

1) indicates that each compound shows its own polarographic behavior irrespective of the pH of the medium (Fig. 2). The diffusion currents obtained for the first wave of azoxybenzene at the same concentrations (Tables II and III) change very little when studied alone or in the presence of hydrazobenzene and indicate that very little reaction occurs between the two compounds. The results for hydrazobenzene in general substantiate this conclusion. Complications, however, arise in comparisons with this compound if traces of oxygen are present, since hydrazobenzene is very easily oxidized to azobenzene. The presence of the latter puts part of the polarographic curve observed for hydrazobenzene above the zero line of the galvanometer (polarograms E and D in Fig. 2). The occurrence of such a reaction was found only at pH 2.0 (47%), 5.1 (19%), 6.2 (12%) and 11.1 (31%). The concentration of azoxybenzene in these buffers, as indicated by the diffusion currents, was decreased signifi-

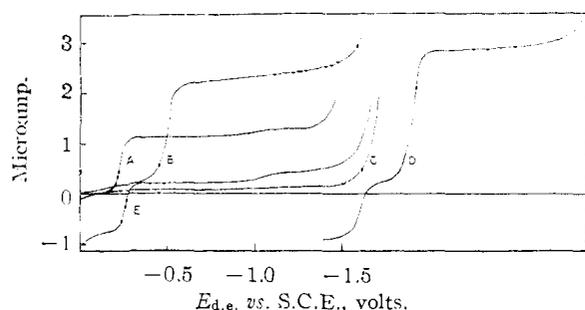


Fig. 2.—Polarograms for *cis*-azobenzene, azoxybenzene and hydrazobenzene in a buffer of pH 5.1: A, *cis*-azobenzene; B, azoxybenzene; E, hydrazobenzene; C, residual current; D, mixture of hydrazobenzene and azoxybenzene.

cantly only in the buffer of pH 11.1. The combined curve for hydrazobenzene and azobenzene under these circumstances was not materially increased and points to some other reason for the decrease in current observed.

The polarographic results obtained not only indicate that *cis*-azobenzene is a definite compound but also preclude the occurrence of a reaction between hydrazobenzene and azoxybenzene in the pH region of 2.0 to 11.1 to form *trans*- or *cis*-azobenzene.

The shift in half-wave potentials of hydrazobenzene in the presence of azoxybenzene illustrates the sensitivity of this system to the presence of maximum suppressors and other compounds in the solution.

The polarographic behavior of azoxybenzene in this work parallels to a great extent the results reported recently.⁷ Due to the more concentrated buffers employed in this work the half-wave potentials when plotted against pH in the range of 2 to 7.5 gave a line with a slope of 0.081 v. as against the 0.1 v. reported.⁷ In the pH range of 7.5 to 11 the half-wave potentials were not constant but showed a slight increase with an increase in pH .

In the present investigation a second wave was obtained at a pH 2.0 which was approximately equal to one half of the first wave in height and pointed to the further reduction of azoxybenzene to aniline. This wave appeared in the buffer of pH 3.0 but was complicated by the appearance of the adsorption wave which has been found previously with hydrazobenzene and *cis*- and *trans*-azobenzenes.⁵ The latter wave was found also in one of the acetate buffers.

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IOWA CITY, IOWA

[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY]

The Partial Hydrolysis of Methyltriethoxysilane

BY M. M. SPRUNG AND F. O. GUENTHER

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The action of three molar equivalents of water and catalytic amounts of acid on a benzene solution of methyltriethoxysilane gave small yields of distillable liquids. These are principally cyclic polysiloxanes having both ethoxyl and hydroxyl "end groups." In alcohol solution, under similar conditions, only polymeric "methylsilicone gel" was obtained. Using 50 or 25% of the calculated quantity of water, complex mixtures of linear and cyclic products resulted. In the former case, the two major products isolated are a monocyclic polysiloxane (1,3,5,7-tetraethoxy-1,3,5,7-tetramethylcyclotetrasiloxane) and a closely related bicyclic structure. In the latter case the products are mixtures of the linear partial hydrolysis products, $\text{EtO}[\text{CH}_3(\text{EtO})\text{SiO}]_n\text{Et}$, with minor amounts of the cyclic products, $[\text{CH}_3(\text{EtO})\text{SiO}]_n$, where n is 3 to 5. Under certain conditions, it is possible to isolate small amounts of sublimable solids having the composition, $(\text{CH}_3\text{SiO}_{1.5})_n$, where n is probably 6 and 8.

Introduction

Trifunctional silanes of general structure RSiX_3 , where R is an alkyl or aryl group and X is a functional group such as halogen, alkoxy or acyloxy, produce cross-linked polymeric structures when hydrolyzed. Among organic silicon products, these structures are at present least well understood.

The characterization of partial hydrolysis products of trifunctional silanes was undertaken some years ago by Andrianov.^{1,2} Several alkyltriethoxy-

silanes were hydrolyzed in alcohol with considerably less than equivalent quantities of water. The high-boiling, distillable products obtained were of the general type $\text{C}_2\text{H}_5\text{O}[\text{R}(\text{C}_2\text{H}_5\text{O})\text{SiO}]_n\text{C}_2\text{H}_5$, where R was ethyl, isobutyl, isoamyl and *n*-hexyl; and n , fixed roughly by the molar ratio of water to triethoxysilane, varied from 2 to 7. Andrianov and Breitman³ hydrolyzed diphenyldichlorosilane, phenyltrichlorosilane and equimolecular mixtures of the two by passing moist air into heated chlorobenzene solutions. Diphenyldichlorosilane and the mixture gave crystalline products which were not

(1) K. A. Andrianov, *J. Gen. Chem. (USSR)*, **8**, 1235 (1938); *C.A.*, **33**, 4193 (1939).

(2) K. A. Andrianov, *J. Gen. Chem. (USSR)*, **16**, 633 (1946); *C.A.*, **41**, 1206 (1947).

(3) K. A. Andrianov and B. M. Breitman, *J. Gen. Chem. (USSR)*, **17**, 1522 (1947); *C.A.*, **42**, 2239 (1948).

further characterized; and phenyltrichlorosilane gave a brittle solid of m.p. 103–107° and 19.81% silicon content.

