TABLE II

OTHER p-PHENYLENEDISILANES

Compound	B.P., Mm.	M.P.	Yield, %	Analysis Calcd. C	Calcd. H	Calcd. Si	Found C	Found H	Found Si
p-$[C_6H_5Si(OC_2H_5)_2]_2C_6H_4$[a]	188–197 (0.30–0.07)	—	27.9	66.91	7.34	12.04	67.45	7.15	12.10
p-$[4\text{-}ClC_6H_4Si(OC_2H_5)_2]_2C_6H_4$	210–246 (0.25–0.8) 239–239 (1)	54–55[b]	26.5	58.30	6.02	10.49	58.14	5.82	10.35
p-$[4\text{-}(CH_3)_2NC_6H_4Si(OC_2H_5)_2]_2C_6H_4$	*ca.* 270 (0.1)	104–105[b]	43.5	65.17 N = 5.07	8.02	10.16	65.57 N = 5.09	7.83	10.56 10.16
p-$[4\text{-}CH_3OC_6H_4Si(OC_2H_5)_2]_2C_6H_4$	230–250 (0.2–0.6)	55–56[b]	43.9	63.84	7.27	10.67	63.52	7.21	10.68 10.74

[a] n_D^{25} 1.5345. [b] From anhydrous ethanol.

g.-atoms) of magnesium turnings, and the mixture was stirred at reflux for 7 hr., a negative Gilman Color Test I was obtained. After 500 ml. of heptane was added to the mixture, 400 ml. of the solvents were removed by distillation, and the salts were removed by filtration. When the product, containing 1 wt. % hydroquinone, was fractionally distilled at 3.3 mm. three fractions were obtained: A, b.p. 74–139°, 25 g.; B, b.p. 139–144°, 42 g.; n_D^{25} 1.4930, d_4^{25} 0.9605; C, b.p. 144–155°, 5 g., n_D^{25} 1.4958, d_4^{25} 0.9587. Fraction B represented a 9% yield of the product.

Anal. Calcd. for $C_{16}H_{26}O_2Si_2$: Si, 18.33; MR_D, 92.78. Found: Si, 18.75, 18.81; MR_D, 92.75.

p-Phenylenebis(diethoxyvinylsilane). Similarly, 5.3 g. (0.2 g.-atom) of magnesium, 23.6 g. (0.1 mole) of p-dibromobenzene, 38 g. (0.2 mole) of triethoxyvinylsilane, and 160 ml. of tetrahydrofuran gave 5.6 g. (15%) of p-phenylenebis(diethoxyvinylsilane), b.p. 125–129° at 0.15 mm.; n_D^{25} 1.4743; d_4^{25} 0.9852, MR_D calcd., 103.56, found, 104.63.

Other p-phenylene(disilanes). Compounds listed in Table II were prepared by the concomitant addition of mixtures of p-dibromobenzene and the appropriate dialkoxyarylchlorosilane in tetrahydrofuran to magnesium and were purified by fractional distillation.

p-Phenylenebis(diethoxyphenylsilane), prepared by treating a cooled, preformed Grignard reagent with chlorodiethoxyphenylsilane, was purified by method B. The product, 26.5 g. (28.5%), boiled at 160–170° at 0.1 mm.

When the reaction products were purified directly by filtration and distillation, the crude reaction mixtures were treated with an equal volume of heptane, and a large part of the tetrahydrofuran was removed by distillation. More complete precipitation of the magnesium halides was obtained, eliminating the necessity for several filtrations.

KANSAS CITY 10, MO.

[CONTRIBUTION FROM THE CORNING GLASS WORKS AND DOW CORNING CORP. MULTIPLE FELLOWSHIP AT MELLON INSTITUTE AND THE DOW CORNING CORP.]

