column at 140°. Pure samples of each $C_{12}$ product analyzed were not available thus precluding a determination of their relative response factors. The results reported are based only on the relative peak area. The assignment of glpc peaks is as follows: CDA (10.8 min), *trans*-CDE (12.9 min), *cis*-CDE (14.3 min), CDD (15.1 min), CDD (16.4 min), *trans,trans,trans*-CDT (17.2 min), CDD (18.4 min), CDD (19.7 min), *cis,trans-trans*-CDT (21.2 min), CDD (22.5 min), *cis,cis,trans*-CDT (24.7 min), and *cis,cis,cis*-CDT (26.4 min). As a check on this procedure, samples were occasionally reanalyzed by glpc on a 150-capillary squalane column at 120°. The relative yields obtained with this column were always within 3% of those obtained with the TCEP column. For hydrogenations carried out at temperatures over 160°, by-products were formed which had retention times very close to *cis*- and *trans*-CDE on the TCEP column. This interference did not occur with the capillary column, and the yields were obtained with this procedure.

**Registry No.**—**1a,** 29079-66-1; *all-trans*-CDT, 676-22-2; *trans,trans,cis*-CDT, 706-31-0; *cis*-CDE, 1129-89-1; *trans*-CDE, 1486-75-5.

**Acknowledgments.**—Rewarding discussions with Dr. E. A. Zuech are gratefully acknowledged. Thanks are also extended to Dr. W. B. Hughes for helpful suggestions and to G. R. Birdsong and C. G. Long for experimental assistance.

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# Silicon Heterocyclic Compounds. Ring Closure by Hydrosilation[1,2]

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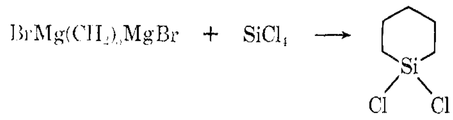
The hydrosilation reaction has been utilized for the synthesis of silicon heterocyclic compounds. With an appropriately substituted silane, the ring-closure reaction results in a silacyclopentane rather than the expected silacyclohexane. 5-(Dimethylsilyl)-1-hexene, upon treatment with chloroplatinic acid, yields equal amounts of *cis*- and *trans*-1,1,2,5-tetramethylsilacyclopentane.

The principal methods for the preparation of silicon heterocyclic compounds utilize some type of organometallic ring-closure reaction. For example, the standard method for the preparation of silacycloalkanes is the reaction of a di-Grignard reagent with a dichlorosilane.[3] The major disadvantage of this method is the limited number of functional groups that can be introduced into the ring system.



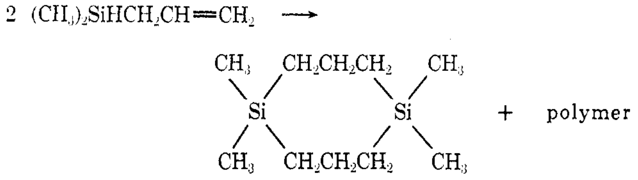
The present study was aimed at the exploration of the use of the hydrosilation reaction for a ring-closure method with particular emphasis on ring systems that contain an α-alkyl substituent.

Silicon hydrides add cleanly across terminal double bonds to yield *n*-alkylsilanes in the presence of both free-radical catalysts[4] (dibenzoyl peroxide) and ionic catalysts[5] (chloroplatinic acid). If the olefin contains an internal double bond and with chloroplatinic acid as catalyst, the double bond migrates to a terminal position before the addition occurs. For example, 2-pentene yields only *n*-pentylsilane.[5]

$$Cl_3SiH + CH_2{=}CHCH_2CH_2CH_3 \xrightarrow{H_2PtCl_6} Cl_3SiCH_2CH_2CH_2CH_2CH_3$$

