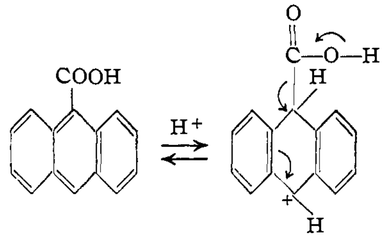
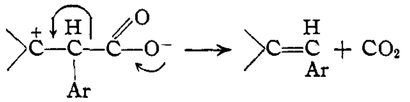
The acid-catalyzed decarboxylation of anthracene-9-carboxylic acid XVI,[1b] may also be treated by the β-carbonium ion mechanism. The relationship of the ionic form XVII to the relatively stable benzhydril carbonium ion suggests that the energy level of the transition-state would be correspondingly low, and leads to the prediction that the acid would be relatively susceptible to decarboxylation.


XVI XVII

The formation of olefins by loss of carbon dioxide in the Meerwein reaction can be treated similarly from the postulated intermediate $>\overset{+}{C}-CHArCOO^-$,[20] *viz.*



It is equally plausible to envisage the decarboxylation as proceeding through the acid $>\overset{+}{C}-CHArCOOH$, but in any event the postulation of a β-lactone intermediate[20] seems unnecessary.

In other experiments which will be described in a future communication it will be shown that the well-known decarboxylation of paraconic acids is probably acid-catalyzed and can be treated satisfactorily by the β-carbonium ion theory.

Acknowledgment.—We are deeply grateful to Dr. Gilbert Stork for inquiring discussions which afforded much of the stimulation for the initiation of this work, and to Drs. P. D. Bartlett and S. Winstein for helpful criticisms relating to the theoretical considerations.

Summary

It has been demonstrated that certain α,β-unsaturated acids of the cinnamic acid type will undergo a truly acid-catalyzed decarboxylation, and that the rates are dependent upon the concentration of catalyst. The relative rates of decarboxylation of variously substituted unsaturated acids have been examined, and the mechanism is discussed.

MADISON, WISCONSIN RECEIVED JANUARY 15, 1949

---

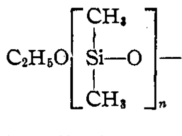
[20] Meerwein, Büchner and Emster, *J. prakt. Chem.*, **152**, 237 (1939).

[CONTRIBUTION FROM THE DOW CORNING CORPORATION]

Organosilicon Polymers. V. Linear Dimethylsiloxanes with Ethoxyl End-Groups

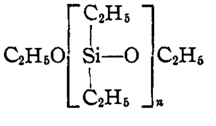
BY H. J. FLETCHER AND M. J. HUNTER

In recent papers[1,2,3] the preparation and properties of several series of low polymer dimethylsiloxanes have been described. This paper is a continuation of the work carried out by this group and will describe the series of open-chain dimethylsiloxanes[4] with ethoxyl end-groups represented by formula I where *n* may vary from 1 to a very large number.



$$C_2H_5O\left[\begin{array}{c}CH_3\\ |\\ Si-O\\ |\\ CH_3\end{array}\right]_n-C_2H_5 \qquad \text{I}$$

Andrianov[5] described a mechanism for the hydrolysis and condensation of dialkyldiethoxysilanes and has given data on the series represented by formula II where *n* varies from 1 to 10.



$$C_2H_5O\left[\begin{array}{c}C_2H_5\\ |\\ Si-O\\ |\\ C_2H_5\end{array}\right]_n C_2H_5 \qquad \text{II}$$

The methylpolysiloxanes of formula I may be prepared by partially hydrolyzing diethoxydimethylsilane.[6] The condensation products from this reaction will have a molecular weight dependent upon the quantity of water used.

When hydrolysis was carried out with 0.75 mole of water per mole of diethoxydimethylsilane a series of polymers was obtained which were separated on fractional distillation as progressively higher boiling plateaus. The first plateau, after the removal of the alcohol formed, was unreacted diethoxydimethylsilane, and subsequent plateaus were the succeeding members of the series. Analyses and physical properties of the redistilled compounds are given in Table I. Data on diethoxydimethylsilane are included for the sake of comparison.