Fletcher and Hunter⁴ isolated a series of linear polyethoxymethylsiloxanes formed by partial hydrolysis of methyltriethoxysilane. These products were similar to those described by Andrianov,³ and corresponded to the formula $C_2H_5O[CH_2(C_2H_5O)SiO]_n C_2H_5$, where n was in this case 2 to 5.

Tamborski and Post⁵ isolated the linear dimer, trimer and tetramer of the general formula $CH_3O[CH_2(CH_3O)SiO]_n CH_3$, as by-products during the preparation of methyltrimethoxysilane from methyltrichlorosilane and methanol.

A preliminary discussion of the kinetics of hydrolysis of trialkoxysilanes, methyltrialkoxysilanes and tetraalkoxysilanes has appeared recently.⁶

Linear polyalkoxysiloxanes having no organic substituents attached directly to silicon were prepared by Morgan, Olds and Rafferty⁷ from silicon tetrachloride and methylisobutyl carbinol or 2-ethylhexanol, by stepwise hydrolysis and condensation reactions. These products were, in general, easily distillable liquids, and several contained free silanol groups.

The isolation and identification of organic silanols has claimed the attention of numerous investigators; yet the total number of authentic members of this class can be confined to a one-page table.^{8,9} Several interesting examples of this relatively unstable class of compounds have been described more recently.¹⁰

The isolation of organic silanetriols has presented an even more formidable problem, since there was not an authentic sample on record until the isolation of phenylsilanetriol was announced very recently by Tyler.¹¹

Complex polymeric silanols certainly exist in the hydrolysis products of many halogeno or alkoxy-silanes, and in conventional silicone resins. For example, brittle polymers obtained by hydrolysis of vinyltrichlorosilane were reported recently by Wagner, *et al.*, to have as high as 9.5% silanol hydroxyl.¹² So far, no generally effective means have been found for the isolation and characterization of these complex intermediates.

Barry and Gilkey¹³ disclosed the very interesting low molecular weight, polycyclic hydrolysis products ($n-C_3H_7SiO_{1.5}$)₃, (C₂H₅SiO_{1.5})₃ and ($n-C_4H_9SiO_{1.5}$)₃ produced by heating initially oily hydrolysis

products of the corresponding alkyltrichlorosilane with powdered alkali.

Thus, only a few relatively simple cyclic products have been isolated from hydrolysis products of trifunctional silicon compounds, and polycyclic structures usually have not been characterized, although it is evident that many must exist. They might be expected to be related structurally to the high-temperature cracking products obtained by Scott¹⁴ from hydrolyzates of mixtures of methylchlorosilanes and silicon tetrachloride, described as methylpolycyclopolysiloxanes and methylspiro-polysiloxanes in the molecular weight range 300 to 600. The difficulty of isolating such complex cyclic intermediates without resorting to cracking or other destructive procedures is accentuated both by the paucity of existing data and by the known labile nature of structurally similar products. The study of such intermediates is not only interesting in itself, but is also likely to furnish useful information about the more highly polymeric products with which they are normally associated.

Hydrolysis in Benzene with the Theoretical Amount of Water.—Methyltriethoxysilane, dissolved in benzene, was treated first with the quantity of water calculated for formation of the hypothetical triol, MeSi(OH)₃, using HCl as catalyst. The initial reaction product was liquid except for a small amount of "methylsilicone gel." After filtering, it was distilled directly under vacuum until the residue gelled. Only a small fraction was distillable.

Percentage analyses of the distillate from several runs, gave the following averages: C, 25.2; H, 5.9; Si, 34.6; OH, 2.7; OC₂H₅, 16.8; mol. wt., 503. Infrared analyses confirmed the presence of appreciable amounts of silanol. These analytical data do not conform to a single empirical formula. However, since carbon-silicon bonds are not affected by the mild conditions involved, and since ethoxyl and hydroxyl must be present, in a sense, as "end groups," two empirical formulas can most reasonably be entertained: namely, C₁₀H₂₈Si₆O₁₁ and C₁₀H₂₈Si₆O₁₀. These differ significantly by a molecule of water. Unique structures cannot be assigned either species. However, reasonable structures are suggested if it is assumed that only 6- and 8-membered polysiloxane rings are present; these are, of course, the most frequently encountered ring sizes in polysiloxane chemistry. The composition C₁₀H₂₈Si₆O₁₁ could be represented by a structure containing two condensed cyclotetra-siloxane rings, as in Ia, or two adjoined cyclo-trisiloxane rings, as in IIa; and the composition C₁₀H₂₈Si₆O₁₀ could be represented most simply by III.¹⁵

Less likely isomeric structures also can be written, and possibly a mixture of several isomers is actually present, since there are numerous ways in which siloxane bond closures hypothetically can occur. The important point is, of course, the high degree of intramolecular "cross-linking" which must be assumed to account for the data. By reasonable

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(6) H. Reuther, *Z. anorg. anal. Chem.*, **272**, 122 (1953).

(7) C. R. Morgan, W. F. Olds and A. L. Rafferty, *THIS JOURNAL*, **73**, 5193 (1951).

(8) E. G. Rochow, "An Introduction to the Chemistry of the Silicones," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1951, p. 182.

(9) C. A. Burkhard, E. G. Rochow, N. S. Booth and J. Hartt, *Chem. Revs.*, **41**, 124 (1947).

(10) G. R. Lucas and R. W. Martin, *THIS JOURNAL*, **74**, 5225 (1952); K. C. Frisch, P. A. Goodwin and R. E. Scott, *ibid.*, **74**, 4584 (1952); L. A. Sommer and L. J. Tyler, *ibid.*, **76**, 1030 (1954); J. F. Hyde, *ibid.*, **75**, 2166 (1953); S. W. Kantor, *ibid.*, **75**, 2712 (1953).