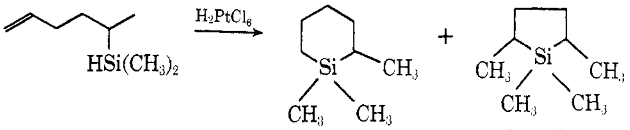
$$Cl_3SiH + CH_3CH{=}CHCH_2CH_3 \xrightarrow{H_2PtCl_6} Cl_3SiCH_2CH_2CH_2CH_2CH_3$$

Ring closure reactions involving hydrosilation have been reported.[6]



## Results and Discussion

Syntheses of the appropriate starting materials are presented in the Experimental Section. Treatment of 5-(dimethylsilyl)-1-hexene with chloroplatinic acid in pentane yields a mixture principally composed of *cis*- and *trans*-1,1,2,5-tetramethylsilacyclopentane (**2**) (73% yield) and only a trace of the expected 1,1,2-trimethylsilacyclohexane (**1**). The five-membered ring was also observed as the major product when 5-(methylchlorosilyl)-1-hexene was used as the starting material.



**1**, trace

**2**, major

This unexpected path of ring closure finds probable explanation in the mechanism for hydrosilation as proposed by Chalk and Harrod.[7] In their proposed mechanism, a seven-membered ring would be required as the key intermediate in the formation of **1**, whereas a six-membered ring intermediate would lead to **2**.

Using the hydrosilation ring-closure reaction, 1,1-dimethylsilacyclopentane was obtained in 60% yield from dimethyl(3-butenyl)silane. The hydrosilation

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(2) Taken in part from the Ph.D. Thesis of William D. Kray, University of Montana.

(3) R. West, *J. Amer. Chem. Soc.*, **76**, 6012 (1954).

(4) C. Eaborn, "Organosilicon Compounds," Academic Press, New York, N. Y., 1960, p 45.

(5) J. L. Speier, J. A. Webster, and G. Barnes, *J. Amer. Chem. Soc.*, **79**, 974 (1957).

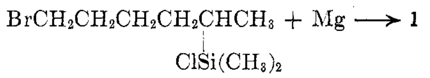
(6) J. W. Curry and G. W. Harrison, *J. Org. Chem.*, 1219 (1958).

(7) A. J. Chalk and J. F. Harrod, *J. Amer. Chem. Soc.*, **87**, 16 (1965).

compares very favorably to dilithium reagent ring-closure reactions (54–76% yield).[8]

To obtain an authentic sample of **1**, an organometallic ring closure was employed. 1-(Trichlorosilyl)-5-chlorohexane was prepared; however, all attempts to ring close this compound met with failure.

When the silyl group was placed at the secondary position and ring closure was attempted to the primary position, the desired compound was obtained in 23% yield.



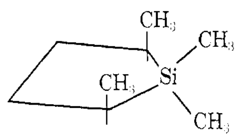
$$BrCH_2CH_2CH_2CH_2\underset{ClSi(CH_3)_2}{\underset{|}{C}}HCH_3 + Mg \longrightarrow \textbf{1}$$

**Structure Assignments.**—The assignment of structures to **1**, *cis*-**2** (**2a**), and *trans*-**2** (**2b**) is based principally upon their comparative spectral data. The carbon–hydrogen analyses of **1** and **2** were consistent with the empirical formulas. Compound **1** contained only one peak in glpc analysis. However, glpc analysis of compound **2** showed that it was a mixture of two components. These two compounds, **2a** and **2b**, were separated using preparative glpc and spectral data was obtained on all three compounds.

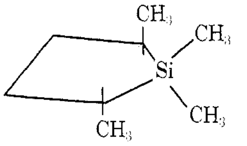
The main distinguishing feature in the ir was that **1** showed a band at 11.4 μ while **2a** and **2b** were clear in this region. Oshesky and Bentley[9] have assigned a band in the 10.93–11.00-μ region as being characteristic of silacyclohexanes. However, the ring systems in their study were all without alkyl substituents on the ring.