Dehydration of 1,3-Bis(hydroxyalkyl)tetramethyldisiloxanes

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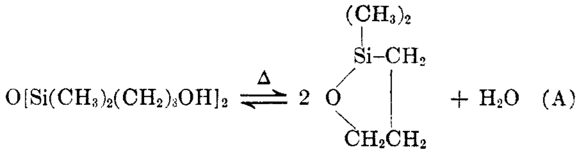
Three 1,3-bis(hydroxyalkyl)tetramethyldisiloxanes of the formula $[(CH_3)_2Si(CH_2)_nOH]_2O$ were prepared in which n = 1, 2, or 3. When subjected to dehydration, each reacted differently. When n = 1, dehydration in the presence of sulfuric acid caused the formation of ethers having the formula, $[-(CH_3)_2SiCH_2OCH_2(CH_3)_2SiO-]_{1,2,\ldots x}$. The cyclic compound in which x = 1 was isolated. In the presence of lime, a product was obtained having the formula, $[-(CH_3)_2SiCH_2O-]_{2,3,\ldots x}$. Under either alkaline or acidic conditions, when n = 2, ethylene, water, and polydimethylsiloxanes formed. When n = 3, a reactive cyclic compound was formed having the formula $\underline{(CH_3)_2Si(CH_2)_3O}$.

The synthesis of a series of three *sym*-(hydroxyalkyl)tetramethyldisiloxanes of the formula $[HO(CH_2)_n(CH_3)_2Si]_2O$ has recently been completed with n = 1, 2 or 3, and the dehydration of these three structures has been studied. Although these three compounds form an homologous series, each loses water in a different manner.

1,3-Bis(hydroxypropyl)tetramethyldisiloxane, (I), prepared by the methanolysis of 1,3-bis(acetoxypropyl)tetramethyldisiloxane[2] lost water on distillation to form a cyclic structure (II) according to equation A:



I II

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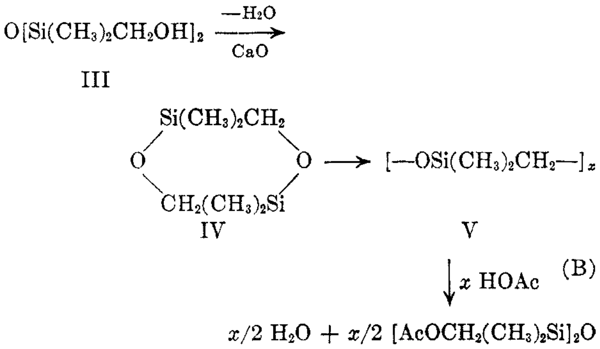
At room temperature the equilibrium is far to the left, but in the presence of a drying agent such as lime, 2,2-dimethyl-1-oxa-2-silacyclopentane (II) is obtained in good yield by distillation, b.p. 103°. In the absence of a drying agent, water and II codistilled and recombined on cooling to reform I.

The cyclic II polymerized readily at room temperature in the presence of minute amounts of water, presumably to form products of the formula $HO[(CH_3)_2Si(CH_2)_3O—]_nH$. In very carefully dried receivers, the polymer was of sufficiently high molecular weight so as to be somewhat rubbery. In the presence of the moisture in conventionally dried glassware, the polymers remained as extremely viscous liquids.

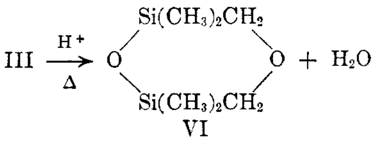
1,3-Bis(hydroxymethyl)tetramethyldisiloxane (III) was prepared by the method of Speier, *et al.*,[3] who noted that the compound was unstable even at room temperature and that heat caused the formation of water and a resinous mass which became quite fluid on exposure to water. Some years later, an opportunity arose to re-examine III somewhat more closely. Distillation from lime caused the formation of 40 to 60% of a volatile product, the properties of which changed rapidly at room temperature, much as described for II. The distillate reacted exothermally with very dilute hydrochloric acid or with glacial acetic acid. With the latter reagent 1,3-bis(acetoxymethyl)tetramethyldisiloxane formed. These phenomena are explained as being due to the changes summarized by Equations B.



