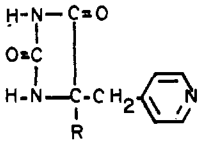
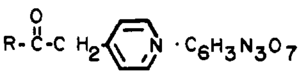
Table II. Hydantoin[a] and Picrate[a] Derivatives of Alkyl 4-Pyridylmethyl Ketones





R	Mp, °C	Mp, °C
CH_3	259–60	156–7.5[b]
C_2H_5	211.5–3.5	163.5–5.5[c]
n-C_3H_7	219.5–20.5	137–8
iso-C_3H_7	241.5–2.5	119–21[d]
n-C_4H_9	217.5–8.5	97.5–9.5
iso-C_4H_9	287–8	138.5–9.5
sec-C_4H_9	217.5–9.5	142–3.5
tert-C_4H_9	220.5–1.5	158.5–9.5[e]
n-C_5H_{11}	223.5–4.5	93–3.5

[a] Elemental analyses (N) in agreement with theoretical values have been obtained and submitted for review. [b] Reported mp, 154°C (2). [c] Reported mp, 163.2–4°C (3). [d] Reported mp, 121–1.7°C (3). [e] Reported mp, 157.3–7.8°C (3).

The mixture was cooled to 0 ± 5°C, and 90 grams (0.9 mole) of diisopropylamine in 126 ml of benzene was added, after which the mixture was stirred for an additional hour at 0 ± 5°C. To the solution of sodium diisopropylamide was added 85 grams (0.9 mole) of 4-picoline in 89 ml of benzene, to give the 4-pyridylmethylsodium. The mixture was stirred for an additional 30 min at 0 ± 5°C, and 51 grams (0.45 mole) of methyl 2-methylbutyrate in 58 ml of benzene was added. After 1 additional hr of stirring at 0 ± 5°C, the mixture was poured onto ice and made strongly acidic with concentrated hydrochloric acid.

This mixture was extracted several times with benzene to remove unreacted ester, then made strongly alkaline with 20% sodium hydroxide, and extracted several times with ether. The ether extracts were dried over anhydrous sodium sulfate, the ether was removed by flash distillation, and the ketone distilled through a Nester-Faust annular Teflon spinning-band column under reduced pressure. There was obtained 30 grams (33%) of 1-(4-pyridyl)-3-methyl-2-pentanone, bp, 100/(1.0 mm), $n^{20}D$ 1.5048, $d^{20}4$ 1.006. A picrate was prepared by the method of Shriner et al. (*5*), mp, 142–3.5°C.

5-sec-Butyl-5-(4-pyridylmethyl) hydantoin. A mixture of 4.5 grams of ammonium carbonate, 1.3 grams of potassium cyanide, and 1.0 gram of 1-(4-pyridyl)-3-methyl-2-pentanone in 50 ml of water was placed in a flask fitted with an air condenser. The flask was placed in a 70°C water bath for 4 hr, carefully acidified with concentrated hydrochloric acid to pH 6–7, and cooled. The hydantoin precipitate was removed by filtration and recrystallized from water, mp, 217.5–9.5°C.

Acknowledgment

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Some New Cyclic Organopolysiloxanes

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Eight new cyclosiloxanes containing five- and seven-membered rings, fused rings, spiro rings, and separated rings were prepared. Yields, melting points, and infrared spectra are given for these compounds.

Organic cyclotrisiloxanes and cyclotetrasiloxanes are well known as useful intermediates which can be rearranged into high-molecular-weight linear polysiloxanes. In a study of polysiloxanes with unconventional structures, several new cyclosiloxanes were made. These compounds, whose structures are shown in Figure 1, were prepared by condensing an α,ω-dichloro compound with a suitable α,ω-diol in the presence of an acid acceptor such as pyridine. The starting materials are given in Table I. Properties of the new cyclosiloxanes are given in Table II, and their infrared spectra are tabulated in Table III.

Experimental

The condensation reactions were carried out in toluene solution with pyridine as an acid acceptor and occasionally as a solvent for the diol as well. A typical procedure is described below.

Preparation of compound I. Into a 2-liter three-necked flask equipped with two dropping funnels, a stirrer, and drying tube, was placed a solution containing 10 ml of pyridine and 500 ml of toluene. To this were added two 300-ml toluene solutions, one containing 22.7 grams (0.05*m*) of tetra-o-tolyldisilane-1,2-diol, the other containing 6.1 ml (0.05*m*) of dichlorodimethylsilane. Both solutions were added simultaneously and at the same rate over a period of 1 hr with stirring at room temperature. The resulting mixture was stirred for a few hours and

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then filtered. The filtrate was washed three times with water, separated, dried over sodium sulfate, and evaporated. On standing, the residue solidified. After washing oily material from the residue with methanol, there was obtained 4.9 grams (19%) of crude product melting at 120–126°C. One recrystallization from hexane, followed by another from ethyl acetate, gave 2.2 grams (9%) of pure crystals melting at 125–126°C. (Melting points were uncorrected.)

