# ORGANIC AND BIOLOGICAL CHEMISTRY

[CONTRIBUTION FROM THE MELLON INSTITUTE]

## Highly Strained Cyclic Paraffin-Siloxanes

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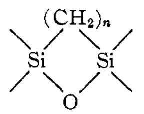
A series of six addition compounds with the structure $ClR_1R_2SiCH_2CH_2SiR_3R_4Cl$, where $R_1$, $R_2$, $R_3$ and $R_4$ = $CH_3$– or $C_6H_5$–, was prepared by a chloroplatinic acid-catalyzed silane addition reaction. Hydrolysis of the adducts, followed by base-catalyzed rearrangement of the hydrolysates at high temperatures yielded a corresponding series of six novel 5-membered paraffin-siloxane cyclic monomers with the structure $R_1R_2SiCH_2CH_2SiR_3R_4O$. A significant shift toward higher wave lengths of the Si–O–Si stretching vibration in the infrared region on ring closure suggests a high order of ring strain in these monomers. An estimate of the strain energy is placed at 8–12 kcal./mole. Polymers of high molecular weight can be obtained from bulk or solution polymerization of the cyclic monomers.

### Introduction

Important cyclic structures in organosilicon chemistry have an even number of alternating silicon and oxygen ring atoms. Noteworthy is the work of Hunter and co-workers[2] describing the preparation and properties of a series of dimethylsiloxane cyclics containing six to sixteen ring atoms. The presence of ring strain was believed by these authors to exist in the 6-ring siloxane since X-ray data revealed this ring to be planar.

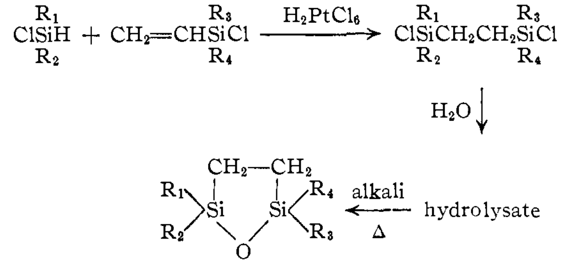
Similar to the cyclic siloxanes is a group of cyclic compounds containing a paraffin as well as a siloxane ring portion. These may be represented by the general structure



In this group ring expansion occurs in the paraffin portion, resulting in rings which can be odd- or even-membered and which can possess varying degrees of strain for the smaller values of $n$. Kumada and Habuchi[3] have described the preparation of the 6-ring member, $(CH_3)_2SiCH_2CH_2CH_2Si(CH_3)_2O$, of this group. The 7-ring compound, $(CH_3)_2SiCH_2CH_2CH_2CH_2Si(CH_3)_2O$, was first reported by Sommer and Ansul,[4] and appropriately termed by them as a "paraffin-siloxane." Since the existence of the 4-ring structures in this group is improbable, the most highly strained and hence most reactive paraffin-siloxanes toward polymerization will be the 5-ring compounds.

The purpose of this paper is to describe the preparation and properties of a series of strained 5-ring paraffin-siloxanes containing methyl and phenyl substituents on the ring silicon atoms.

Syntheses of the various cyclics were accomplished in high yield *via* well-known reactions, as shown in the sequence



$R_1$, $R_2$, $R_3$ and $R_4$ = $CH_3$– or $C_6H_5$–

The sequence further indicates that a series of six adducts is possible when any R group is either methyl or phenyl. All six adducts were prepared in yields ranging from 68–94% by reaction of the appropriate silicon hydrides and vinylsilanes in the presence of chloroplatinic acid[5] as the catalyst. Hydrolysis of the adducts, followed by catalytic rearrangement of the hydrolysates over strong alkali[2] at temperatures above 230° gave a corresponding series of six 5-ring compounds in 68–87% yield.