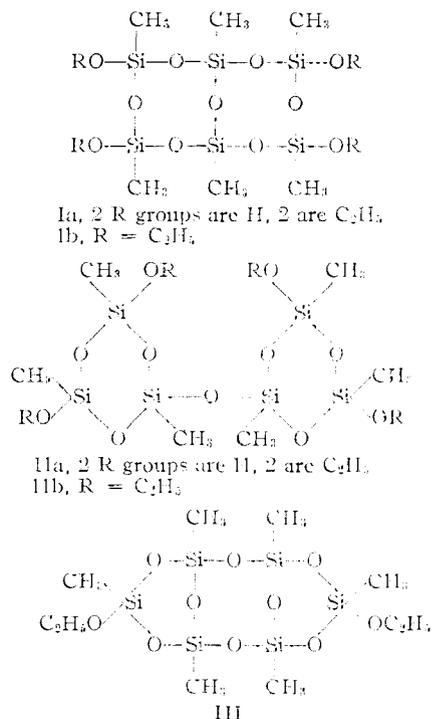
(11) L. J. Tyler, *ibid.*, **77**, 771 (1955).

(12) G. H. Wagner, D. L. Bailey, A. N. Pines, M. L. Dunham and D. B. McIntire, *Ind. Eng. Chem.*, **45**, 367 (1953).

(13) A. J. Barry and J. W. Gilkey, U.S. Patent 2,465,188, March 22, 1949.

(14) D. W. Scott, *THIS JOURNAL*, **68**, 356 (1946).

(15) Species having more or less than this number of -OH groups and (compensatingly) less or more -OC₂H₅ groups conceivably may be present in small amounts.



analogy, it is apparent that a multiplicity of such small rings also must be present in the high polymeric resinous structures formed under similar circumstances.

Increased yields of the volatile components could not be obtained by running larger batch hydrolyses. The longer times involved led instead to decreased yields. Hydrolysis could be accomplished without the acid catalyst, but this strategem resulted in the formation of more gel, and less distillable oil, rather than more.

Hydrolysis in Alcohol Solution.—Hydrolysis in ethanol solution with three molar equivalents of water gave insoluble methylsilicone gel as the sole product; no liquid or even resinous intermediates were obtained. With 1.5 molar equivalents of water, a good yield of distillable oil was obtained. However, this oil contained a highly complex mixture of products. Redistillation into eleven fractions was accomplished in an efficient fractionating column. Only one of these was a fraction of constant boiling point that conformed, analytically, to a single, reasonable composition. This product is similar to I or II, but contains four residual ethoxy groups instead of two, and has no free silanol groups. The empirical formula is (CH₃)₆Si₂O₂(OC₂H₅)₄. Reasonable structural assignments are 1,3,5,7,9,11-hexamethyl-1,3,7,9-tetraethoxy-5,11-epoxycyclohexasiloxane (Ib) or bis-1,3,5-trimethyl-3,5-diethoxycyclotrisiloxyl ether (IIb). Other less likely isomeric forms again are conceivable.¹⁶ A lower-boiling fraction of constant composition was apparently an azeotrope of 1,3,5-

(16) The infrared absorption spectrum of this fraction shows a relatively strong peak at 9.4 μ , generally associated with methylcyclo-tetrasiloxane rings. There is no absorption peak at 9.8-9.9 μ , where hexamethylcyclotrisiloxane absorbs strongly. Other features of the curve, however, were difficult to interpret. Therefore, on this basis alone, it is not possible to conclude that the structure is entirely that of Ib, exclusive of IIb.

trimethyl-1,1,3,5,5-pentaethoxytrisiloxane (previously described by Fletcher and Hunter)⁴ and 1,3,5,7-tetraethoxy-1,3,5,7-tetramethylcyclo-tetrasiloxane. Other fractions contained mixtures of homologous linear and cyclic polysiloxanes.

With 0.75 mole of water per mole of methyltriethoxysilane (this approximates the molar ratio of Fletcher and Hunter's alkaline hydrolysis) the yield was 100 g. of distillable oil from a 1-mole run. Redistillation into 59 cuts was effected, but only five of these represented the mid-points of well-defined "flats." Analyses indicated that only the lowest-boiling of the mid-cuts was pure; this was the linear dimer, 1,3-dimethyl-1,1,3,3-tetraethoxydisiloxane. The higher-boiling "flats" were mixtures of the straight-chain polymer-homologs having 3, 4, and 5 silicon atoms, with the corresponding polyethoxymethylcyclopolysiloxanes. Under alkaline hydrolysis conditions, Fletcher and Hunter obtained these particular partial hydrolysis products, free from cyclic by-products.

Total Hydrolysis Products.—The usual total hydrolysis product of a methyltrialkoxo or methyltrihalosilane, so-called "T-gel," has the empirical composition (CH₃SiO_{1.5})_n. It is a granular, insoluble, infusible, and generally intractable solid. Molecular weights have not been assigned to this type of product for obvious reasons.

The formation of T-gel frequently is observed during partial hydrolysis experiments. Sometimes small amounts of solids having the general appearance of T-gel are formed which, however, are found to be quite different on closer examination. Whereas T-gel can be heated above 250° in vacuum without appreciable physical change, slow sublimation could be accomplished with several of these solid by-products under similar conditions. The sublimate usually did not melt below 300°. In one experiment, however, the sublimable, high melting solid was accompanied by a very small amount of a lower melting (~210°) solid, from which it was separated by fractional sublimation. The two compounds had the same empirical composition.

It is believed that the chief component of these high-melting sublimate is the completely condensed, cage-like molecule having eight silicon atoms, with one methyl group attached to each silicon (IV). For lack of a simple systematic name, the designation "octamethyl T₈" is used for this molecule. It is quite likely that Scott's¹⁴ sublimable cracking product was, in fact, "octamethyl T₈." Barry and Gilkey¹³ suggested similar structures for their cyclic hydrolysis products.

The lower melting sublimable solid was recognized as a polymer homolog. It could differ from "methyl T₈" by any multiple of the unit C₂H₆Si₂O₃. That is, it could be "methyl T₆," "T₁₀," "T₁₂" . . . etc., but not "methyl T₄," which is presumably sterically impossible. The determined molecular weight is very close to that calculated for "hexamethyl T₆," V.

