2=\overset{7}{C}H\overset{5}{C}H_2\overset{4}{C}H_2\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{S}i(CH_3)_2Cl$	9.65 (s, H^1), 9.00-9.35 (complex, H^2), 8.56 (p, J 3 Hz, $H^{3,4}$), 7.96 (q, J 6 Hz, H^5), 4.85-5.25 (m, H^6) 3.90-4.65 (m, H^7)
$\overset{7}{C}H_2=\overset{8}{C}H\overset{6}{C}H_2\overset{5}{C}H_2\overset{4}{C}H_2\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{S}i(CH_3)_2\overset{6}{H}$	9.95 (d, J 4 Hz, H^1), 9.26-9.50 (complex, H^2), 8.61 (p, J 3.5 Hz, $H^{3,4}$), 7.98 (q, J 6 Hz, H^5), 6.12 (h, J 3.5 Hz, H^6), 4.89-5.27 (m, H^7), 3.97-4.63 (m, H^8)
$\overset{7}{C}H_2=\overset{8}{C}H\overset{6}{C}H_2\overset{5}{C}H_2\overset{4}{C}H_2\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{S}i(CH_3)_2Cl$	9.65 (s, H^1), 9.00-9.45 (envelope, H^7), 8.62 (broad singlet, $H^{3,4,5}$) 7.97 (q, J 6 Hz, H^6), 4.86-5.33 (m, H^7), 3.87-4.70 (m, H^8)
$\overset{8}{C}H_2=\overset{9}{C}H\overset{6}{C}H_2\overset{5}{C}H_2\overset{4}{C}H_2\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{S}i(CH_3)_2\overset{7}{H}$	10.00 (d, J 4 Hz, H^1), 9.24-9.65 (envelope, H^2), 8.70 (broad singlet, $H^{3,4,5}$), 8.06 (q, J 6 Hz, H^6), 6.17 (h, J 3.5 Hz, H^7), 5.00-5.38 (m, H^8), 4.00-4.82 (m, H^9)
$\overset{8}{C}H_2=\overset{9}{C}H\overset{7}{C}H_2\overset{6}{C}H_2\overset{5}{C}H_2\overset{4}{C}H_2\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{S}i(CH_3)_2Cl$	9.65 (s, H^1), 9.00-9.40 (envelope, H^2), 8.64 (broad singlet, $H^{3,4,5,6}$), 7.96 (q, J 6 Hz, H^7), 4.81-5.21 (m, H^8), 3.81-4.70 (m, H^9)
$\overset{9}{C}H_2=\overset{10}{C}H\overset{7}{C}H_2\overset{6}{C}H_2\overset{5}{C}H_2\overset{4}{C}H_2\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{S}i(CH_3)_2\overset{8}{H}$	10.00 (d, J 4 Hz, H^1), 9.21-9.66 (envelope, H^2), 8.66 (broad singlet, $H^{3,4,5,6}$), 8.00 (q, J 6 Hz, H^7), 6.10 (h, J 3.5 Hz, H^8), 4.88-5.33 (m, H^9), 3.90-4.73 (m, H^{10})
$\overline{\overset{5}{C}H_2\overset{4}{C}H_2\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{S}i(CH_3)_2}$	9.91 (s, H^1), 9.37-9.63 (complex, $H^{2,5}$), 8.41 (p, J 3.5 Hz, $H^{3,4}$)
$\overline{\overset{7}{C}H_3\overset{6}{C}H\overset{5}{C}H_2\overset{4}{C}H_2\overset{3}{C}H_2\overset{}{S}i}\underset{\overset{2}{C}H_3}{\overset{\overset{1}{C}H_3}{\diagdown}}$	10.00 (s, H^1), 9.90 (s, H^2), 9.30-9.65 (complex, H^3), 7.98-9.17 (complex, $H^{4,5,6}$), 9.03 (d, H^7)
$\overline{\overset{6}{C}H_2\overset{5}{C}H_2\overset{4}{C}H_2\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{S}i(CH_3)_2}$	10.00 (s, H^1), 9.26-9.58 (complex, $H^{2,6}$), 8.13-8.56 (complex, $H^{3,4,5}$)
$\overline{\overset{8}{C}H_3\overset{7}{C}H\overset{6}{C}H_2\overset{5}{C}H_2\overset{4}{C}H_2\overset{3}{C}H_2\overset{}{S}i}\underset{\overset{2}{C}H_3}{\overset{\overset{1}{C}H_3}{\diagdown}}$	9.99 (s, H^1), 9.92 (s, H^2), 7.92-9.85 (complex, $H^{3,4,5,6,7}$), 9.07 (d, H^8)