**Preparation.**—The addition reactions appear to yield $\beta$-adducts exclusively. While formation of $\alpha$-addition compounds is possible during adduct preparation, no evidence for their formation has been found from n.m.r. examination of several hydrolysates and forecuts from adduct distillations. In addition, the high yields of the desired $\beta$-adducts indicate that $\alpha$-adduct formation must be of a low order of magnitude, if they are formed at all.

Both lithium and potassium hydroxides have been used as catalysts for the rearrangement of hydrolysates into cyclic compounds. At the high temperatures of this procedure, phenyl cleavage by potassium hydroxide has been observed. Use of the weaker base, lithium hydroxide, minimizes this tendency and is considered to be more satisfactory in the preparation of the cyclics containing phenyl substituents.

Cyclic compounds with more than five ring atoms have not been successfully isolated. Only with the preparation of 2,2,5,5-tetramethyl-1-oxa-2,5-disilacyclopentane has material approximating the 10-ring cyclic been obtained and identification of this material has not been unequivocal.

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[1] Multiple Fellowship on Silicones sustained by Dow-Corning Corporation and Corning Glass Works.

[2] M. J. Hunter, J. F. Hyde, E. L. Warrick and H. J. Fletcher, This Journal, **68**, 667 (1946).

[3] M. Kumada and A. Habuchi, *J. Inst. Polytech. Osaka City Univ.*, **3**, Ser. C, 65 (1952).

[4] L. H. Sommer and G. R. Ansul, This Journal, **77**, 2482 (1955).

[5] J. L. Speier, J. A. Webster and G. H. Barnes, *ibid.*, **79**, 974 (1957).

Formation of cyclic siloxanes by hydrolysis of chlorosilanes has been widely reported.[6] In the synthesis route described here, no attempt was made to isolate cyclic materials which may have formed directly upon hydrolysis of the adducts. Recent investigations in this area, however, have revealed that 5-ring compounds can be obtained in high yield directly from hydrolysis. These results will be discussed in a future publication.

**Spectra and Ring Strain.**—In the cyclic siloxanes, the infrared Si–O–Si stretching vibration is located at 9.15–9.25 $\mu$ in the 8-ring compounds and at 9.8–9.9 $\mu$ in the 6-ring compounds.[7] Reducing the ring size has the effect of shifting the band to higher wave lengths. The case is similar for the cyclic paraffin-siloxanes. Reduction of ring size from the 7-ring system[4] to the 5-ring system results in a large shift of this band from 9.86 to the 10.8–11.05 $\mu$ region. In linear polyparaffin-siloxanes the Si–O–Si band is observed near 9.4 $\mu$. This large shift from 9.4 $\mu$ in the open chain form to 10.8 $\mu$ or greater in the cyclic form is indicative of the high order of ring strain in the 5-ring system.

An estimation of the strain energy of the 6-ring siloxane and the 5-ring paraffin-siloxane systems has been made from heats of polymerization of these cyclics. The estimated values of 3–4 kcal./mole for dimethylsiloxane cyclic trimer and 8–12 kcal./mole for the 5-ring cyclics suggest at least a twofold increase in ring strain in the 5-ring over the 6-ring system and, as a consequence thereof, a greater reactivity toward polymerization by the 5-ring cyclics. This latter point has been recently demonstrated by Merker and Scott.[8]

Cyclopentane, a hydrocarbon comparable in structure to the 5-ring cyclics discussed here, possesses a strain energy of 7 kcal./mole.[9] A comparison of this value with that estimated for the 5-ring paraffin-siloxanes shows that in effect the replacement of $-(CH_2)_3-$ by –Si–O–Si– in the cyclopentane ring results in an increase of ring strain.

Extra-annular atoms or groups contribute to ring strain energy, such as, for example, the energy due to hydrogen–hydrogen repulsion in cyclopentane.[10,11] In addition to this expected repulsion effect in the paraffin portion of the paraffin-siloxane ring, an effect of the substituent on the ring silicon atom also appears to influence ring strain. As phenyl groups are substituted for methyl groups in the 5-ring paraffin-siloxanes, a small shift of the Si–O–Si infrared band toward higher wave lengths occurs and a similar shift toward lower field strengths is observed in the $Si^{29}$ n.m.r. spectra.