Re-examination of several distillates obtained from partial hydrolysis products of methyltriethoxysilane disclosed that very small amounts of "methyl T₆" frequently were present in solution, especially in the lower boiling fractions. By

appropriate treatment it again was possible to isolate small amounts of this completely condensed, cyclic product.

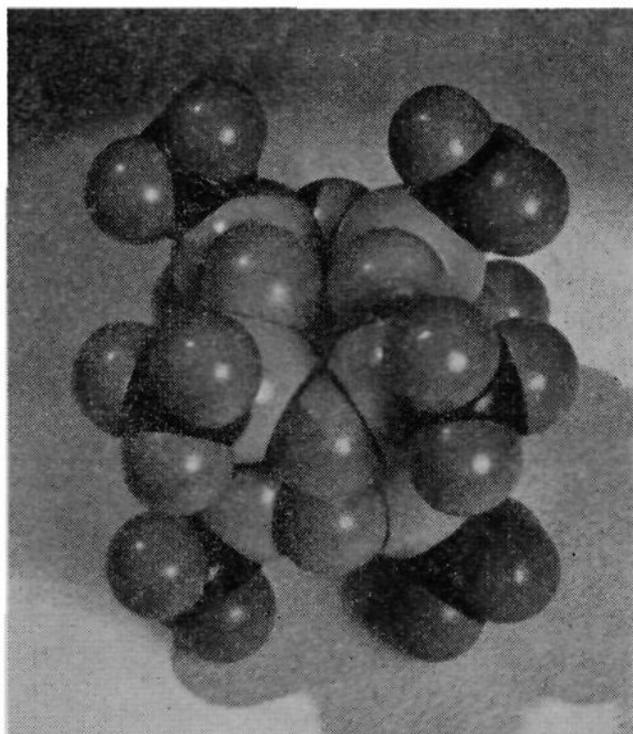
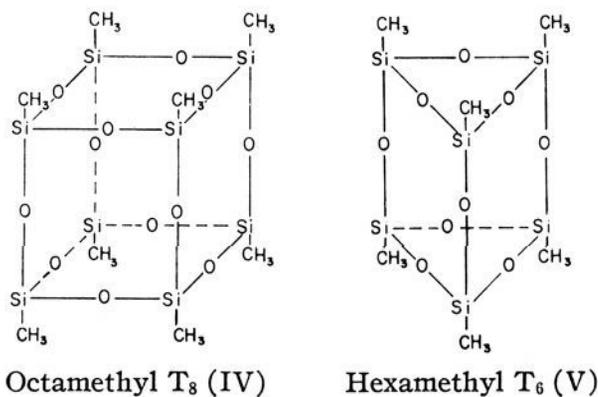


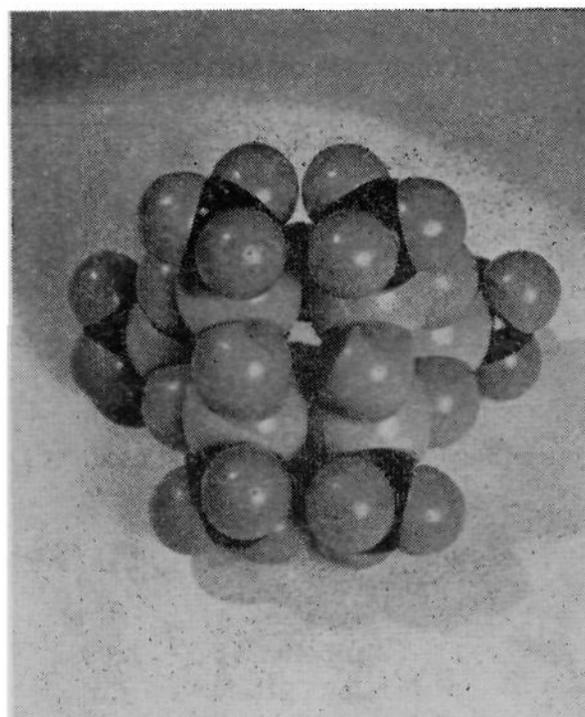
Fig. 1.—Photograph of "octamethyl T₈," constructed from Fisher-Hirschfelder models.

Figure 1 is a photograph of a Fisher-Hirschfelder model of "octamethyl T₈," in which the highly symmetrical, cage-like character of this molecule is illustrated. A model of "hexamethyl T₆" cannot be constructed satisfactorily. Figure 2 is a view of the nearly completed model, showing the spatial relation of the 6- and 8-membered rings and the resulting dissymmetry. Figure 2a shows the extent to which the model fails to allow closure of the last ring.