---

[1] Hunter, Hyde, Warrick and Fletcher, THIS JOURNAL, **68**, 667 (1946).

[2] Patnode and Wilcock, *ibid.*, **68**, 358 (1946).

[3] Hunter, Warrick, Hyde and Currie, *ibid.*, **68**, 2284 (1946).

[4] U. S. Patent 2,415,389, February 4, 1947, by Hunter, Fletcher and Currie.

[5] Andrianov, *J. Gen. Chem., U. S. S. R.*, **16**, 633-638 (1946).

[6] (a) U. S. Patent 2,380,057, July 10, 1945, by McGregor and Warrick; (b) U. S. Patent 2,384,384, September 4, 1945, by McGregor and Warrick.

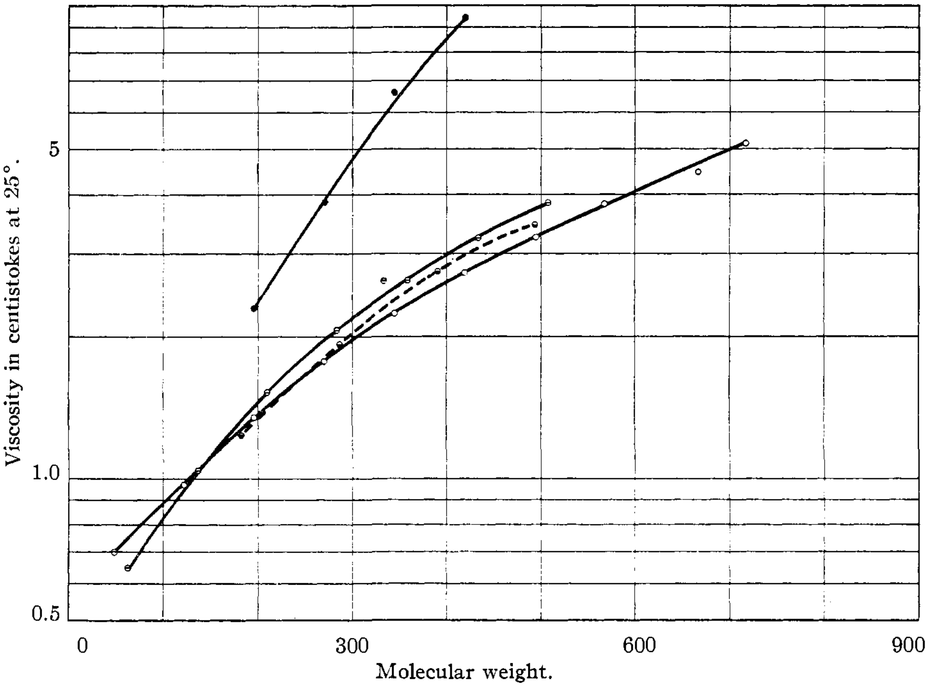


Fig. 1.—Relationship between viscosity and molecular weight for various siloxanes: ●, dimethylsiloxane cyclics; O, ethoxyl end-blocked dimethylsiloxanes; ⊖, trimethyl end-blocked dimethylsiloxanes; ◒, ethoxyl end-blocked ethoxymethylsiloxanes.

Since in several cases the boiling points of this series fall rather close to those of the cyclic dimethylsiloxanes,[1] it is not always possible to obtain complete separation by fractional distillation. In this case, however, the amount of cyclics present was small, and in the fractional distillation small inflections were noted for both the cyclic tetramer and pentamer. Any cyclic trimer which may have formed was subsequently polymerized under the conditions of reaction. The amount of cyclics formed is a measure of the probability of the termination of chain growth by cyclicization and it is significant that the amount of cyclic tetramer is greater than the amount of cyclic pentamer. There is an indication that a small amount of cyclic hexamer was present, but there is no evidence for higher cyclics. The proportion of cyclics as compared to the linear compounds is shown on Fig. 2.