Infrared spectra. The infrared spectra were recorded on a Perkin-Elmer Model 137 spectrometer equipped with a NaCl prism.

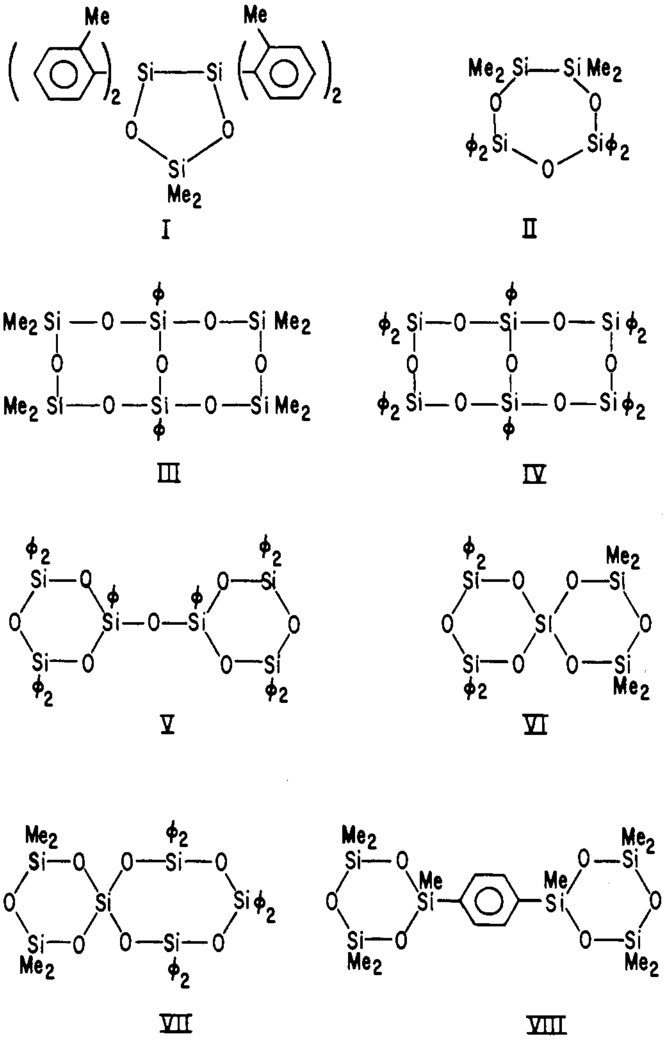

Figure 1. Structures of cyclic organopolysiloxanes

Table II. Organopolysiloxanes

Compound designation[a]	Formula	Mp, °C	Yield, %
I	$C_{30}H_{34}O_2Si_3$	125–126	9
II	$C_{28}H_{32}O_3Si_4$	64–65	79
III	$C_{20}H_{34}O_7Si_6$	74.5–75.5	29
IV	$C_{60}H_{50}O_7Si_6$	231–232	4
V	$C_{60}H_{50}O_7Si_6$	234–236	7
VI	$C_{28}H_{32}O_6Si_5$	155–156	10
VII	$C_{40}H_{42}O_7Si_6$	113.5–115.5	28
VIII	$C_{16}H_{34}O_6Si_6$	102–104	5

[a] Elemental analyses (Si) in agreement with theoretical values were obtained and submitted for review.

Table III. Infrared Spectra of Cyclic Organopolysiloxanes

Band positions in microns[a]