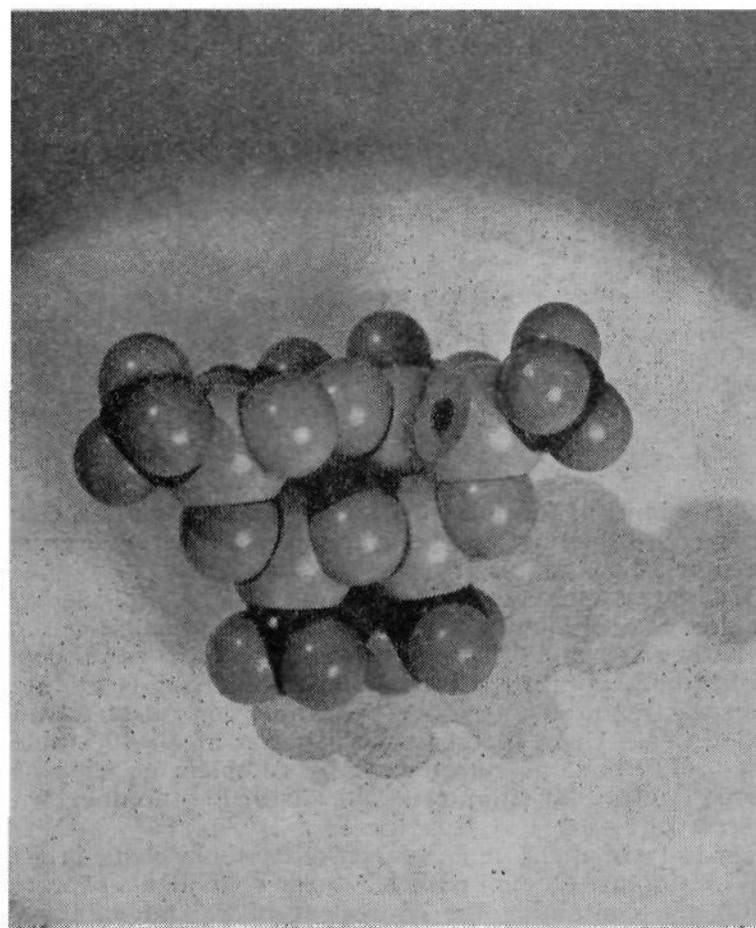


Experimental

Hydrolysis of Methyltriethoxysilane in Benzene with Three Molar Equivalents of Water.—One mole (178.4 g.) of methyltriethoxysilane (Dow-Corning Corp., 99% purity, b.p. 143.5°), dissolved in 500 ml. of C.P. benzene, was stirred rapidly, and the mixture heated to boiling (81°) under a reflux condenser. Three moles (54.0 g.) of water containing 0.2 ml. of 35.4% HCl was added in 15 minutes. The temperature dropped to 68.0°; then, as heating and stirring were continued, the equilibrium liquid temperature dropped to 64.6° in one hour. A modified Dean-Stark trap was attached, and 33 ml. of aqueous distillate was removed in one hour at 64.7–65.5°. This contained some ethanol and benzene and some of the HCl, in addition to water. The solvents then were distilled (500 g., b.p. to 81°, d. 0.85, *n*_D²⁰ 1.4640, containing approximately 134 g. of ethanol and an additional 11 ml. of aqueous distillate). The residue (106.5 g.) was filtered to remove suspended gel (1.0 g.), and subjected to vacuum distillation. After residual solvents were removed, 10.2 g. of oil boiling at 130–



a



b

Fig. 2.—a: photograph of model of "hexamethyl T₆," showing 6 and 8-membered polysiloxane rings. b: reverse side of "hexamethyl T₆," showing failure of model to allow complete ring closure.

140° at 3 mm. came over. The remainder (60.5 g.) then rapidly gelled. The final pot temperature was 200°.

A run with double the quantities of reagents yielded only 6.3 g. of oil, and resulted in 128.5 g. of gelled resin.

Table I summarizes the data obtained in a number of similar runs.

Anal. Calcd. for C₁₀H₃₀Si₆O₁₁: C, 24.4; H, 6.1; Si, 34.0; OH, 6.9; OC₂H₅, 18.2; mol. wt., 495.7. Calcd. for C₁₀H₂₈Si₆O₁₀: C, 25.3; H, 5.9; Si, 35.4; OH, 0.0; OC₂H₅, 18.9; mol. wt., 477.7. Found (oils from runs 1, 2, and 5): C, 25.9, 25.5, 25.0; H, 6.0, 5.9, 6.5; Si, 34.3, 33.2, 33.9, 35.7; OH, 2.5, 2.4; OC₂H₅, 17.6, 17.0; mol. wt., 478, 525. Calcd. for (C₁₆H₄₈Si₁₂O₂₀)_n: C, 21.4; H, 5.4; Si, 37.5; OC₂H₅, 10.0. Found (gel from run 2): C, 20.9; H, 5.6; Si, 37.6; OC₂H₅, 9.0.

TABLE I
 HYDROLYSIS OF METHYLTRIOXOSILANE IN BENZENE WITH THREE MOLES OF WATER

Run	MTS, ^a moles	Benzene ml.	Oil				Gel, g.	Resin, g.
			Wt., g.	Obsd. b. p. °C.	Mm.	<i>n</i> _D ²⁰		
1	0.5	500	2.0	135-155	15	...	11.2	16.5
2	1.0	500	10.2	130-140	3	1.4168	1.0	55.9
3	2.0	1000	6.3	120-130	1	1.4223	1.0	128.5
4	1.0	1000	11.5	135-145	1	1.4168	25.0	32.5
5 ^b	1.0	1000	7.0	125-135	1	1.4208	30.0	30.0
6 ^c	1.0	1000	5.2	130-135	3	1.4183	30.0	34.0
9	0.5	500	6.6	140-165	0.4	...	14.5	14.0

^a Methyltriethoxysilane. ^b No catalyst used. ^c Distillation through the Dean-Stark trap omitted.

 TABLE II
 HYDROLYSIS IN ETHANOL WITH 1.5 MOLAR EQUIVALENTS OF WATER

Fraction	Vol. ml.	B. p., °C. at 1 mm.	<i>n</i> _D ²⁰	Analyses, %			OC ₂ H ₅	Mol. wt.	
				C	H	Si			
2	1.5	107-108.5	1.3998	35.5	8.2	25.9	50.2	399	
				Calcd. for C ₁₂ H ₃₂ Si ₄ O ₈ (A)	34.7	7.7	26.9	43.4	416.5
				Calcd. for C ₁₃ H ₃₄ Si ₃ O ₇ (B)	40.5	8.8	21.8	58.3	386.4
				Calcd. for 85% (A) + 15% (B)	35.5	7.9	25.6	44.6	403.5
7	1.5	143-144	1.4060	29.9	6.9	29.6	...	531	
				Calcd. for C ₁₄ H ₃₈ Si ₅ O ₁₁	30.5	7.0	30.5	...	551.7

 TABLE III
 HYDROLYSIS IN ETHANOL WITH 0.75 MOLAR EQUIVALENT OF WATER

Fraction	°C.	B. p.	Mm.	<i>n</i> _D ²⁰	<i>d</i> ₄ ²⁰	Analyses, %		Mol. wt.
						C	H	
8, 9, 10	85.5		11	1.3911	0.959	43.3	9.7	267
						43.0	9.5	
21	91.5		10	1.3912	0.953	42.0	9.2	...
31, 32	119.5		7.5	1.3955	0.986	39.2	8.8	342
44	99		0.7	1.3972	1.004	38.4	9.1	362
49, 50	120		.5	1.3983	1.006	37.6	8.7	448
58	138		.5	1.4004	1.022	36.9	8.5	607

The empirical formula (C₁₆H₄₈Si₁₂O₂₀)_n represents a composition still having, on the average, one functional group per three silicon atoms.