**Structural Features.**—The effect of symmetry on the physical state of the adducts can be conveniently shown. Those adducts—1,2-bis-(dimethylchlorosilyl)-ethane, 1,2-bis-(phenylmethylchlorosilyl)-ethane and 1,2-bis-(diphenylchlorosilyl)-ethane—which have planes or centers of symmetry are solids at ordinary temperatures. One exception is 1-dimethylchlorosilyl-2-diphenylchlorosilylethane, which is liquid but does have a plane of symmetry.

While theory predicts the existence of stereoisomers for certain adduct and cyclic structures, no effort has been made toward their separation or identification.

**Reactivity.**—Catalytic amounts of strong acids or bases readily attack the 5-ring paraffin-siloxane system at the siloxane linkage to yield linear high molecular weight polymers. Weight average molecular weights as high as 870,000 have been obtained from bulk polymerization of the cyclic monomers at moderate temperatures. As expected from the higher strain energy of the 5-ring systems, polymerizations are more exothermic and proceed more rapidly than those of the 6- and 8-ring siloxanes. A comprehensive treatment of 5-ring monomer reactivity and of factors influencing reactivity is in the process of being published.[8]

## Experimental

**Materials.**—All chlorosilanes used in this work were supplied by Dow–Corning Corporation with the exception of phenylmethylchlorosilane which was prepared in a Grignard process from phenyl bromide and methyldichlorosilane. Phenylchlorosilanes of varying purities were generally used in the crude form without additional purification.

The catalyst for the addition reaction was prepared by the solution of 1.161 g. of $H_2PtCl_6 \cdot 6H_2O$ in 22.4 ml. of isopropyl alcohol to give a 0.1 *M* solution. Each drop of solution at 50 drops/ml. was equivalent to 2 × $10^{-6}$ mole Pt.

**Monomers. 2,2,5,5-Tetramethyl-1-oxa-2,5-disilacyclopentane (A).**—Dimethylchlorosilane (378 g., 4.0 moles) was added dropwise to a mixture of dimethylvinylchlorosilane (483 g., 4.0 moles) and $H_2PtCl_6$ catalyst solution (16 × $10^{-6}$ mole Pt) initially at 75°. A reaction temperature of 110–120° was then maintained by controlling the addition rate. Distillation yielded 780 g. (91%) of solid adduct, **1,2-bis-(dimethylchlorosilyl)-ethane (I)**, b.p. 198° (734 mm.), f.p. 37°.

*Anal.* Calcd. for $C_6H_{16}Cl_2Si_2$: Si, 26.1; neut. equiv., 78.5. Found: Si, 26.3; neut. equiv., 77.6.

Compound I (366 g., 1.7 moles) was melted and hydrolyzed by adding the compound slowly to vigorously stirred cold water (400 ml.). The hydrolysate was dissolved in a mixture of toluene (300 ml.) and ethyl ether (100 ml.), washed with water and aqueous sodium bicarbonate to remove residual chloride, and stripped of solvents by distillation. To catalytically rearrange the hydrolysate into cyclic products, a portion of the hydrolysate (249 g.) was mixed with potassium hydroxide (1.8 g.) and heated to 270–280°. Refluxing liquid was collected as a crude distillate, which was then fractionated to yield 169 g. (68%) of pure cyclic A, b.p. 124° (735 mm.), $n^{25}\text{D}$ 1.4142, $d^{25}_{4}$ 0.855, $r\text{D}$ 0.2922 (calcd. 0.2919).

*Anal.* Calcd. for $C_6H_{16}OSi_2$: C, 45.0; H, 10.1; Si, 35.1. Found: C, 44.0; H, 10.2; Si, 35.0.