Viscosities of this present series may be compared with those reported previously by noting the curves of Fig. 1. The viscosities of this series fall quite close to the corresponding molecular weight members of the trimethylsiloxy end-blocked series.[3]

The molecular refraction as calculated may be compared with the theoretical figure arrived at from a consideration of bond refractivities using the values given by Warrick.[7] These data are listed in Table I. It can be noted that the difference in molecular refraction between consecutive members of the series has a value of about 18.6, which is in close agreement with the refraction of a dimethyl siloxane unit as observed in the study of the cyclics.[1] This is further confirmation of the fact that this is a homologous series differing only by the number of dimethyl siloxane units in the molecule. If it is assumed that the interior of the molecule is made up entirely of dimethyl siloxane units, and the calculated group refraction for the number of repeated dimethyl siloxane units is subtracted from the molecular refraction of the linear molecule then the result should be the group refraction of the end-group. Using 18.64 for the group refraction of a dimethyl siloxane unit and carrying out the above operations gives an average value of 22.32 for the refraction of the end-group. This compares with a value of 22.42 calculated for diethyl ether using Denbigh's[8] bond refractions. This is further confirmation of structure.

The surface tension values were determined on the various members of the series and found to be low. From these data the parachors and parachor equivalents for silicon have been calculated, using the values obtained from Glasstone.[9] These results are found in Table I. The data are in good agreement with that from the cyclic and trimethylsiloxy end-blocked series.[1,3]

The distribution of low polymers obtained from the hydrolysis of diethoxydimethylsilane with

---

(7) Warrick, THIS JOURNAL, **68**, 2455 (1946).

(8) Denbigh, *Trans. Faraday Soc.*, **36**, 936 (1940).

(9) Glasstone, "Textbook of Physical Chemistry," D. Van Nostrand Co., New York, N. Y., 1940, p. 516.

TABLE I

PHYSICAL PROPERTIES AND ANALYSES OF OPEN-CHAIN DIMETHYL SILOXANE POLYMERS WITH ETHOXY DIMETHYLSILOXY END-GROUPS

Polymer size 1	Name 2	Formula 3	Boiling point, °C. 4	Melting point, °C. 5	Viscosity, cstks. at 25° 6
Monomer	Diethoxydimethylsilane	$C_2H_5O((CH_3)_2SiO)_1C_2H_5$	114	− 87	0.70
Dimer	1,3-Diethoxytetramethyldisiloxane	$C_2H_5O((CH_3)_2SiO)_2C_2H_5$	161	−134	0.97
Trimer	1,5-Diethoxyhexamethyltrisiloxane	$C_2H_5O((CH_3)_2SiO)_3C_2H_5$	196	−126	1.35
Tetramer	1,7-Diethoxyoctamethyltetrasiloxane	$C_2H_5O((CH_3)_2SiO)_4C_2H_5$	227	−124	1.78
Pentamer	1,9-Diethoxydecamethylpentasiloxane	$C_2H_5O((CH_3)_2SiO)_5C_2H_5$	253	−123	2.24
Hexamer	1,11-Diethoxydodecamethylhexasiloxane	$C_2H_5O((CH_3)_2SiO)_6C_2H_5$	274	−118	2.75
Heptamer	1,13-Diethoxytetradecamethylheptasiloxane	$C_2H_5O((CH_3)_2SiO)_7C_2H_5$	292	−112	3.28
Octamer	1,15-Diethoxyhexadecamethyloctasiloxane	$C_2H_5O((CH_3)_2SiO)_8C_2H_5$	311	−110	3.86
Nonamer	1,17-Diethoxyoctadecamethylnonasiloxane	$C_2H_5O((CH_3)_2SiO)_9C_2H_5$	...	− 53	4.50
Decamer	1,19-Diethoxyeicosamethyldecasiloxane	$C_2H_5O((CH_3)_2SiO)_{10}C_2H_5$	...	−100	5.17
Undecamer	1,21-Ethoxydocosamethylundecasiloxane	$C_2H_5O((CH_3)_2SiO)_{11}C_2H_5$	...	...	5.89

0.75 mole of water per mole of silicon is shown in Fig. 2. It is significant that the peak of the distribution curve is at the molecular size favored by the amount of water used. This, coupled with the fact that all molecular sizes were found, leads to the conclusion that the ethoxyl group has about the same stability toward hydrolysis regardless of the size molecule on which it occurs; however, in the larger molecules, probability and mobility factors may decrease the possibilities for reaction.