In the mass spectra, all three compounds showed a parent peak at *m/e* 142. The mass spectra of **2a** and **2b** were identical and differed from that of **1** by an *m/e* peak at 114, which appeared in the spectrum of **1** but not in those of **2a** and **2b**. This P − 28 peak can be interpreted as the loss of ethylene from the unsubstituted side of the silacyclohexane.[10]

In the nmr, the $SiCH_3$ signal for **1** and **2b** was a singlet but was a doublet for **2a**. This allows assignment of the cis structure to **2a** and the trans structure to **2b**.



**2a**



**2b**

## Experimental Section

The ir spectra were obtained either with neat samples or with 7–10% solutions in $CHCl_3$ using a Beckman IR-5a spectrophotometer. Nmr spectra were obtained with 10% solutions in $CCl_4$ using a Varian HA-60 instrument with either TMS or benzene as the internal standard. Mass spectra were obtained using a modified CEC-103 instrument.

*cis*- and *trans*-1,1,2,5-Tetramethyl-1-silacyclopentane (2). **5-Chloro-1-hexene.**—To 82 g (1.0 mol) of biallyl[11] was added 300 ml of concentrated HCl. The mixture was stirred at room temperature for 16 hr. The product (bp 121°, $n^{30}D$ 1.4308) was isolated by distillation. The yield was 18 g (14%). Unreacted biallyl (80%) was recovered.

*Anal.* Calcd for $C_{11}H_6Cl$: C, 60.75; H, 9.35. Found: C, 60.48; H, 9.49.

**5-(Dimethylchlorosilyl)-1-hexene.**—A Grignard reagent was prepared from 40 g (0.33 mol) of 5-chloro-1-hexene and 12 g (0.5 g-atom) of Mg. To this was added 50 g (0.4 mol) of dimethyldichlorosilane, and the mixture was heated at reflux overnight. The mixture was filtered through Celite, and the product, bp 118° (12 mm), was isolated by distillation. The yield was 10 g (18%). A sample of the product was reduced with $LiAlH_4$ in ether and characterized as the hydride, 5-(dimethylsilyl)-1-hexene (see below).

**5-(Chloromethylsilyl)-1-hexene.**—To a slurry of 12 g (0.5 g-atom) of Mg powder in 400 ml of ether was added 24 g (0.19 mol) of 5-chloro-1-hexene. After the addition was complete, 45 g (0.40 mol) of methyldichlorosilane was added, and the mixture was heated at reflux overnight. After filtration through Celite and distillation, there was obtained 23 g (72%), bp 110° (15 mm). A sample of this material was converted to 5-(dimethylsilyl)-1-hexene with methylmagnesium bromide for characterization (see below).

**5-(Dimethylsilyl)-1-hexene.**—To excess $LiAlH_4$ in 100 ml of ether was added 5 g (0.03 mol) of 5-(dimethylchlorosilyl)-1-hexene. The mixture was heated at reflux overnight, then poured over cracked ice. The ether layer was decanted, and the aqueous layer was extracted with 100 ml of ether. The product, bp 70° (12 mm), $n^{25}D$ 1.4411, was isolated by vacuum distillation. The yield was 3.6 g (75%): ir 3.3, 6.1, 10.0, 10.9 (monosubstituted ethylene), 4.45 (SiH), and 8.0 μ ($SiCH_3$); nmr δ 5.1–6.0 (monosubstituted ethylene pattern, 3 protons), 3.8 (m, 1 proton, assigned as the SiH), 2.1 (vinyl methylene, 2 protons), 1.1–1.8 (m), 0.95 (d, 6 protons), and 0.05 (d, $J$ = 7 Hz, 6 protons, $SiCH_3$).

*Anal.* Calcd for $C_8H_{18}Si$: C, 67.51; H, 12.74. Found: C, 67.60; H, 12.58.