**2,2,5-Trimethyl-5-phenyl-1-oxa-2,5-disilacyclopentane (B).**—As described for I, dimethylchlorosilane (483 g., 5.1 moles) and phenylmethylvinylchlorosilane (731 g., 4.0 moles) were allowed to react in the presence of $H_2PtCl_6$ catalyst (16 × $10^{-6}$ mole Pt) to give 1045 g. (94%) of liquid adduct, **1-dimethylchlorosilyl-2-phenylmethylchlorosilylethane (II)**, b.p. 191° (50 mm.), $n^{25}\text{D}$ 1.5118, $d^{25}_{4}$ 1.072, $r\text{D}$ 0.2798 (calcd. 0.2792).

*Anal.* Calcd. for $C_{11}H_{18}Cl_2Si_2$: Si, 20.3; neut. equiv., 138.7. Found: Si, 20.4; neut. equiv., 138.6.

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(6) (a) F. S. Kipping and R. Robinson, *J. Chem. Soc.*, **105**, 484 (1914); (b) J. F. Hyde and R. C. De Long, THIS JOURNAL, **63**, 1194 (1941); (c) W. F. Gilliam, H. A. Liebhafsky and A. F. Winslow, *ibid.*, **63**, 801 (1941); (d) R. O. Sauer, W. J. Scheiber and S. D. Brewer, *ibid.*, **68**, 962 (1946); (e) W. Patnode and D. F. Wilcock, *ibid.*, **68**, 358 (1946).

(7) C. W. Young, P. C. Servais, C. C. Currie and M. J. Hunter, *ibid.*, **70**, 3758 (1948).

(8) R. L. Merker and M. J. Scott, presented at the 136th National Meeting of the American Chemical Society, Atlantic City, N. J., September 14, 1959.

(9) K. S. Pitzer, *Science*, **101**, 672 (1945).

(10) J. B. Conn, G. B. Kistiakowsky and E. A. Smith, THIS JOURNAL, **61**, 1868 (1939).

(11) R. Spitzer and H. M. Huffman, *ibid.*, **69**, 211 (1947).

Compound II (834 g., 3.0 moles) was hydrolyzed by slow addition of the compound to a stirred cold mixture of toluene (500 ml.) and water (750 ml.). After washing to remove residual chloride, lithium hydroxide (2.4 g.) was added to a portion of the toluene solution containing 488 g. of hydrolysate and the toluene was distilled off at atmospheric pressure. The catalytic rearrangement of linear polymers into cyclic product was carried out at 225–285° and at a pressure of less than 1 mm. with an apparatus consisting merely of a reaction flask and an attached distillation head. Cyclics which formed were collected as a crude distillate. Fractionation then yielded 426 g. (87%) of pure cyclic B, b.p. 146° (50 mm.), $n^{25}\mathrm{D}$ 1.4962, $d^{25}_{4}$ 0.974, $r\mathrm{D}$ 0.3001 (calcd. 0.2995).

*Anal.* Calcd. for $C_{11}H_{18}OSi_2$: C, 59.4; H, 8.2; Si, 25.3. Found: C, 58.1; H, 7.8; Si, 25.3.

**2,5-Dimethyl-2,5-diphenyl-1-oxa-2,5-disilacyclopentane (C).**—The dropwise addition of crude phenylmethylchlorosilane (86.6 g., b.p. 105–117° (100 mm.), $n^{25}\mathrm{D}$ 1.5141) to a heated mixture (125°) of phenylmethylvinylchlorosilane (121 g., 0.66 mole) and $H_2PtCl_6$ catalyst ($6 \times 10^{-6}$ mole Pt), followed by heating at 125° for 1.5 hours, yielded upon distillation 140 g. (68%) of solid adduct, **1,2-bis-(phenylmethylchlorosilyl)-ethane (III)**, b.p. 215° (11 mm.), m.p. 68°.

*Anal.* Calcd. for $C_{16}H_{20}Cl_2Si_2$: Si, 16.6; neut. equiv., 169.7. Found: Si, 16.6; neut. equiv., 168.9.