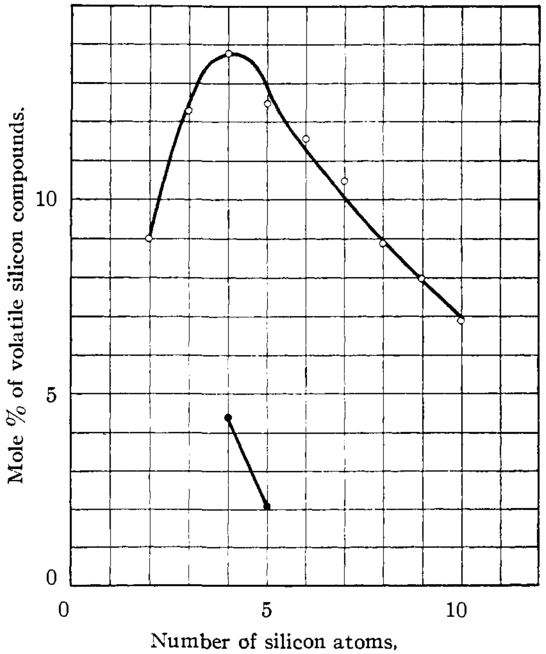


Fig. 2.—Distribution of low polymers from the hydrolysis of $(C_2H_5O)_2Si(CH_3)_2$ with 0.75 mole of water per mole of Si: O, ethoxyl end-blocked dimethyl siloxanes; ●, dimethylsiloxane cyclics.

The low-polymer linear dimethylsiloxanes described above comprise the lower range of an homologous series in which *n* may vary from one to a very large number. Fluids, in this series, with progressively higher molecular weights may be prepared in a controlled manner to cover all viscosity ranges from those just described up to completely non-volatile, highly viscous materials. This is accomplished by the hydrolysis and removal of additional ethoxyl end-blocking groups. Data as to the amount of water used to obtain a given viscosity fluid, the properties of the fluid before and after removing the lower polymers, and the nature of the low polymers removed are given in Table II, and shown in Fig. 3.

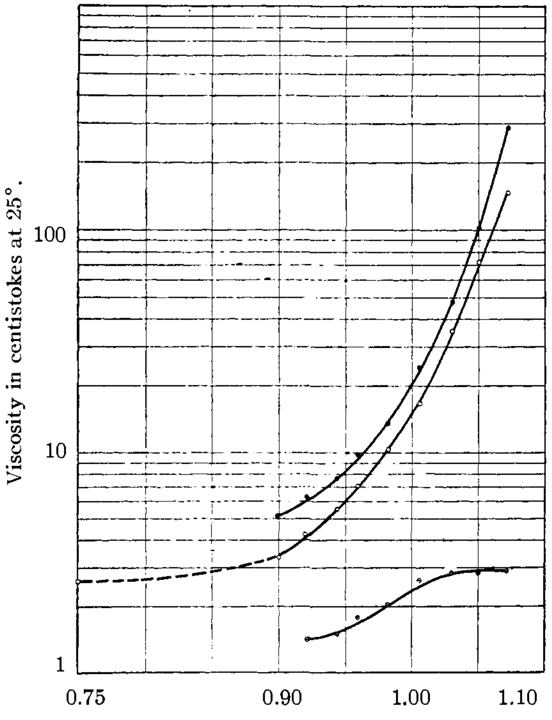


Fig. 3.—Relation between amount of water added to $(C_2H_5O)_2Si(CH_3)_2$ and viscosity of polymer obtained; O, polymer as formed; ●, high polymer portion; ⊖, low polymer portion.