**Ring Closure. Method A.**—A catalytic amount of chloroplatinic acid was placed in 100 ml of olefin-free hexane and heated to reflux. Then 10 g (0.071 mol) of 5-(dimethylsilyl)-1-hexene in 100 ml of hexane was added dropwise over a 4-hr period. The mixture was heated at reflux for an additional 4 hr, and then the solvent was removed by distillation. The product mixture, 7.3 g (73%), bp 145–150°, was isolated by distillation. Glpc analysis showed that the mixture contained three components, later shown to be *cis*- and *trans*-1,1,2,5-tetramethyl-1-silacyclopentane (48%, each isomer) and 1,1,2-trimethyl-1-silacyclohexane (4%). The two silacyclopentanes were separated using preparative glpc (see below).

**Method B.**—Into 200 ml of olefin-free pentane were placed 5.0 g (0.02 mol) of 5-(chloromethylsilyl)-1-hexene and a catalytic amount of chloroplatinic acid. The mixture was placed in a pressure bottle and shaken at 60° for 24 hr. The product mixture, 2.1 g (55%), was isolated by distillation. The product ratios were the same as in method A. Of several catalysts tried, only chloroplatinic acid was effective. With other catalysts, either starting material or polymeric material (in the case of dibenzoyl peroxide) was obtained.

*Anal.* Calcd for $C_8H_{18}Si$: C, 67.51; H, 12.74. Found: C, 67.75; H, 12.59.

**Separation of *cis*- and *trans*-1,1,2,5-Tetramethyl-1-silacyclopentane (2a and 2b).**—The mixture of cis and trans silacyclopentanes was separated by preparative glpc using a 20 ft × 0.5 in. SE-30 column at 110° with a flow rate of 80 ml/min He. The trans (**2b**) and cis (**2a**) isomers had retention times of 3.7 and 4.4 min, respectively. The refractive indices of the trans and cis isomers were $n^{25}D$ 1.4364 and 1.4399, respectively.

The mass spectra of the two isomers were identical: *m/e* (rel intensity) 27 (38), 31 (12), 43 (15), 58 (12), 59 (22), 67 (20), 72 (15), 73 (20), 85 (base peak), 86 (35), 99 (35), 100 (99), 127 (15), 142 (25); ir (both isomers) 3.4, 6.9, 8.05, 14.5 μ; ir (cis isomer) four symmetrical bands at 11.05 (s), 12.3 (w), 13.05 μ (s); ir (trans isomer) three symmetrical bands at 12.05, 12.6, 13.2 μ, equal intensity; the 12.05-μ band had two shoulders at 11.8 and 12.2 μ. In the nmr, the cis isomer showed a doublet ($SiCH_3$) at δ 0 ($J$ = 7 Hz), and the trans isomer showed a singlet ($SiCH_3$) at δ 0. Both isomers showed an unresolved multiplet at δ 1.

**1,1-Dimethyl-1-silacyclopentane.**—To 150 ml of pentane were added 5 g (0.044 mol) of dimethyl(3-butenyl)silane, bp 95°, $n^{30}D$ 1.4190 [lit.[12] bp 98.5° (735 mm), $n^{25}D$ 1.4161], and a catalytic

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[8] R. J. Fessenden and M. D. Coon, *J. Org. Chem.*, **26**, 2530 (1961).

[9] G. D. Oshesky and F. F. Bentley, *J. Amer. Chem. Soc.*, **79**, 2057 (1957).

[10] N. Y. Chernyak, R. A. Khmel'nitskii, T. V. D'yakova, and V. M. Vdovin, *Zh. Obshch. Khim.*, **36**, 96 (1966); *Chem. Abstr.*, **64**, 13524*e* (1966).

[11] A. Turk and H. Chanan, *Org. Syn.*, **27**, 7 (1947).

[12] A. D. Petrov, N. P. Smetankina, and G. I. Nikishin, *Izv. Akad., Nauk SSSR, Otd. Khim. Nauk*, 1468 (1958); *Chem. Abstr.*, **53**, 8117 (1959).

amount of chloroplatinic acid. The mixture was stirred for 16 hr at room temperature. The pentane was removed by distillation through a 24-in. spinning-band column yielding the product, 3.1 g (60%), bp 102°, $n^{30}\mathrm{D}$ 1.4288 (lit.[8] bp 103–105°, $n^{22}\mathrm{D}$ 1.4340).