TABLE 2 (continued)   87

Compounds	τ value
$\overset{7\quad 6\quad 5\quad 4\quad 3\quad 2\quad 1}{CH_2CH_2CH_2CH_2CH_2CH_2Si(CH_3)_2}$	9.98 (s, H^1), 9.11-9.44 (envelope, $H^{2,7}$), 8.39 (broad singlet, $H^{3,4,5,6}$)
$\overset{9\quad 8\quad 7\quad 6\quad 5\quad 4\quad 3}{CH_3CHCH_2CH_2CH_2CH_2CH_2Si}\overset{1}{\underset{2}{\overset{CH_3}{\diagdown}\underset{CH_3}{\diagup}}}$	10.00 (s, H^1), 9.94 (s, H^2), 7.86-9.68 (complex, $H^{3,4,5,6,7,8}$), 9.15 (d, H^9)[b]
$\overset{8\quad 7\quad 6\quad 5\quad 4\quad 3\quad 2\quad 1}{CH_2CH_2CH_2CH_2CH_2CH_2CH_2Si(CH_3)_2}$	10.00 (s, H^1), 9.22-9.56 (envelope, $H^{2,8}$), 8.52 (broad singlet, $H^{3,4,5,6,7}$)
$\overset{10\quad 9\quad 8\quad 7\quad 6\quad 5\quad 4\quad 3}{CH_3CHCH_2CH_2CH_2CH_2CH_2CH_2Si}\overset{1}{\underset{2}{\overset{CH_3}{\diagdown}\underset{CH_3}{\diagup}}}$	10.00 (s, H^1), 9.94 (s, H^2), 7.89-9.70 (complex, $H^{3,4,5,6,7,8,9}$), 9.18 (d, H^{10})

[a] These spectra were determined either neat or in carbon tetrachloride with tetramethylsilane as an internal standard. [b] Poor resolution.

SCHEME 1
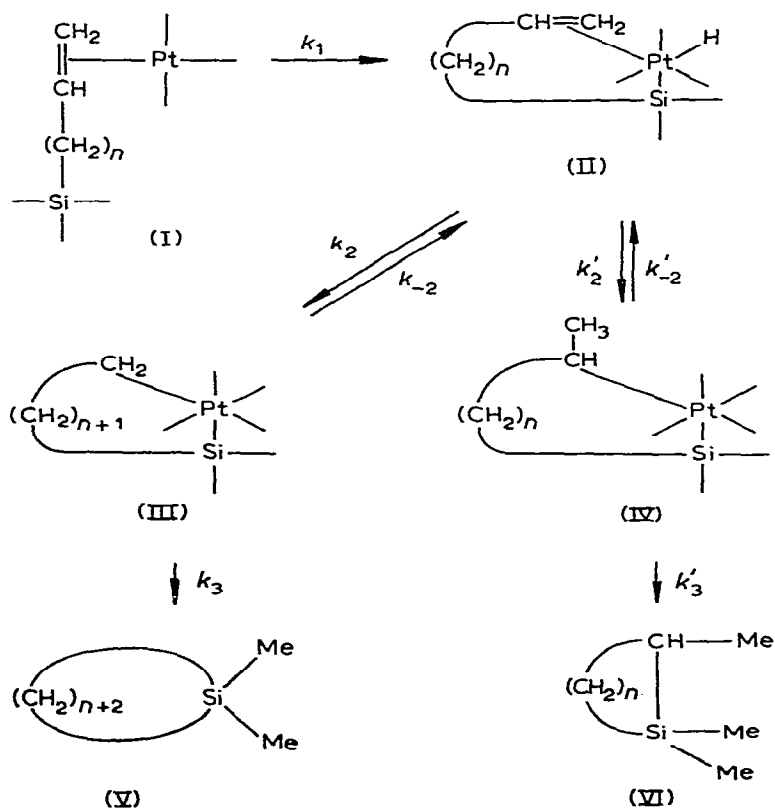
When $n = 3$, the two possible complexes are the seven- and six-membered ring complexes III and IV. The seven-membered ring complex III leads to a six-membered ring product and the six-membered ring complex IV gives a five-membered ring product. As expected, the six-membered ring complex should predominate over the seven-membered one, so 1,1,2-trimethyl-1-silacyclopentane is favored over 1,1-dimethyl-1-silacyclohexane by a 9/1 ratio. This result is consistent with literature reports [2,3].