(B)

Dehydration of III in the presence of a small amount of sulfuric acid caused the formation of unreactive products, part of which (15%) was obtained as the cyclic ether, 2,2,6,6-tetramethyl-1,4-dioxa-2,6-disilacyclohexane (VI), with the remainder as a high boiling liquid polymer. These products were quite unlike those obtained with lime. Concentrated hydrochloric acid or refluxing dilute sodium hydroxide had no effect upon these products.

Proof of structure for the cyclic compound was obtained as outlined below.



(C)

$$3\ (VI) + 2\ BF_3.Et_2O \longrightarrow$$
$$3\ \underset{VII}{F(CH_3)_2SiCH_2OCH_2Si(CH_3)_2F} + 2\ Et_2O + B_2O_3 \quad (D)^4$$

$$VII + 2\ NaOH \longrightarrow VI + 2\ NaF + H_2O \qquad (E)$$

The cyclic VI and the polymer both had the same H^1 NMR spectra. The polymer also formed the precipitate of boric oxide (Eq. D) characteristically obtained from siloxanes. From these data, along with analyses and general behavior, we feel the polymer is probably linear forms of VI with hydroxymethyl end groups.

The infrared spectrum of VI showed two strong absorption maxima, one at 10.15 μ and one at 9.4 μ believed to be characteristic of the siloxane and ether bonds in a strained six-membered ring.

1,3-Bis(hydroxyethyl)tetramethyldisiloxane (VIII) was prepared by the methanolysis of 1,3-bis(acetoxyethyl)tetramethyldisiloxane. As isolated from the methanol, VIII was of reasonably high purity without further purification. When completely neutral, VIII was much more resistant to dehydration than I or III and distilled in the expected boiling range without change.

Elevated temperatures caused cleavage in VIII at the silicon-carbon bond of the hydroxyethyl group in the presence of even trace amounts of acid or base. Only dimethylpolysiloxanes remained after the rapid evolution of ethylene had ceased. Acid catalysis promoted a fairly rapid reaction accurately described by Equation F. Potassium hydroxide was also an effective catalyst, but apparently promoted cleavage also by a second route leading to ethanol, according to Equation G. Freshly calcined lime was effective only at high temperatures and did not equal potassium hydroxide in promoting the formation of ethanol.

$$[(CH_3)_2SiCH_2CH_2OH]_2O \xrightarrow[OH^-]{H^+} 2\ [(CH_3)_2SiO]_x +$$
$$2\ CH_2{=}CH_2 + H_2O \quad (F)$$

$$\equiv SiCH_2CH_2OH \xrightarrow{OH^-} \equiv SiO^- + CH_3CH_2OH \qquad (G)$$

EXPERIMENTAL

1,3-Bis(hydroxypropyl)tetramethyldisiloxane (I) was prepared by methanolysis of 1,3-bis(acetoxypropyl)tetramethyldisiloxane[3] in an eight-fold excess of methanol with a small amount of potassium hydroxide as catalyst. After re-

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(2) J. L. Speier, J. A. Webster, and G. H. Barnes, *J. Am. Chem. Soc.*, **79**, 974 (1957).

(3) J. L. Speier, B. F. Daubert, and R. R. McGregor, *J. Am. Chem. Soc.*, **71**, 1474 (1949).

(4) L. H. Sommer and G. R. Ansul, *J. Am. Chem. Soc.*, **77**, 2482 (1955), have described this procedure for making fluorosilanes.

moval of methyl acetate by distillation, followed by removal of all volatile compounds, the product had the following properties[5]: n_D^{25}, 1.4472; d_D^{25}, 0.9531; R_D, 0.2804; calcd. R_D, 0.2817.

2,2-Dimethyl-1-oxa-2-silacyclopentane (II). Seventy-five grams of I was distilled at 50 mm. The vapor temperature varied erratically but remained much too low to be correct for the disiloxane (I). The distillate showed striations initially and became very viscous, but the striations disappeared on standing with no agitation. Soon after the distillation, the distillate had the physical constants of I. This behavior suggested that I decomposed on distillation and reformed in the receiver according to Equation A.