**1,1,2-Trimethyl-1-silacyclohexane (1). 1-(Trichlorosilyl)-5-chlorohexane.**—To 20 g (0.16 mol) of 5-chloro-1-hexene in 250 ml of cyclohexane were added 60 g (0.50 mol) of trichlorosilane and 3.6 g of dibenzoyl peroxide catalyst. The temperature of the mixture was maintained at 65° for 90 hr. The solvent and excess trichlorosilane were removed by atmospheric distillation, and the product, bp 110–112° (0.12 mm), was isolated by vacuum distillation. The reaction yield was 21 g (87%). The product was converted to trimethyl-*n*-hexylsilane for characterization (see below).

**Trimethyl-*n*-hexylsilane.**—To 50 g of 1-(trichlorosilyl)-5-chlorohexane was added 50 ml of 3 *M* methylmagnesium bromide in ether. The mixture was stirred at ambient temperature for 1 hr, then poured over cracked ice, and extracted with two 50-ml portions of ether. The ether was removed by distillation, and the product, bp 195–197°, $n^{25}\mathrm{D}$ 1.4125, was distilled. The 1-(trimethylsilyl)-5-chlorohexane was treated with magnesium in ether, and the resulting Grignard reagent was hydrolyzed with $H_2O$. The product was distilled and shown to be trimethyl-*n*-hexylsilane by comparison of its spectra (nmr, ir) with those of an authentic sample prepared from the reaction of *n*-hexylmagnesium bromide and trimethylchlorosilane.[13]

**Attempted Ring Closure of 1-(Trichlorosilyl)-5-chlorohexane.**—To a large excess of Mg in 500 ml of ether was added 20 g (0.063 mol) of 1-(trichlorosilyl)-5-chlorohexane. The mixture was heated at reflux overnight, and then 35 g (0.25 mol) of methyl iodide was added. The mixture was again heated at reflux for 24 hr. Water (100 ml) was then added and the organic material was extracted. The ether was removed by careful fractionation, and the volatile product was distilled. This material was shown to be trimethyl-*n*-hexylsilane by comparison of its spectra (nmr, ir) with those of an authentic sample.[13]

**1-Bromo-5-(dimethylchlorosilyl)hexane.**—Anhydrous HBr was bubbled through a mixture of 20 g (0.11 mol) of 5-(dimethylchlorosilyl)-1-hexene and 0.5 g of dibenzoyl peroxide in cyclohexane for 6 hr. During the reaction period, an oil separated from the cyclohexane solution. The ir of this oil showed a strong band at 9.5 μ (SiO). After separation of the oil and removal of the solvent, distillation yielded 18 g of product mixture, bp 80–100° (3 mm). Glpc analysis of this material showed it to be composed of equal amounts of two components. The material was taken into the ring-closure step without further purification.

**Ring Closure.**—A solution of 18 g of crude 1-bromo-5-(dimethylchlorosilyl)hexane in 500 ml of ether was added to an excess of Mg turnings, and the mixture was heated at reflux overnight. Water was then added and the ether phase was decanted and dried ($Na_2SO_4$). The ether was removed by distillation, and the product (bp 150–153°, $n^{25}\mathrm{D}$ 1.4410) was distilled. The product yield of the reaction was 3.8 g [23.6% from 5-(dimethylchlorosilyl)-1-hexene]: ir 8.0 ($SiCH_3$), 7.25 ($-CH_3$), 11.4 μ (silacyclohexane[9]); nmr δ 1.1 (d, α-Me), 1.0–2.2 (m), 0.1 ($SiCH_3$); there was no olefinic signal; mass spectrum *m/e* (rel intensity) 26 (19), 43 (12), 59 (35), 72 (25), 73 (25), 85 (35), 86 (25), 87 (11), 99 (base), 101 (15), 114 (35), 114 (35), 127 (60), 142 (65).