With $n = 4$ or 5, complex II initially would be expected to produce complex III and complex IV almost equally ($k_2/k_{-2} \approx k_2'/k_{-2}'$) and the rates of product formation from complexes III and IV should not differ greatly (k_3, k_3'). Thus, when $n = 4$, the ratio of 1,1-dimethyl-1-silacycloheptane to its isomer 1,1,2-trimethyl-1-silacyclohexane is nearly one, and when $n = 5$, the ratio of the two isomers, 1,6-dimethyl-1-silacyclooctane and 1,1,2-trimethyl-1-silacycloheptane is also almost equal to one. However, the yield for $n = 5$ is only one fourth of that for $n = 4$ due to the increased formation of polymer.

Finally, with $n = 6$, the competition between ring closure and polymerization should be the major factor. This is definitely shown by the 2.4% yield of only one ring product. That product is 1,1,2-trimethyl-1-silacyclooctane with no 1,1-dimethyl-1-silacyclononane detected, but a large amount of polymer was left.

The attempted formation of 1,1-dimethyl-1-silacyclobutane and 1,1,2-trimethyl-1-silacyclopropane by cyclizing dimethylallylsilane ($n = 1$) in the presence of chloroplatinic acid was unsuccessful. Only high-boiling polymeric material was obtained (eqn. 4).

$$CH_2=CHCH_2SiMe_2H \xrightarrow[\text{pentane}]{H_2PtCl_6} \text{polymer} \qquad (4)$$
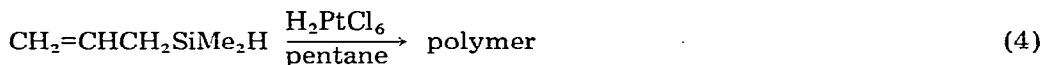
Cyclization of methylethylvinylsilane in the presence of chloroplatinic acid catalyst was also attempted in hope of obtaining 1-methyl-1-ethyl-1-silacyclopropane. Again, only high-boiling polymeric material was observed (eqn. 5).

$$CH_2=CH\underset{\underset{H}{|}}{\overset{\overset{Me}{|}}{Si}}-Et \xrightarrow[\text{pentane}]{H_2PtCl_6} \text{polymer} \qquad (5)$$
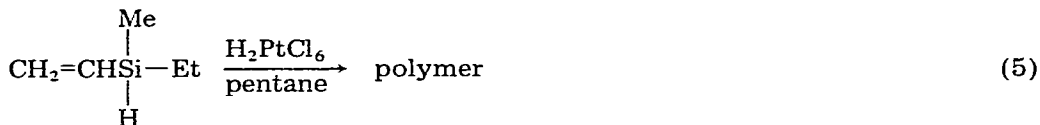
The total yield of products is also in good agreement with what would be expected in ring formation. Five-, six-, and seven-membered rings should predominate with the small ones produced in higher yield because of the proximity of the atoms involved in ring closure. The chance of polymerization becomes important with the larger ring precursors.

Structure assignments

The assignment of structures to the reaction products is based principally upon their spectral data as shown in Table 2, carbon and hydrogen analysis, and the spectral data of similar compounds [3,7,8,9]. The cyclic products were normally separated using preparative GLPC.

In the NMR, the Si—H heptet and the olefinic signals of the ω-dimethylsilyl-1-alkenes disappeared during the course of hydrosilation. A characteristic set of Si—CH$_3$ signals grew in. The 1,1-dimethyl-1-silacycloalkanes show a single Si—CH$_3$ peak, while the isomeric 1,1,2-trimethyl-1-silacycloalkanes show two peaks of equal intensity for the Si—CH$_3$ *cis* and *trans* to the C—CH$_3$ on the ring. A distinct absorption for the methine proton in the latter type of cyclic isomer could not be picked out, but the presence of the methine proton was indicated in each case by the extent of the complex multiplet for the ring protons beginning at about τ 7.9. In each of the 1,1,2-trimethyl-1-silacycloalkanes the C—CH$_3$ signal was obvious as a doublet rising out of the complex multiplet for the ring protons.

The main distinguishing feature in the IR was that ω-dimethylsilyl-1-alkenes showed two bands at 3.24 and 6.10 μm (C=C) and a band at 4.73 μm (Si—H) while cyclization products were clear in those regions.

Experimental

General comments. All boiling points reported here are uncorrected and obtained from distillation or boiling-point apparatus. All GLPC work was done on a Varian Aerograph A-90-P or Series 1700. Isomer distributions reported were determined directly from peak areas without correction for variable detector response. The IR spectra were obtained from a Perkin—Elmer Grating 457 Spectrophotometer. NMR spectra were determined with a Varian A-60 NMR Spectrometer. All elemental analyses were performed by M-H-W Laboratories, Garden City, Michigan.