To verify this, a 40-g. sample of I was distilled through a small column packed with dehydrated alumina pellets. The alumina adsorbed much of the product as well as the water, so that only 10 g. of distillate was obtained. This distillate, however, was the heterocyclic II, b.p. 32° at 50 mm.; 103° at 740 mm.; n_D^{25}, 1.4415; d_4^{25}, 0.9178; R_D, 0.2880. Calcd. R_D, 0.2886. Infrared spectra showed no absorption maximum corresponding to hydroxyl.

Anal. Calcd. for $C_5H_{12}OSi$: Si, 24.2. Found: Si, 23.8.

The preparation was repeated more successfully by distillation of I from freshly calcined calcium oxide. Recovery was simplified by this technique and II was obtained in 93% yield, b.p. 102–103° at 740 mm.; n_D^{25}, 1.4409, d_D^{25}, 0.9180, R_D, 0.2876; % Si, 24.1.

The refractive index and density of this product changed rapidly after distillation. The indices reported above are those existing at the time the density was determined. The possibility of error cannot be disregarded. In 6 hr. the refractive index rose to 1.4503 in a tightly closed bottle. In 7 days it rose to 1.4535[6] as the product became a soft, gelatinous mass.

1,3-Bis(acetoxypropyl)tetramethyldisiloxane. A sample of II, 5.8 g., was mixed with 6.0 g. of glacial acetic acid and 0.36 g. of sulfuric acid at room temperature. After 24 hr. ether was added so that the mixture could be washed thoroughly with water. The product, free of ether and dry, was essentially pure diacetate ester of (I), $[Si(CH_3)_2(CH_2)_3OOCCH_3]_2O$,[7] n_D^{25}, 1.4323; d_4^{25}, 0.9747; R_D, 0.2663; sapon. equiv., 173.6. Calcd. sapon. equiv., 167.

2,2,5,5-Tetramethyl-1,4-dioxa-2,5-disilacyclohexane (IV). 1,3-Bis(hydroxymethyl)tetramethyldisiloxane (III) (150 g., 0.774 mole) was distilled at 100 mm. from calcined lime (45 g.). Three fractions were obtained: (a) 19.4 g.; b.p. 29–32° at 100 mm.; n_D^{25}, 1.3400; % Si, 3.50; % C, 36.9; % H, 12.6. This fraction was not identified. (b) 60.9 g. of sweet-smelling liquid; b.p. 95–104° at 100 mm. (c) A residue (115.7 g.) made up of the lime and an orange oil having n_D^{25}, 1.4259; d_4^{25}, 0.966.

Fraction (b) increased in viscosity and refractive index on standing in clean, tightly stoppered bottles under an atmosphere of nitrogen. The lowest index measured was n_D^{25} 1.4169, but after several days this value rose as high as 1.4290. The infrared spectrum of (b) was not that of the cyclic VI and showed no hydroxyl groups.

Anal. Calcd. for $[—(CH_3)_2SiCH_2O—]_x$: Si, 31.9; C, 40.9; H, 9.1. Found: Si, 32.0; C, 39.9; H, 9.6.

Boron trifluoride ethereate produced no precipitate of boric oxide from (b). At room temperature 2,4-dinitrobenzoyl chloride did not react with (b). With water, (b) reacted slowly. When a trace of acid was added, the reaction became noticeably exothermic.

To determine the stoichiometry of the reaction with water, 0.0001*N* hydrochloric acid was added to (b) in small portions and the change in viscosity of the solution was measured. From an original viscosity of 10.9 cs. at 25° (n_D^{25}, 1.4278) a smooth rise to a high of 29.4 cs. (n_D^{25}, 1.4309) was noted when 0.0108 mole of water per g. of sample had been added. Additional water caused the viscosity to decrease. Equation H requires 0.0114 mole of water per g. of sample for complete hydrolysis. The dehydration of III was repeated and the

$$[—(CH_3)_2SiCH_2O—]_x + H_2O \longrightarrow x\ HOSi(CH_3)_2CH_2OH \qquad (H)$$