Hydrolysis in Ethanol.—Hydrolysis of 1 mole of methyltriethoxysilane dissolved in 1000 ml. of ethanol with 3 moles of water and 0.2 ml. of concentrated HCl was accomplished in 20 minutes at the boiling point. Eighty minutes then was required to remove the major portion of solvent and water. Upon further concentration at 35-40° under 100 to 110 mm. pressure, virtually complete gelation occurred within 30 minutes. No distillable product was observed.

Hydrolysis of 0.5 mole of methyltriethoxysilane in 500 ml. of absolute ethanol with 1.5 molar equivalents of water (13.5 g.), containing the equivalent of 2.5 ml. of 0.5 N HCl, was accomplished in 1.5 hours at the reflux temperature. The crude distillate obtained after stripping solvents weighed 28.7 g., boiled over the range 81-208° at 0.3 to 0.8 mm., and had an ethoxyl content of 34.2%. The resin, which weighed 16.5 g. and had 26.9% ethoxyl, was a stiff, gummy, balsam-like, thermoplastic material.

Redistillation of the volatile oil into 11 fractions was accomplished under 1 mm. pressure in a precision column of the spinning-band type. Data concerning two fractions are given in Table II.

The major constituents of both fractions 2 and 7 are cyclic polysiloxanes. The compound C₁₂H₃₂Si₄O₈ is 1,3,5,7-tetraethoxy-1,3,5,7-tetramethylcyclotetrasiloxane. The sample isolated apparently contains a minor proportion of the congeneric straight-chain compound, 1,1,3,5,5-pentaethoxy-1,3,5-trimethyltrisiloxane. The compound C₁₄H₃₈Si₅O₁₁ can be represented most simply by structure Ib or IIb.

The acid-catalyzed hydrolysis of a mole of methyltriethoxysilane in absolute ethanol with 0.75 mole of water gave 100 g. of a limpid oil boiling between 48 and 190° at 3 mm. and 8.5 g. of a highly viscous, gummy residue. Careful refractionation of the oil from two runs into 59 fractions was

carried out in a spinning-band column under vacuum. The distillation curve is shown in Fig. 3. Table III summarizes the properties of six fractions which seemed to be uniform in composition, but which actually turned out to be mixtures in all but one case.

Fractions 8, 9, 10, 21 and presumably the intermediate fractions 11 to 20 are nearly pure 1,3-dimethyl-1,1,3,3-tetraethoxydisiloxane (calcd.: C, 42.6; H, 9.2; mol. wt., 282.4). The higher-boiling fractions listed in Table III contain from 65 to 80% of the higher linear polymer-homologs, C₂H₅O[CH₂(C₂H₅O)SiO]_nC₂H₅, where *n* is 3, 4, or 5. The cyclic component of each mixture is probably the corresponding cyclopolysiloxane, [CH₂(C₂H₅O)SiO]_n.

Co-hydrolysis of Methyltriethoxysilane and Methyltrichlorosilane.—Three-eighths mole of each component was dissolved in 750 ml. of benzene. The water (40.5 g.) was added in 20 minutes at 5-10°, after which the temperature was raised slowly to boiling (69°) and held there for an hour. Evolved HCl gas was trapped in an absorber containing aqueous caustic. After removal of solvents, 13.8 g. of gel was filtered off. On further heating under vacuum, the residual charge (34.2 g.) gelled.

In a second attempt, the benzene solution was washed repeatedly with sodium bicarbonate and separated from 7.8 g. of gel before distillation was begun. After stripping solvents, vacuum distillation resulted in 4.9 g. of volatile oil, b. p. 112-165° at 1 mm. The distillation residue (32.6 g.) was a brittle, thermoset resin.

This distillate was allowed to stand at room temperature for over a year, at which time it had gelled. The gel was then crushed in a mortar and transferred to a sublimation chamber held under about 0.4 mm. pressure. With the temperature held at 120-130°, 0.17 g. of solid sublimed and was collected on the cold finger. It was dissolved in benzene, the solution filtered and the filtrate evaporated to dryness in a nitrogen stream. This sublimate was soluble in benzene, ether, pentane and acetone. It was crystallized from 3-4 ml. of acetone, giving 0.07 g. of tiny, color-