*Anal.* Calcd for $C_8H_{18}Si$: C, 67.51; H, 12.74. Found: C, 67.27; H, 12.59.

**Registry No.**—1, 30102-80-8; 2a, 36982-63-5; 2b, 36982-64-6; 5-chloro-1-hexene, 927-54-8; 5-(chloromethylsilyl)-1-hexene, 36982-66-8; 5-(dimethylsilyl)-1-hexene, 36982-67-9.

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[13] F. C. Whitmore, L. H. Sommer, P. A. DiGiorgio, W. A. Strong, R. E. Van Strien, D. L. Bailey, H. K. Hall, E. W. Pietrusza, and G. T. Kerr, *J. Amer. Chem. Soc.*, **68**, 475 (1946).

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# One-Electron *vs.* Two-Electron Oxidations. The Vanadium(V) and Manganese(III) Oxidations of Cyclobutanol

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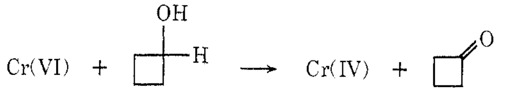
*Received August 4, 1972*

Vanadium(V) oxidizes cyclobutanol in high yields to the ring cleavage product, γ-hydroxybutyraldehyde. The observations that 1-methylcyclobutanol reacts about nine times faster than cyclobutanol, that the oxidation of 1-deuteriocyclobutanol is accompanied by a low deuterium isotope effect ($k_H/k_D$ = 1.21), and that cyclobutanol is about 1000 times more reactive than cyclohexanol, all support the mechanism consisting of a rate-limiting ring opening reaction leading to the $\cdot CH_2CH_2CH_2CHO$ radical as the first reaction product. The presence of manganese(II) in chromic acid oxidations of cyclobutanol has a strong accelerating effect on the reaction, and leads to a large decrease in the deuterium isotope effect and to a large increase in the reactivity of 1-methylcyclobutanol. The yield of cyclobutanone decreases and that of hydroxybutyaldehyde increases with increasing concentration of manganese(II) in the system. These observations are consistent with a mechanism in which the effective oxidant is manganese(III), formed probably by the reaction Cr(VI) + Mn(II) ⇄ Cr(V) + Mn(III), reacting *via* the same free radical intermediate as vanadium(V). Both results strongly indicate that cyclobutanol reacts rapidly and smoothly with one-electron oxidizing agents under ring cleavage, and can be successfully employed as a probe for one-electron oxidants.

Cyclobutanol reacts with chromium(VI), which is a two-electron oxidant, to yield, by carbon–hydrogen bond breaking, the corresponding ketone, cyclobutanone[2] (eq 1), while cleavage of the carbon–carbon bond occurs in the reaction with one-electron oxidants like chromium(IV)[2] or cerium(IV)[3] (eq 2 and 3). It has been proposed[3] that the property of cyclobutanol to react by either carbon–hydrogen or carbon–carbon cleavage could make it a valuable tool for determining the ability of oxidants to react as either one- or two-electron reagents. However, before one can use cyclobutanol oxidations as a diagnostic tool, one has to gain more confidence that the observed pattern is indeed generally valid.



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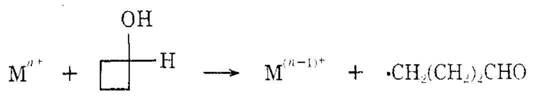

(2)

$$\cdot CH_2(CH_2)_2CHO \longrightarrow HO(CH_2)_3CHO \quad (3)$$

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[2] J. Roček and A. E. Radkowsky, *J. Amer. Chem. Soc.*, **90**, 2986 (1968).

[3] K. Meyer and J. Roček, *ibid.*, **94**, 1209 (1972).