After the hydrolysis of III (139.8 g., 0.41 mole) and removal of residual chloride, the rearrangement of the hydrolysate was carried out over lithium hydroxide (0.33 g.) as described for B. Fractionation of the crude distillate (82 g.) gave 72 g. (69%) of pure cyclic C, b.p. 182° (10 mm.), $n^{25}\mathrm{D}$ 1.5492, $d^{25}_{4}$ 1.047, $r\mathrm{D}$ 0.3039 (calcd. 0.3039).

*Anal.* Calcd. for $C_{16}H_{20}OSi_2$: C, 67.6; H, 7.1; Si, 19.8. Found: C, 67.5; H, 7.2; Si, 19.7.

**2,2-Dimethyl-5,5-diphenyl-1-oxa-2,5-disilacyclopentane (D).**—Crude diphenylchlorosilane (228 g.) was added dropwise to a mixture of dimethylvinylchlorosilane (121 g., 1.0 mole) and $H_2PtCl_6$ catalyst ($4 \times 10^{-6}$ mole Pt) at 110°. To ensure completeness of the reaction, the mixture temperature was raised to 145° over 1.5 hours before distillaton, which then gave 257 g. (76%) of liquid adduct, **1-dimethylchlorosilyl-2-diphenylchlorosilylethane (IV)**, b.p. 215° (10 mm.), $n^{25}\mathrm{D}$ 1.5566, $d^{25}_{4}$ 1.118, $r\mathrm{D}$ 0.2865 (calcd. 0.2868).

*Anal.* Calcd. for $C_{16}H_{20}Cl_2Si_2$: Si, 16.6; neut. equiv., 169.7. Found: Si, 16.8; neut. equiv., 169.2.

Following the hydrolysis of IV (225 g., 0.66 mole), the rearrangement of the hydrolysate was carried out as for B at 270-280° and 1 mm. over lithium hydroxide (1.88 g.). The collected crude cyclic material polymerized on standing. Rearrangement was repeated at 290–350° and 1 mm. without addition of further catalyst. Fractionation of the crude distillate then gave 141 g. (75%) of pure cyclic D, b.p. 181° (11 mm.), $n^{25}\mathrm{D}$ 1.5492, $d^{25}_{4}$ 1.044, $r\mathrm{D}$ 0.3048 (calcd. 0.3039).

*Anal.* Calcd. for $C_{16}H_{20}OSi_2$: C, 67.6; H, 7.1; Si, 19.8. Found: C, 67.6; H, 7.2; Si, 20.0.

**2-Methyl-2,5,5-triphenyl-1-oxa-2,5-disilacyclopentane (E).**—At a temperature of 120°, as described for IV, diphenylchlorosilane (219 g.) was added to phenylmethylvinylchlorosilane (183 g., 1.0 mole) in the presence of $H_2PtCl_6$ catalyst ($4 \times 10^{-6}$ mole Pt). Further heating at 150° for 2.5 hr. and distillation yielded 266 g. (67%) of liquid adduct, **1-phenylmethylchlorosilyl-2-diphenylchlorosilylethane (V)**, b.p. 256° (8 mm.), $n^{25}\mathrm{D}$ 1.5878, $d^{25}_{4}$ 1.152, $r\mathrm{D}$ 0.2920 (calcd. 0.2918).

*Anal.* Calcd. for $C_{21}H_{22}Cl_2Si_2$: Si, 14.0; neut. equiv., 200.7. Found: Si, 14.1; neut. equiv., 200.6.

The hydrolysis of V (224 g., 0.56 mole) from 1 liter of toluene solution followed by washing and rearrangement, as described for B, over lithium hydroxide (0.58 g.) at 250–350° and 1 mm. yielded 182 g. of crude distillate, of which 161 g. was fractionated to give 148 g. (86%) of cyclic E, b.p. 241° (11 mm.), $n^{25}\mathrm{D}$ 1.5860, $d^{25}_{4}$ 1.092, $r\mathrm{D}$ 0.3073 (calcd. 0.3063).