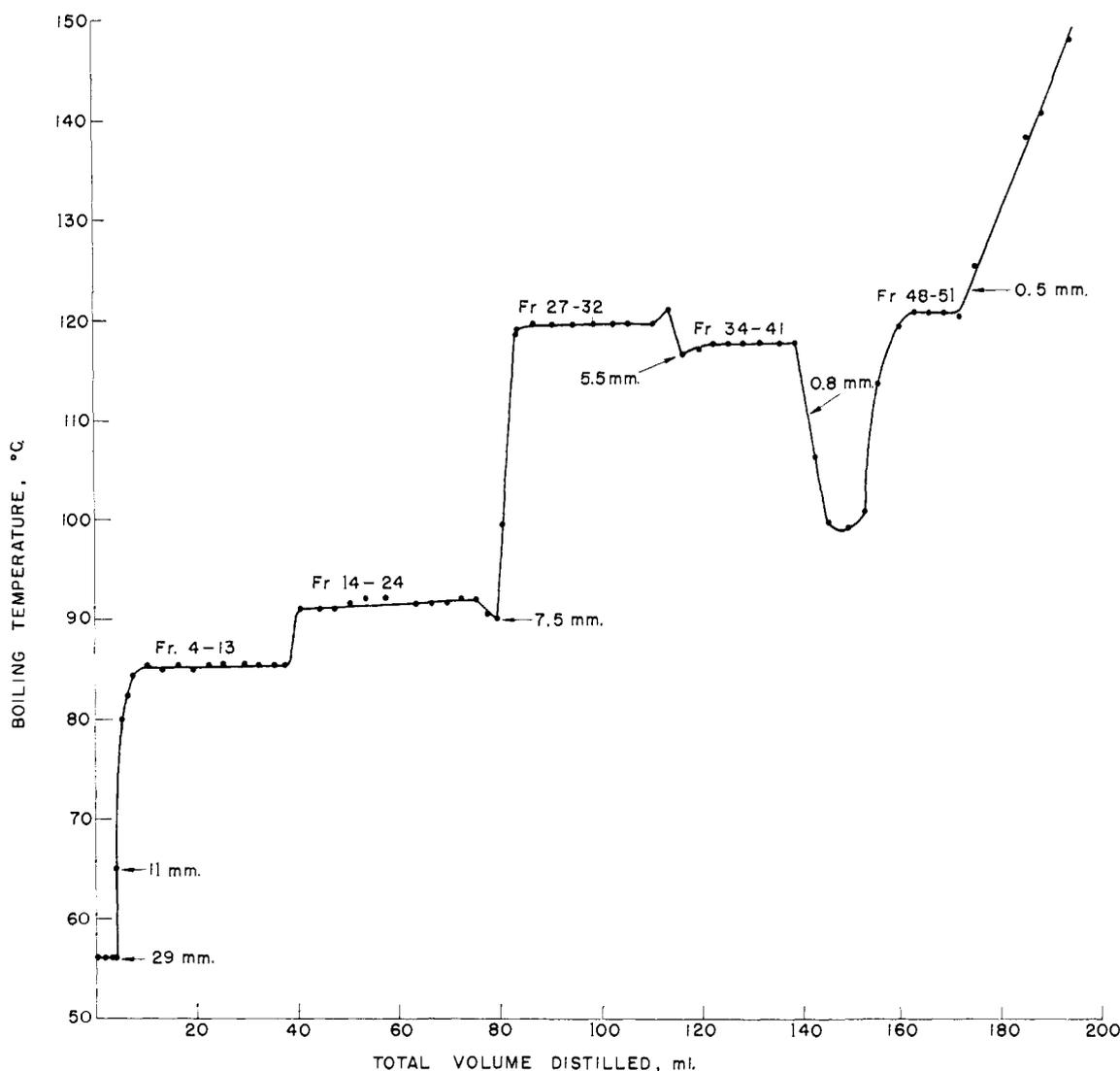


Fig. 3.—Distillation curve, product of hydrolysis of $\text{CH}_3\text{Si}(\text{OC}_2\text{H}_5)_3$ with 0.75 mole of H_2O .

less, rod-like crystals, m.p. 210–211° uncor. with preliminary softening at about 202°. Because of the limited sample available, further purification was impossible.

Anal. Calcd. for $(\text{CH}_3\text{SiO}_{1.5})_n$: C, 17.9; H, 4.5; Si, 41.8. Found: C, 16.9; H, 4.9; Si, 40.0.

The temperature in the sublimation chamber was now raised further. After 2 hours at 180–220° and 0.5 mm., 0.06 g. of a second sublimate was collected. This product did not melt below 330°, the limit to which the melting point apparatus could be raised.

A half mole each of methyltrichlorosilane and methyltriethoxysilane were then hydrolyzed in 500 ml. of benzene with 27.0 ml. of water (50% of the stoichiometric amount) in 13 minutes at 4–9°. The mixture was warmed slowly to the boiling point (65°) and maintained at 64.5–67.5° for 75 min. Insoluble "T-gel" weighing 8.6 g. was filtered off. The benzene solution was concentrated until the vapor temperature reached 86° and the liquid temperature was 113°. The viscous liquid (80.5 g.) gelled upon attempted distillation under vacuum, after only 0.73 g. of distillate was obtained. The gelled residue was transferred to a sublimation chamber, and, upon heating at 170–210° and 0.5–0.6 mm. for 2 hr., 1.2 g. of a semi-solid product was collected. This was combined with the earlier distillate, and the part that did not dissolve in hot acetone (0.25 g.) was resublimed by heating at 185–195° at 0.5 mm. pressure. This gave 0.20 g. of a colorless solid, m.p. >330°, insoluble in benzene, pentane, acetone, chloroform and carbon tetrachloride.

Based on its close resemblance to a better characterized product obtained upon hydrolysis of methyltri-*n*-butoxysilane, this high melting solid is presumably "octamethyl T_8 ."¹⁷

Anal. Calcd. for $(\text{CH}_3\text{SiO}_{1.5})_n$: C, 17.9; H, 4.5; Si, 41.8. Found: C, 18.3, 18.3; H, 4.4, 4.7; Si, 41.3.

Isolation of "Hexamethyl T_6 " from Hydrolysis Products of Methyltriethoxysilane.—The oily distillates from several hydrolysis experiments were observed to contain very small amounts of solids that settled out slowly upon standing. In a typical example, a distillate weighing 11.5 g., b.p. 120–143° at 1 mm., obtained upon hydrolysis of a mole of methyltriethoxysilane in benzene with 3.0 moles of water, was allowed to stand at room temperature for several weeks. A slightly sticky solid (0.63 g.) was filtered off. Upon heating at 86–120° at 0.7–0.9 mm. for 140 min. almost the entire sample sublimed. Upon crystallization from acetone, however, only 0.065 g. was recovered, m.p. 209–210°. The original oily distillate next was redistilled through a small Vigreux column ($\frac{1}{4}$ " \times 12"). An intermediate fraction (3.24 g., b.p. 113–121° at 0.9 mm.) slowly deposited more

(17) A larger amount of "methyl T_8 " was isolated from a hydrolysis product of methyltri-*n*-butoxysilane, and its molecular weight was ascertained from vapor density measurements. It is assumed to be identical with the sublimate described above on the basis of the sublimation temperature and rate, general appearance and analytical data.

solid (0.45 g.) upon standing in a freeze chest. After crystallization from acetone, there was thus obtained 0.08 g. more of purified solid, m.p. 209–210°.