4-Dimethylsilyl-1-butene. A Grignard reagent was prepared from 10 g (0.074 mole) of 4-bromo-1-butene and 1.8 g (0.074 g-atom) of magnesium turnings in ether. To this was added 6.9 g (0.074 mole) of dimethylchlorosilane in a dropwise manner, and the mixture was refluxed for 4 h. The mixture was then hydrolyzed with dilute hydrochloric acid until the ether and aqueous layers were clearly separated. The aqueous layer was extracted with ether. The combined ether extracts were dried over anhydrous magnesium sulfate. After removal of the ether the residue was distilled under reduced pressure yielding 4.43 g (52.6%) of product, b.p. 35-36° (94 mm), n_D^{28} 1.4137 (lit. [11] b.p. 98.5° (735 mm), n_D^{25} 1.4161).

5-Dimethylsilyl-1-pentene. The experimental procedure was the same as that described above except that 10 g (0.096 mole) of 5-chloro-1-pentene, 2.33 g (0.11 g-atom) of magnesium turnings, and 9.06 g (0.096 mole) of dimethylchlorosilane were used. The product, b.p. 31-32° (80 mm), n_D^{24} 1.4184 (lit. [2] 120-121° (760 mm), n_D^{20} 1.4219) was isolated by distillation. The yield was 4.59 g (37.4%).

6-Dimethylsilyl-1-hexene was prepared by Kobrakov [1] previously. To 100 ml of cyclohexane containing 2 drops (approximately 50 μl) of a chloroplatinic acid solution (0.20 *M* in isopropyl alcohol) was added an equal molar mixture of 16.4 g (0.20 mole) of 1,5-hexadiene and 18.93 g (0.20 mole) of dimethylchlorosilane. The mixture was stirred for 50 h at reflux. After the solvent was distilled off, vacuum distillation of the residue afforded 12.76 g (36.12%) of 6-dimethylchlorosilyl-1-hexene, b.p. 44° (3.5 mm), n_D^{22} 1.4402 (lit. [1] b.p.

183-184° (760 mm), n_D^{20} 1.4423). The chlorosilane, 12.76 g (0.072 mole), was converted into the desired product, 6-dimethylsilyl-1-hexene, b.p. 26° (4.8 mm), n_D^{24} 1.4213 (lit. [1] b.p. 51° (25 mm), n_D^{20} 1.4274) with excess lithium aluminum hydride. The yield was 4.97 g (48.6%).

7-Dimethylsilyl-1-heptene. The procedure was identical to that described for the previous preparation except that 9.32 g (0.097 mole) of 1,6-heptadiene [12] (prepared from treatment of the Grignard reagent of 4-bromo-1-butene with 3-bromo-1-butene) and 9.1 g (0.097 mole) of dimethylchlorosilane were used. 7-Dimethylchlorosilyl-1-heptene, b.p. 68-70° (3.2 mm), n_D^{28} 1.4373 was obtained by distillation under reduced pressure. The yield was 7.02 g (38.1%). (Found: C, 56.65; H, 9.91. $C_9H_{19}SiCl$ calcd.: C, 56.66; H, 10.04%.)

The 7-dimethylchlorosilyl-1-heptene, 7.02 g (0.037 mole), was reduced to 7-dimethylsilyl-1-heptene, b.p. 65-67° (20 mm), n_D^{28} 1.4275, with excess lithium aluminum hydride. The yield was 3.66 g (63.3%). (Found: C, 69.21; H, 13.18. $C_9H_{20}Si$ calcd.: C, 69.14; H, 12.89%.)

8-Dimethylsilyl-1-octene. The procedure was the same as that previously described. 1,7-Octadiene (11.5 g, 0.106 mole) and 10 g (0.106 mole) of dimethylchlorosilane were used. Vacuum distillation of the residue afforded 10.6 g (50%) of 8-dimethylchlorosilyl-1-octene, b.p. 58° (0.6 mm), n_D^{26} 1.4431. (Found: C, 58.55; H, 10.46. $C_{10}H_{21}SiCl$ calcd.: C, 58.64; H, 10.33%.)

The chlorosilane, 10.6 g (0.052 mole), was converted to 8-dimethylsilyl-1-octene, b.p. 31° (0.37 mm), n_D^{24} 1.4320 with excess vitride [$NaAlH_2(OCH_2CH_2OCH_3)_2$, 70% in benzene]. The yield was 7.2 g (81.4%). (Found: C, 70.18; H, 13.15. $C_{10}H_{22}Si$ calcd.: C, 70.50; H, 13.00%.)