I	Solid film.[b] 3.3(m), 3.4(m), 6.3(m), 6.4(w), 6.8(w), 6.9(m), 7.3(w), 7.8(m), 7.9(s) ($SiCH_3$), 8.3(w), 8.6(w), 8.8(m), 9.3(m), 9.6(w), 10.4(vs) (SiOSi in five-membered ring), 11.0(s), 11.7(m), 12.3(s), 12.4(m), 13.3(s) (*o*-substituted aromatic ring), 13.6(m), 13.8(m), 14.7(m)
II	Solid film.[b] 3.3(m), 3.4(w), 6.3(m), 6.7(w), 7.0(m) (SiC_6H_5), 8.0(m) ($SiCH_3$), 8.4(w), 8.9(s) and 9.0(s) [$Si(C_6H_5)_2$], 9.5(vs) (SiOSi), 9.8(s), 10.0(m), 11.7(w), 12.2(m), 12.6(m), 13.0(s), 13.5(m), 13.9(s), 14.4(s) (C_6H_5)
III	Mull. 6.3(w), 7.0(w) (SiC_6H_5), 7.9(s) ($SiCH_3$), 8.8(s) (SiC_6H_5), 9.3(vs) (SiOSi), 9.7(w), 10.0(w), 11.4(w), 11.8(m), 12.3(s), 13.4(w), 13.7(m), 13.8(sh), 14.3(m) (C_6H_5)
IV	Mull. 6.3(w), 7.0(m) (SiC_6H_5), 8.4(w), 8.8(sh) and 8.9(s) and 9.0(sh) (SiC_6H_5 and SiOSi), 9.2(s) and 9.3(s) (SiOSi), 9.8(m), 10.0(m), 13.5(m), 13.9(s), 14.4(s) (C_6H_5)
V	Mull. 6.3(m), 6.7(w), 7.0(m) (SiC_6H_5), 7.7(w), 7.9(w), 8.4(w), 8.75(s) (SiC_6H_5), 8.85(m) and 8.95(s) [$Si(C_6H_5)_2$], 9.4(w sh), 9.6(s), 9.7(w), 9.8(m), 9.9(vs) (SiOSi in six-membered ring), 10.0(s), 10.4(w), 13.0(w), 13.3(w), 13.6(sh), 13.7(m), 13.9(s), 14.4(s) (C_6H_5), 14.6(w), 14.7(w)
VI	Mull. 6.3(m), 6.7(w), 7.0(m) (SiC_6H_5), 7.7(w), 7.9(s) ($SiCH_3$), 8.4(w), 8.6(w), 8.9(s) and 9.0(s) [$Si(C_6H_5)_2$], 9.65(vs) (SiOSi in six-membered ring), 9.8(m), 10.0(m), 10.3(w), 11.4(sh), 11.7(m), 12.4(s), 12.9(w), 13.0(w), 13.5(m), 13.6(m), 13.9(m), 14.3(s) (C_6H_5), 14.7(m)
VII	Mull. 6.3(w), 7.0(m) (SiC_6H_5), 7.9(m) ($SiCH_3$), 8.4(sh), 8.6(sh), 8.7(sh), 8.9(s) and 9.0(s) [$Si(C_6H_5)_2$], 9.1(m) and 9.3–9.4(m) (SiOSi), 9.65(vs) (SiOSi in six-membered ring), 10.0(m), 10.4(w), 11.4(sh), 11.8(m), 12.3(s), 13.0(w), 13.5(m), 13.7(w), 13.9(m), 14.3(s) (C_6H_5)
VIII	Mull. 3.3(w), 6.4(w), 7.9(s) ($SiCH_3$), 8.8(m) (*p*-SiC_6H_4Si), 9.1(w sh), 9.7(s), 9.9(vs) (SiOSi in six-membered ring), 10.2(w sh), 11.4(w), 11.7(m), 12.3(s), 12.7(m), 13.3(m), 14.1(w)

[a] s, strong; m, medium; w, weak; sh, shoulder; v, very. [b] Deposited from trichloroethylene solution.

Table I. Starting Materials for Preparation of Organopolysiloxanes

Compound designation	Starting materials	
	Si–Cl compound	Si–OH compound
I	Dichlorodimethylsilane	Tetra-*o*-tolyldisilane-1,2-diol
II	1,2-Dichlorotetramethyldisilane	Tetraphenyldisiloxane-1,3-diol
III	1,3-Diphenyltetrachlorodisiloxane	Tetramethyldisiloxane-1,3-diol
IV[a]	1,3-Diphenyltetrachlorodisiloxane	Tetraphenyldisiloxane-1,3-diol
VI	2,2-Dichlorotetraphenylcyclotrisiloxane	Tetramethyldisiloxane-1,3-diol
VII	2,2-Dichlorotetramethylcyclotrisiloxane	Hexaphenyltrisiloxane-1,5-diol
VIII	1,4-Bis(dichloromethylsilyl)benzene	Tetramethyldisiloxane-1,3-diol

[a] Compound V was obtained as a by-product from the preparation of IV.

Discussion

All the compounds show one or more strong infrared bands between 9.1 and 10.4 μ owing to the asymmetric SiOSi stretching vibration (*4*). Compounds V–VIII show a strong SiOSi band in the 9.65–9.9 μ range characteristic of the strained, six-membered cyclotrisiloxane ring. In the two spiro compounds, VI and VII, the siloxane band is at the short-wavelength end of this range, in agreement with the band position reported previously (*6*) for a series of octaaryl spirosiloxanes.

Compounds III, IV, and VII, which contain cyclotetrasiloxane rings, show SiOSi bands in the range 9.1–9.4 μ, whereas compound II, with a seven-membered ring, shows the SiOSi band at 9.5 μ, between the band positions for six- and eight-membered rings. Compound II, when treated with KOH at 210°C rearranged to a polymer. Completely aromatic-substituted compounds of this type were unaffected under these conditions (*5*).

Compound I shows a strong SiOSi band at 10.4 μ. This band position is consistent with spectra of other five-membered, strained-ring siloxanes (*1–3*). Unlike the cyclotrisiloxanes, I is very resistant to base-catalyzed rearrangement. After 2 hr at 210°C in the presence of KOH, compound I was recovered unchanged. However, in the presence of H_2SO_4 at 140°C, rearrangement occurred rapidly to form a polymer. The basicity of I apparently is due to the decrease in pi overlap of the bent SiOSi bond in the highly strained five-membered ring.

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