TABLE I (*Continued*)

Density at 20° 7	Refractive index n^{20}_D 8	Molar refraction 9	Molar refraction calcd. from bond refractivities 10	Surface tension dynes/cm. 25° 11	Parachor 12	Parachor equiv. for Si 13	Molecular weight theory 14	% OC_2H_5 Found 15	% OC_2H_5 Theory 15	% Si Found 16	% Si Theory 16	% C Found 17	% C Theory 17
0.8395	1.3805	40.89	41.06	18.8	369	27.2	148.25	60.6	60.79	...	18.93	...	48.61
.8788	1.3880	59.61	59.70	18.7	532	27.3	222.38	39.5	40.53	25.71	25.24	43.32	43.21
.9024	1.3922	78.14	78.38	18.9	687	27.3	296.50	29.0	30.39	29.20	28.34	...	40.50
.9157	1.3950	96.87	96.98	19.1	850	28.3	370.63	23.8	24.32	30.66	30.28	38.81	38.89
.9207	1.3964	115.98	115.62	19.2	1020	30.3	444.76	19.8	20.26	31.50	31.55	38.48	37.80
.9317	1.3980	134.19	134.26	19.2	1170	28.3	518.89	17.2	17.37	...	32.45	...	37.03
.9364	1.3990	152.92	152.90	19.3	1330	28.3	593.02	15.1	15.20	33.25	33.12	36.50	36.45
.9409	1.3996	171.44	171.54	19.9	1500	29.6	667.14	13.4	13.51	...	33.65	...	36.00
.9442	1.4002	190.41	190.18	19.9	1660	29.5	741.27	12.1	12.16	33.76	34.07	35.24	35.64
.9471	1.4009	209.13	208.82	19.3	1810	28.4	814.40	10.8	11.05	34.40	34.41	...	35.35
.9495	1.4012		227.46				889.53	9.98	10.13	...	...	...	...

In the lower viscosity range, one can readily observe the effect of the ethoxyl end-group on the physical properties, refractive index and density, but in the higher polymers these properties vary only slightly with increasing molecular weight. The data on the low polymer portion show that the low polymers approach a constant composition that is made up principally of cyclics.

The fluids described here have been studied viscosimetrically by Barry[10] and the results are summarized in the paper by him.

TABLE II

PROGRESSIVE WATER ADDITION TO $(CH_3)_2Si(OC_2H_5)_2$

	Fluid as made				Low polymer portion			High polymer portion				
Moles H_2O per mole Si	Visc., cstks. at 25°	n^{20}_D	OC_2H_5, %	%	Visc.	n^{20}_D	OC_2H_5, %	Visc.	n^{20}_D	d^{20}	OC_2H_5, %	Mol. wt. from OC_2H_5
0.90	3.34	1.39 5	17.0	21.8	..	1.3899	31.1	5.15	1.3996	0.9444	12.06	747
.921	4.29	1.3989	13.8	18.1	1.42	1.3902	27.1	6.30	1.4003	.9476	10.76	837
.943	5.55	1.4001	11.4	15.7	1.53	1.3915	23.0	7.71	1.4010	.9518	8.95	1005
.959	7.13	1.4008	9.39	15.8	1.80	1.3940	16.9	9.9	1.4015	.9554	7.83	1150
.982	10.40	1.4017	7.87	13.3	2.05	1.3941	12.03	13.5	1.4024	.9597	6.13	1468
1.006	16.85	1.4028	4.77	16.7	2.64	1.3964	8.93	24.1	1.4035	.9655	3.55	2535
1.030	35.7	1.4037	2.57	11.9	2.85	1.3969	3.55	48.0	1.4046	.9695	2.30	3910
1.050	72.5	1.4043	1.40	11.7	2.85	1.3976	1.60	102	1.4049	.9720	1.06	8500
1.072	148.0	1.4045	0.77	11.5	2.94	1.3971	1.45	290	1.4050	.9736	0.42	21400

Experimental

Preparation of Low Polymer Mixtures.—In a three-neck 12-liter flask fitted with a reflux condenser, agitator, dropping funnel and thermometer, was placed 8051 g. (54.4 moles) of diethoxydimethylsilane. To this was slowly added, over a period of two hours, a solution containing 733 g. (40.7 moles) of water and 21.8 g. (0.544 mole) of sodium hydroxide. The temperature of the mixture rose spontaneously to 70° during the addition. Heat was then applied and the mixture was refluxed for one hour. The reflux condenser was replaced with a downward condenser, and alcohol was distilled off until a pot temperature of 100° was attained. Carbon dioxide gas was bubbled through the fluid for one and one-half hours, and the mixture was filtered through a Filter-Cel cake.