distillate was taken in two fractions: (a) 10 g.; b.p. 79° at 55 mm.; n_D^{25}, 1.4150, and (b) 70 g.; b.p. 79° at 55 mm. Fraction (b) was added directly to 100 g. of glacial acetic acid. A slightly exothermic reaction took place. The solution was heated to 115° for 2 hr. and distilled to remove 60 g. (59.7 calcd.) of water and acetic acid. The residue weighed 107 g. Distillation of the residue gave 89 g. (81%) of 1,3-bis(acetoxymethyl)tetramethyldisiloxane, b.p. 69–70° at 0.1 mm.; n_D^{25}, 1.4200; d_4^{25}, 0.999; R_D, 0.2533; calcd. R_D, 0.2514.[8] The infrared spectrum was that of authentic 1,3-bis(acetoxymethyl)tetramethyldisiloxane.

2,2,6,6-Tetramethyl-1,4-dioxa-2,6-disilacyclohexane (VI). With 15 drops of sulfuric acid III (509 g., 2.61 moles) was heated to reflux with a small amount of benzene under a trap for water. Water (34. g., 73%) was collected at a temperature of 180° in the flask. Distillation under vacuum removed the benzene followed by VI (52.5 g., 11%), b.p. 57–57.5° at 24 mm.; n_D^{25}, 1.4244; d_D^{25}, 0.9293; R_D, 0.2748; calcd. 0.2753. About 13.5 g., 4% of the same material (n_D^{25}, 1.4255), was caught in a Dry Ice trap along with water as ice (8 g., 17%).

The residue boiling above 250° at 24 mm., weighed 369 g., 81% of theory calculated as $[—(CH_3)_2SiCH_2O—]_x$, n_D^{25}, 1.4344; d_D^{25}, 0.9495; R_D, 0.2745; calcd. 0.2753.

Anal. Calcd. for $[(C_3H_8OSi)]_x$:Si, 31.8; OH, 0.00. Found: Si, 31.6; OH, 1.9.

Bis(dimethylfluorosilylmethyl)ether (VII). A mixture of 26.5 g. (0.15 mole) of VI and 15.6 g. (0.11 mole) of boron trifluoride etherate was placed in a 100-ml. round bottom flask attached to a small still head and heated. At 71°, ether started to distill. The temperature was gradually raised over a period of 3 hr. to the boiling point of the etherate (125°), during which time 7 g. of ether was collected (7.4 g. calcd.). The mixture was cooled and 3.2 g. (0.02 mole) of hexamethyldisiloxane added to react with the excess boron trifluoride ethereate. The mixture was heated again, and a total of 28.7 g. of volatile material was collected up to a flask temperature of 160°. The residue, 7 g., included the expected solid boron oxide, 3.8 g. theory. Fractional distillation through a small Podbielniak column gave 2 g. of ether, b.p. 28–30°; intermediate 1 g.; and 19 g. of VII, b.p. 144° at 738 mm.; n_D^{25}, 1.3795; d_4^{25}, 0.9444; R_D, 0.2450. Calcd. R_D, 0.2441. Residue, 5 g., n_D^{25}, 1.3820; neut. equiv., 99.8; was also calculated as VII, making the total yield 80%.

Anal. Calcd. for $C_6H_{16}F_2OSi_2$: neut. eq., 99.2. Found, 97.2.

Inspection of the H^1 NMR spectrum of V substantiated the structure assigned.

Preparation of VI *from* VII. Approximately 50 ml. of 1*N* sodium hydroxide was added to a stirred solution of 5 g. of VII in 25 ml. of benzene so that the solution became basic to phenolphthalein. The benzene solution was washed, dried over anhydrous sodium sulfate, filtered, and distilled. A quantitative yield of VI was obtained: b.p. 152.6° at 738 mm.; n_D^{25}, 1.4245; d_4^{25}, 0.926; R_D, 0.2759. Calcd. R_D, 0.2753.

Anal. Calcd. for $C_6H_{16}O_2Si_2$: Si, 31.8. Found, 32.0.