Several small lots of this solid, obtained as described above, were combined, resublimed, and again crystallized from acetone, m.p. 210–211° (uncor.) in a sealed tube. The solubility and superficial appearance were the same as were described above.

Anal. Calcd. for $C_6H_{18}Si_6O_9$: C, 17.9; H, 4.5; mol. wt., 402.66. Found: C, 18.1; H, 4.5; mol. wt., 374.

Infrared spectrograms of "hexamethyl T_6 " and "octamethyl T_8 " also were obtained, both as Nujol mulls. Both curves confirmed the complete absence of silanol, and showed no features inconsistent with the assumed structures. Evidence was sought for the presence of six-membered (cyclotrisiloxane) rings in "hexamethyl T_6 ,"¹⁸ but an unequivocal answer to this question was not obtained.

Analyses.—For determination of alkoxy, samples of suitable weight to give 0.03 to 0.09 g. OR were refluxed in aqueous 50% potassium hydroxide. Solution usually was complete in 0.5 hour. Free alcohol was distilled directly

(18) C. W. Young, P. C. Servais, C. C. Currie and M. J. Hunter, *THIS JOURNAL*, **70**, 3758 (1948).

from the alkaline solution and was collected as a water-alcohol mixture. The alcohol was determined by measuring the percentage absorption at 475 $m\mu$ in 5-mm. cells of the colored complex formed with ammonium hexanitrate cerate.¹⁹

Silanol usually was determined by reaction with methylmagnesium iodide in dibutyl ether solution. In some cases, lithium aluminum hydride was used instead of the Grignard reagent. It is believed that the Grignard method, as employed for this work, is accurate to within 5 or, at most, 10%. Silanol values usually were checked qualitatively by infrared spectrograms.

The molecular weight determinations were carried out cryoscopically in benzene.

Acknowledgment.—We are indebted to E. M. Hadsell for precision distillations, to various members of the Analytical Chemistry Unit of this Laboratory for elementary analyses and molecular weight determinations, and to C. A. Hirt for the infrared absorption curves.

(19) F. R. Duke, *Ind. Eng. Chem., Anal. Ed.*, **17**, 572 (1945).

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[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY]

The Partial Hydrolysis of Ethyltriethoxysilane

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Appreciable yields of distillable liquids result from the acid-catalyzed reaction of three molar equivalents of water with ethyltriethoxysilane in benzene solution. The major components are polycyclic polysiloxanes that contain free silanol groups and residual ethoxyl groups. Lower yields are obtained in ethanol solution with an acid catalyst, and only gels are obtained with an alkaline catalyst. If smaller amounts of water are used, the major products are first less highly cyclic, and finally predominantly straight-chain polysiloxanes. Several ethoxy-substituted linear and monocyclic polysiloxanes were isolated. Co-hydrolysis of equimolar mixtures of ethyltriethoxysilane and ethyltrichlorosilane gives products similar in physical properties to those derived from the trialkoxysilane alone, but with much less residual ethoxyl and silanol. A sublimable high-melting solid obtained in small amounts was identified as octa-(ethylsilsesquioxane), $(C_2H_5SiO_{1.5})_8$. A lower melting solid frequently present in even smaller amounts was identified as hexa-(ethylsilsesquioxane), $(C_2H_5SiO_{1.4})_6$.

Introduction

The distillable liquids isolated in low yields when methyltriethoxysilane was treated with three molar equivalents of water in benzene solution are principally complex polycyclic polysiloxanes with ethoxyl and hydroxyl end-groups.¹ It was of considerable interest that complex silanols survived the rigorous catalytic and thermal treatment involved, including distillation at high still-pot temperatures.

Ethyltriethoxysilane is considerably more stable toward hydrolysis. Under the standard conditions previously described (*i.e.*, 1.5 moles of water allowed to react with 0.5 mole of the alkoxy silane, dissolved in 500 ml. of benzene and stirred rapidly at the boiling point¹), about 2.5 to 3 hours is required to reach the equilibrium conditions that are established. An acid or alkaline catalyst must be employed. Two high-boiling fractions were obtained: (1) b.p. 149–158° at 1 mm., n_D^{20} 1.4263; (2) b.p. 167–176° at 1 mm., n_D^{20} 1.4308. The residue was a heavy, balsam-like liquid, in contrast to the gelled resin obtained from methyltriethoxysilane. The results of ultimate analyses, ethoxyl, hydroxyl and molecular weight determinations are shown in Table I. Infrared spectra of the distillable fractions confirmed the presence

of Si-OH, Si-OC₂H₅ and Si-C₂H₅ bonds (peaks at 2.93, 7.73 and 7.99 μ). The two infrared curves were nearly indistinguishable.

TABLE I
HYDROLYSIS PRODUCTS OBTAINED WITH THREE MOLAR EQUIVALENTS OF WATER

	Fraction 1	Fraction 2	Residue
Mol wt. (in benzene)	540	574	1167, 1330
Carbon, %	33.9	33.1	31.8
Hydrogen, %	7.4	7.3	6.9
Silicon, %	29.2	29.9	31.2
—OC ₂ H ₅ , %	15.6	13.5	9.2
—OH, %	4.0	4.3 (av. of 6)	...

The close similarity of the analytical constants, and the trends from lower to higher molecular weight components, suggest that the individual components are very closely akin. The data for the lower boiling fraction conform closely to those required for a compound of the empirical composition $C_{14}H_{36}Si_5O_9$; *i.e.*, $(C_2H_5)_5Si_5O_6(OC_2H_5)_2(OH)$ (calcd.: mol. wt., 488.7; C, 34.4; H, 7.4; Si, 28.7; —OC₂H₅, 18.4; —OH, 3.5²). The analytical data for the higher boiling fraction do not lead

(2) Reasonable structural formulas would be 5,7-diethoxy-(3,9)-epoxy-1-hydroxy-1,3,5,7,9-pentaethylcyclopentasiloxane or 1,7-diethoxy-(3,9)-epoxy-5-hydroxy-1,3,5,7,9-pentaethylcyclopentasiloxane.

(1) M. M. Sprung and F. O. Guenther, *THIS JOURNAL*, **77**, 3990 (1955).