A series of 3 identical runs was made yielding fluids with the following viscosities at 25°: 2.53, 2.71 and 2.62 centistokes.

The filtrates were combined and placed in a 12-liter Claisen flask for strip distillation. The distillate was collected in successive 2-liter portions until a vapor temperature of 150° at 1 mm. was reached. The residue amounted to 28.2% of the load and had a viscosity of 7.4 centistokes at 25°.

Each of the above 2-liter cuts was then redistilled in a fractionating still with a four-foot by one-inch column packed with 0.25-inch single turn glass helices. This divided the material into well defined cuts. All the cuts of the same boiling range were then combined and redistilled through the same column. The final distribution of products is shown on Fig. 2.

Preparation of Intermediate Polymer Series.—In a three-neck 12-liter flask fitted with a reflux condenser, agitator, dropping funnel and thermometer, was placed 8051 g. (54.4 moles) of diethoxydimethylsilane. To this was slowly added, over a period of several hours, a solution containing 882 g. (0.9 mole per mole of silicon) of water, and 21.8 g. (0.544 mole) of sodium hydroxide. The temperature of the mixture rose spontaneously to 70° during the addition. Heat was then applied and the mixture was refluxed for one hour, then the reflux condenser was replaced with a downward condenser, and alcohol was distilled off until a pot temperature of 125° was attained. The total distillate amounted to 4416 g. (theory 4500 g.) and from this distillate 259 g. of silicones was separated by pouring the distillate into a large excess of water. A sample of the oily residue was taken, treated with carbon dioxide, and filtered.

The remainder of the oily residue (3967 g.) was heated to 125° and 17.5 g. (0.021 mole per mole of silicon) of water was added over a period of one and one-half hours. During the water addition 145 g. of volatiles was being removed through a downward condenser, and from this distillate 41 g. of silicones was separated. After the addition was complete the mass was held at 125° for ten minutes, then cooled to 91°. A sample was taken, treated with carbon dioxide, and filtered.

---

[10] Barry, *J. Applied Phys.*, **17**, 1020-1024 (1946).

This process was repeated until a total of 9 samples had been obtained. Portions of each sample were analyzed, and the remainder was subjected to vacuum distillation to remove the lower polymer portion. Data relating the amount of water added and the properties of the recovered fluid, before and after stripping, and the lower polymer portion removed, are given in Table II and in Fig. 3.

Summary

1. Open-chain dimethylsiloxane polymers containing from 2 to 11 silicon atoms with ethoxyl end-groups have been prepared and their physical properties reported.

2. The open-chain low polymers are shown to be the first members of an homologous series of polydimethylsiloxanes. The preparation and properties of higher members of this series are also described.

3. The comparative properties of open-chain and cyclic dimethylsiloxane structures are discussed.

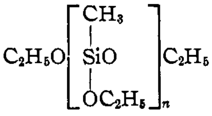
MIDLAND, MICHIGAN RECEIVED FEBRUARY 9, 1949

[CONTRIBUTION FROM THE DOW CORNING CORPORATION]

Organosilicon Polymers. VI. Linear Ethoxymethylsiloxanes

BY H. J. FLETCHER AND M. J. HUNTER

Linear polydimethyl siloxanes have been prepared with both inert[1] and active[2,1b] end-groups. This paper will describe a series of polymers with active groups in the chain as well as on the terminal groups as indicated by formula I.