β-Acetoxyethyldimethylchlorosilane. A mixture of vinyl acetate (172.2 g., 2.0 moles) and 2.4 ml. of 0.1*M* chloroplatinic acid in isopropanol (2.4 × 10^{-4} mole of platinum) was heated to 72° and dimethylchlorosilane (208.3 g., 2.2 moles) was added during 7 hr. The addition of the chlorosilane was

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(5) Ref. 2 cited n_D^{26}, 1.4470.

(6) W. H. Knoth, Jr., and R. V. Lindsay, Jr., *J. Am. Chem. Soc.*, **80**, 4106 (1958), have synthesized II from 3-chloropropoxydimethylchlorosilane and sodium. They report b.p. 95°, n_D^{26} 1.4170 for a freshly distilled sample. They also observed that the cyclic formed polymers spontaneously on standing.

(7) Ref. 3 reported n_D^{25}, 1.4322; d_4^{25}, 0.9732; R_D 0.2666.

(8) Ref. 3 reported b.p. 250° at 760mm.; n_D^{25}, 1.4215; d_4^{25}, 0.993.

controlled so as to keep the temperature of reflux between 60 and 75°. Continued heating of the total quantities of reactants resulted in a maximum temperature of 108°. β-Acetoxyethyldimethylchlorosilane, $(CH_3)_2SiClCH_2CH_2OOCCH_3$, was obtained in 65% yield. The following properties were observed: b.p. 108–109.5° at 50 mm.; n_{D}^{25}, 1.4301; d_4^{25}, 1.031; R_D, 0.2506. Calcd. R_D, 0.2505.

Anal. Calcd. for $C_6H_{14}ClO_2Si$: neut. equiv., 180.8; sapon. equiv., 90.4; Si, 15.5. Found: neut. equiv., 180.1; sapon. equiv., 89.8; Si, 15.3.

A fraction (b.p. 60–75° at 50 mm.) representing approximately 10% by weight of the total product was observed during distillation. This impure fraction may have contained the α-adduct.

1,3-Bis(acetoxyethyl)tetramethyldisiloxane was prepared by hydrolysis of β-acetoxyethyldimethylchlorosilane in ice water. The hydrolyzate was washed with water and dilute sodium bicarbonate solution and fractionally distilled at reduced pressure; yield 93%. The properties observed were: b.p. 166–166.5° at 18 mm.; n_{D}^{25}, 1.4288; d_4^{25}, 0.9886; R_D, 0.2607; Calcd. R_D, 0.2609.

Anal. Calcd. for $C_{12}H_{26}O_5Si_2$: sapon. equiv., 153.2. Found: sapon. equiv., 151.

1,3-Bis(hydroxyethyl)tetramethyldisiloxane (VIII). 1,3-Bis-(acetoxyethyl)tetramethyldisiloxane was dissolved in a 14-fold excess of methanol to which was added several drops of concd. hydrochloric acid. After several days, most of the methanol and methyl acetate were removed by distillation. The residue was freed of all volatile compounds by a sweep of dry nitrogen at 100 mm. pressure up to a temperature of 75°. A quantitative yield of clear, colorless, somewhat viscous VIII was obtained having these properties: n_{D}^{25}, 1.4432; d_4^{25}, 0.966; R_D, 0.2746. Calcd. R_D, 0.2745. The H^1NMR spectrum showed only β-product.

Distillation of neutral 1,3-bis(hydroxyethyl)tetramethyldisiloxane (VIII). In order to remove all traces of hydrochloric acid, 54 g. of VIII was dissolved in 35 ml. of benzene and washed with a mixture of 35 ml. of concd. sodium chloride solution and 25 ml. of saturated sodium bicarbonate solution. After a second washing with aqueous sodium chloride, the neutral organic solution was dried azeotropically, filtered to remove traces of inorganic salts, and rendered free of solvent. A final sweep with dry nitrogen at 70–80° and 100 m. pressure insured removal of the last traces of benzene; yield 50.3 g., n_{D}^{25}, 1.4438.