General method for ring-closure hydrosilation of ω-dimethylsilyl-1-alkenes

The catalyst (50 μl), chloroplatinic acid (0.20 M in isopropyl alcohol), was placed in 250 ml of cyclohexane (pentane was used in the cyclization of 4-dimethylsilyl-1-butene) and heated to reflux. The ω-dimethylsilyl-1-alkene (1.8-7.0 g) in 100 ml of the same solvent was added dropwise over a 24 h period. The mixture was heated at reflux for an additional 48 h, and then the solvent was removed by distillation. The expected products were isolated by distillation followed by GLPC analysis using a 0.25 in. × 20 ft. SE-30 column. A viscous residue remained in the distilling flask.

1,1-Dimethyl-1-silacyclopentane. This compound was obtained following the above procedure, 2.05 g (46.3%), b.p. 57-58° (145 mm), n_D^{24} 1.4377 (lit. [13] b.p. 107°, n_D^{25} 1.4335). GLPC analysis at 90° showed only one component.

Separation of 1,1-dimethyl-1-silacyclohexane and 1,1,2-trimethyl-1-silacyclopentane. The product mixture 2.5 g (58.1%), b.p. 45-50° (50 mm) was isolated by distillation. Two components were detected and collected by GLPC at 99°. 1,1-Dimethyl-1-silacyclohexane had the longer retention time (10 area %), b.p. 132°, n_D^{24} 1.4391 (lit. [14] b.p. 133°, n_D^{25} 1.4380). 1,1,2-Trimethyl-1-silacyclopentane had the shorter retention time, (90 area %), b.p. 124°, n_D^{24} 1.4370 (lit. [2] b.p. 125° (760 mm), n_D^{20} 1.4380).

Separation of 1,1-dimethyl-1-silacycloheptane and 1,1,2-trimethyl-1-silacyclohexane. The product mixture 3.47 g (69.8%), b.p. 62-65° (35 mm) was obtained by distillation. Two components were detected by GLPC at 109° and collected. 1,1-Dimethyl-1-silacycloheptane had the longer retention time, (47.5

area %), b.p. 72° (40 mm), n_D^{24} 1.4512 (lit. [1] b.p. 163-164° (760 mm), n_D^{20} 1.4535). 1,1,2-Trimethyl-1-silacyclohexane had the shorter retention time, (52.5 area %), b.p. 65° (40 mm), n_D^{24} 1.4423 (lit. [1] b.p. 150-152°, n_D^{20} 1.444).

Separation of 1,1-dimethyl-1-silacyclooctane and 1,1,2-trimethyl-1-silacycloheptane. The product mixture 0.3 g (16.4%), b.p. 40-50° (4.8 mm) was obtained by distillation. Two components were detected by GLPC at 190° and collected. 1,1-Dimethyl-1-silacyclooctane had the longer retention time, (45.8 area %), b.p. 78° (20 mm), n_D^{28} 1.4605. (Found: C, 69.08; H, 12.84. $C_9H_{20}Si$ calcd.: C, 69.14; H, 12.89%.) 1,1,2-Trimethyl-1-silacycloheptane had the shorter retention time, (54.2 area %), b.p. 80° (30 mm), n_D^{28} 1.4572. (Found: C, 69.10; H, 13.05. $C_9H_{20}Si$ calcd.: C, 69.14; H, 12.89%.)

1,1,2-Trimethyl-1-silacyclooctane. The product 0.17 g (2.4%), b.p. 42-45° (7 mm) was obtained by distillation. Only one component was detected by GLPC at 220°. (Found: C, 70.33; H, 12.85. $C_{10}H_{22}Si$ calcd.: C, 70.50; H, 13.00%.)

Attempted formation of 1,1-dimethyl-1-silacyclobutane and 1,1,2-trimethyl-1-silacyclopropane from intramolecular hydrosilation of dimethylallylsilane. To a mixture of 150 ml of pentane and chloroplatinic acid catalyst was added 5.0 g (0.05 mole) of dimethylallylsilane prepared by treating dimethylallylchlorosilane with excess lithium aluminum hydride. After the reaction mixture was refluxed for 48 h, the pentane was distilled through a 6 in. Vigreux column and only viscous polymeric material was left.

Attempted formation of 1-methyl-1-ethyl-1-silacyclopropane from intramolecular hydrosilation of methylethylvinylsilane. Methylethylvinylsilane was prepared by treating ethylmagnesium bromide with methylvinyldichlorosilane, followed by reduction with lithium aluminum hydride. The attempted cyclization of this compound was done by following the same procedure described in the previous attempt. Only viscous polymeric material was observed.

Acknowledgement

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