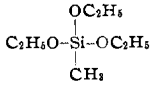
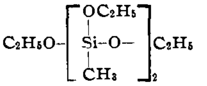
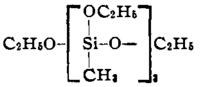
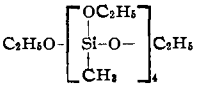
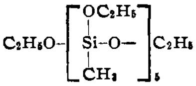
$$C_2H_5O\left[\overset{CH_3}{\underset{OC_2H_5}{SiO}}\right]_nC_2H_5 \qquad I$$

A somewhat similar series was prepared by Andrianov starting with certain other alkyltriethoxysilanes,[3] but the products were not accurately characterized. The method of preparation and characterization of these low polymers is similar to that used in the preparation of the ethoxy end-blocked polydimethylsiloxanes.[2]

Compounds of the above series, I, were prepared by partial hydrolysis of triethoxymethylsilane. On fractional distillation of the mixture it was separated into individual members of a series containing from 2 to 5 silicon atoms. Data on these materials are given in Table I. Properties of the triethoxymethylsilane are included for the purpose of comparison. The viscosities of this series are shown in Fig. 1 of the previous paper.[2]

TABLE I

PHYSICAL PROPERTIES AND ANALYSES OF OPEN-CHAIN ETHOXYMETHYL SILOXANE POLYMERS WITH DIETHOXYMETHYLSILOXY END-GROUPS

Polymer size		Monomer	Dimer	Trimer	Tetramer[a]	Pentamer[b]
Name		Triethoxymethyl silane	Tetraethoxy-1,2-dimethyldisiloxane	Pentaethoxy-1,2,3-trimethyltrisiloxane	Hexaethoxy-1,2,3,4-tetramethyltetrasiloxane	Heptaethoxy-1,2,3,4,5 pentamethylpentasiloxane
Formula		 $C_2H_5O-\overset{OC_2H_5}{\underset{CH_3}{Si}}-OC_2H_5$	 $C_2H_5O-\left[\overset{OC_2H_5}{\underset{CH_3}{Si}}-O-\right]_2C_2H_5$	 $C_2H_5O-\left[\overset{OC_2H_5}{\underset{CH_3}{Si}}-O-\right]_3C_2H_5$	 $C_2H_5O-\left[\overset{OC_2H_5}{\underset{CH_3}{Si}}-O-\right]_4C_2H_5$	 $C_2H_5O-\left[\overset{OC_2H_5}{\underset{CH_3}{Si}}-O-\right]_5C_2H_5$
Boiling point, °C. at mm		143 at 760	100 at 20	73 at 0.5	95 at 0.5	120 at 0.5
Viscosity, centistokes at 25°		....	1.24	1.92	2.77	3.48
Density at 25°		0.8923[c]	0.9441	0.9744	0.9935	1.0060
Refractive index at 25°		1.3835[c]	1.3895	1.3934	1.3955	1.3974
Molar refraction		46.59	70.83	94.77	118.56	142.53
Molar refraction calcd. from bond refractivities[4]		46.57	70.70	94.83	118.96	143.09
Molecular weight calcd.		178.27	282.43	386.58	490.74	594.89
Carbon, %	Theory	47.16	42.52	40.39	39.16	38.36
	Found	...	43.2	40.3	38.7	38.3
Silicon, %	Theory	15.74	19.87	21.78	22.87	23.58
	Found	...	19.7	22.1	23.3	23.9
OC_2H_5, %	Theory	75.83	63.82	58.28	55.09	53.02
	Found	...	60.8	54.5	50.5	49.8

[a] It is possible for this fraction to contain a certain amount of branched isomer. [b] This fraction may also contain portions of two branched isomers. [c] Determinations made at 20°.

Experimental

In a three-neck 12-liter flask fitted with a reflux condenser, agitator, thermometer and dropping funnel was

---

(1) (a) Hunter, Hyde, Warrick and Currie, THIS JOURNAL, **68**, 2284 (1946); (b) Patnode and Wilcock, *ibid.*, **68**, 358 (1946).

(2) Fletcher and Hunter, *ibid.*, **71**, 2918 (1949).

(3) Andrianov, *J. Gen. Chem.* (*USSR*), 8, 1255 (1938); **16**, 639 (1946).

(4) Warrick, THIS JOURNAL, **68**, 2455 (1946).