A small sample (4.8 g.) was flash distilled. At a pressure of 5 mm., distillation proceeded smoothly, and 2.0 g. of distillate (boiling range 151–159°; n_{D}^{25}, 1.4431) was collected before the temperature in the flask reached 200°. The residue, still clear and colorless, weighed 2.8 g.; n_{D}^{25}, 1.4475. Inspection of the H^1 NMR spectra of this distillate, and the residue showed all three samples to have identical curves. These data indicate that VIII when completely neutral may be distilled without change.

Cleavage of 1,3-bis(hydroxyethyl)tetramethyldisiloxane (VIII). a. *Slightly acidic with hydrogen chloride.* A sample of VIII containing a trace of hydrogen chloride decomposed when heated for distillation as above. No distillate was collected up to a temperature of 200° in the flask, and a loss in weight occurred equal to that calculated for complete cleavage of ethylene from the molecule (Equation F).

The experiment was repeated using 10.3 g. (0.046 mole) of VIII in a 50-ml. flask attached to a small condenser, a Dry Ice trap, and a gas collecting bottle in series. Evolution of gas commenced at 75° and a total of 1908 ml. (corr.), 92%, was collected up to a temperature of 220°, where the rate of evolution had essentially ceased. Most of the gas formed below 150°. The flask had lost 3.5 g. (theory for loss of ethylene and water, 3.4 g.) and contained 6.8 g. of a clear, colorless, viscous fluid: n_{D}^{25}, 1.4067; d_4^{25}, 0.972; R_D, 0.2531. Calcd. R_D, $[(CH_3)_2SiO]_x$, 0.2521.

Anal. Calcd. for $(C_2H_6OSi)]$: Si, 37.9. Found, 38.0. The trap contained 0.6 g. of ice (theory requires 0.8 g. water), n_{D}^{25}, 1.3421. The infrared spectrum of the gas was that of ethylene.

b. *Under alkaline conditions. Potassium hydroxide.* A mixture of 10 g. (0.045 mole) of VIII and 0.3 g. of crushed, dry potassium hydroxide was heated as in (a). The evolution of gas started at 80° and continued to a temperature of 218°.

Only 1260 ml. (corr.) of the calculated amount of 2016 ml. of gas was collected. Infrared analysis proved this to be ethylene. The cold trap contained 1.8 g., partly in the form of ice. Only 0.8 g. of water was expected. The contents of the cold trap smelled like ethanol, n_{D}^{25}, 1.3651. The colorless residue was dissolved in benzene and washed free of potassium hydroxide. It was then dried and devolatilized by a stream of nitrogen at 55° and 100 mm. It was essentially pure polydimethylsiloxane: n_{D}^{25}, 1.4037; d_{D}^{25}, 0.966; R_D, 0.2530 (calcd. R_D for $[(CH_3)_2SiO]_x$, 0.2521).

Anal. Calcd. for $(C_2H_6OSi)_n$: Si, 37.9. Found, 37.8.

From these data it appears likely that the cleavage in the presence of alkali formed both ethylene with water as well as ethanol as outlined in Equations F and G.

c. *With calcium oxide.* A mixture of 5 g. (0.0225 mole) of VIII and 2.5 g. of freshly calcined calcium oxide heated as above formed no gas until it reached 170°. The evolution of gas proceeded very slowly in this case. The experiment was continued up to a temperature of 218°, to obtain 780 ml. (corr.) of ethylene, 77% of theory according to Equation D. The trap contained only two drops of colorless liquid, n_{D}^{25}, 1.363, having the odor of ethanol. The residue weighed 6.5 g. The loss of 1.0 g. agrees with the 0.97 g. loss calculated for a 77% yield of ethylene, assuming that the lime would absorb the water also formed.

The residue was diluted with hexane, filtered free of the lime and worked up as in (a) and (b) above to give 3.0 g. of polysiloxane: n_{D}^{25}, 1.4175, d_4^{25}, 0.969; R_D, 0.2598. R_D calcd. for $[(CH_3)_2SiO]_x$, 0.2521.

The infrared spectrum of the gas was again that of ethylene.

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MIDLAND, MICH.