*Anal.* Calcd. for $C_{21}H_{22}OSi_2$: C, 72.8; H, 6.4; Si, 16.2. Found: C, 72.7; H, 6.6; Si, 16.2.

**2,2,5,5-Tetraphenyl-1-oxa-2,5-disilacyclopentane (F).**—After the slow addition of crude diphenylchlorosilane (765 g., 41% purity) over a 3-hour period to a mixture of crude diphenylvinylchlorosilane (857 g.) and $H_2PtCl_6$ catalyst ($14 \times 10^{-6}$ mole Pt) at 115°, the mixture was heated further at 115° for 3.5 hours and at 145° for 1.5 hours. Distillation plus hexane extraction of the residue and crystallization of the adduct from the solvent yielded a total of 535 g. (80%) of solid adduct, **1,2,-bis-(diphenylchlorosilyl)-ethane (VI)**, b.p. 301° (8 mm.), m.p. 98°.

*Anal.* Calcd. for $C_{26}H_{24}Cl_2Si_2$: Si, 12.1; neut. equiv., 231.8. Found: Si, 12.3; neut. equiv., 229.5.

The chloride-free solid hydrolysate obtained from the hydrolysis of VI (535 g., 1.15 moles) was rearranged as for B at 320–425° and 1 mm. over lithium hydroxide (0.89 g.). In this case, a flask was used as both condenser and receiver for the collection of 370 g. (78%) of crude solid cyclic. Recrystallization from hexane gave pure cyclic F, m.p. 80–81°.

*Anal.* Calcd. for $C_{26}H_{24}OSi_2$: C, 76.4; H, 5.9; Si, 13.8. Found: C, 76.7; H, 6.3; Si, 13.7.

**Heats of Polymerization.**—In the homopolymerizations of dimethylsiloxane cyclic trimer and cyclic B, the heats of polymerization are essentially the cyclic strain energies since polymerizations result in conversion of a ring structure to a linear structure without the formation of new types of bonds. Thus there is no significant net change in the number of like bonds since bonds are merely broken and reformed.

In a vacuum-jacketed polymerization cell, a small quantity of powdered potassium hydroxide was added to a weighed amount of cyclic at 90° to initiate the exothermic polymerization. When the temperature of the system appeared to reach a maximum (1–3 minutes), the polymer–cyclic mixtures were rapidly quenched and analyzed. For dimethylsiloxane cyclic trimer, the percentage conversion was determined by dissolving the quenched sample in benzene, precipitating the polymer with 95% methanol, and by isolating, drying and weighing of the polymer. With cyclic B, the percentage conversion was obtained directly from a refractive index of the polymer–cyclic mixture, for the refractive index in this system is a linear function of the weight percentage of the cyclic and polymer components. The heats of polymerization were then estimated from an equation of the type

$$\Delta H = \Delta T C M_w / 1000 f$$

where $\Delta H$ = heat of polymerization or strain energy, kcal./mole; $\Delta T$ = temperature rise, °C.; $C$ = specific heat of polymer–cyclic mixture at $(T_1 + T_2)/2$, cal./°g.; $M_w$ = cyclic molecular weight; and $f$ = weight fraction polymer. Corrections were applied to compensate for heat lost to the glass cell.

**Polymers. Poly-(methyltriphenylsilethylene-siloxane).**—Cyclic E (2.0 g.) and a trace of potassium dimethylsilanolate catalyst were mixed and heated at 120–130° for 20 minutes and cooled. Examination showed the polymer product to be a hard and tough high polymer. A light scattering molecular weight of 870,000 was determined for the polymer.

**Poly-(tetraphenylsilethylene-siloxane).**—Solid cyclic F (3.0 g.) was solution polymerized in 20 ml. of diphenyl ether in the presence of potassium dimethylsilanolate. The polymerization was carried out in an air evacuated and sealed ampoule at 100° for 18.75 hours. A high melting polymer, m.p. 292°, precipitated from solution during polymerization.

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