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.

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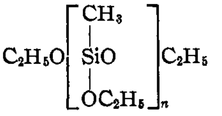
[CONTRIBUTION FROM THE DOW CORNING CORPORATION]

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.



$$C_2H_5O\left[\begin{array}{c}CH_3\\ |\\ SiO\\ |\\ OC_2H_5\end{array}\right]_n C_2H_5$$

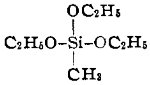
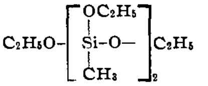
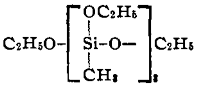
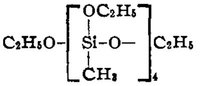
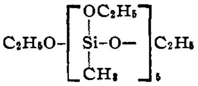
I

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		 $C_2H_5O\text{-}\overset{\overset{\large OC_2H_5}{\vert}}{\underset{\underset{\large CH_3}{\vert}}{Si}}\text{-}OC_2H_5$	 $C_2H_5O\text{-}\left[\begin{array}{c}OC_2H_5\\ \vert\\ Si\text{-}O\text{-}\\ \vert\\ CH_3\end{array}\right]_2 C_2H_5$	 $C_2H_5O\text{-}\left[\begin{array}{c}OC_2H_5\\ \vert\\ Si\text{-}O\text{-}\\ \vert\\ CH_3\end{array}\right]_3 C_2H_5$	 $C_2H_5O\text{-}\left[\begin{array}{c}OC_2H_5\\ \vert\\ Si\text{-}O\text{-}\\ \vert\\ CH_3\end{array}\right]_4 C_2H_5$	 $C_2H_5O\text{-}\left[\begin{array}{c}OC_2H_5\\ \vert\\ Si\text{-}O\text{-}\\ \vert\\ CH_3\end{array}\right]_5 C_2H_5$
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

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(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).

placed 5935 g. (33.3 moles) of triethoxymethylsilane and 1525 g. of ethyl alcohol, formula 2B. To this was slowly added, over a period of two hours, a solution of 13.3 g. (0.33 mole) of sodium hydroxide in 300 g. (16.7 moles) of water. During the addition, heat was evolved. After the addition was completed the mass was allowed to stand overnight. Then the reflux condenser was replaced with a downward condenser, heat was applied and volatiles (principally alcohol) were removed to a pot temperature of 100°. The distillate amounted to 2754 g. (theory, 3055 g.). The residue was blown with carbon dioxide as it cooled to room temperature. The mass was filtered to yield 4160 g. of fluid (theory, 4400 g.).

The filtrate was distilled in a fractionating still with a four-foot by one-inch column packed with 0.25-inch single-turn glass helices. This gave some unreacted triethoxymethylsilane and a series of progressively higher boiling plateaus which were characterized as shown in Table I.

Summary

1. Open-chain ethoxymethylsiloxane polymers with diethoxymethylsiloxy end-groups containing from 2 to 5 silicon atoms have been isolated and characterized.

MIDLAND, MICHIGAN RECEIVED FEBRUARY 9, 1949

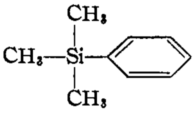
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

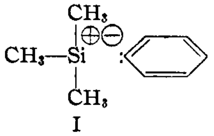
The Electrical Effect of the Trimethylsilyl Group

BY JOHN D. ROBERTS, ELIZABETH A. MCELHILL AND ROSE ARMSTRONG

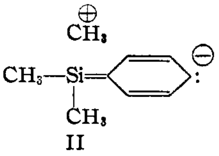
The magnitude and direction of the electrical effect of tetravalent silicon atoms in organosilicon compounds has not been definitely established. The difference in electronegativity between carbon and silicon on the Pauling scale[1] (+0.7 unit) suggests that silicon should be fairly strongly electron-releasing with respect to carbon. Nonetheless, the low reactivity of trimethylsilylmethyl chloride toward ionizing reagents has been interpreted as indicating that tetravalent silicon atoms are "electronically unsaturated" relative to tetravalent carbon.[2] The possibility exists that silicon atoms may tend to be more electron-attracting than otherwise anticipated since resonance forms involving more than four pairs of electrons in the outer atomic valence shells should be energetically more favorable for silicon than carbon. Actually, strong evidence has been obtained for important contributions of resonance forms involving pentacovalent silicon in the transition states of the displacement reactions of organosilicon halides.[3]

For trimethylsilylbenzene, three possible electrical effects due to the trimethylsilyl group can be represented by resonance forms I, II and III.

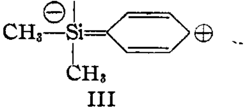




I



II



III

The electropositive nature of silicon relative to carbon is reflected by I while II represents hyperconjugative resonance of the type postulated for alkylbenzenes.[4] III depicts the tendency for silicon to expand its valence shell by the interaction of the 3*d* orbitals of silicon with the unsaturation electrons of the benzene ring. It is expected that I should be somewhat more important than the corresponding resonance forms involving the Si–C bonds of the methyl groups since the phenyl group is more electron-attracting than saturated alkyl groups.[4c]

In the present work a study was made of the dipole moments and relative reactivities of substituted trimethylsilylbenzenes to allow a decision to be made regarding the relative importance of resonance of types I, II and III involving silicon atoms attached to a benzene ring. The dipole moments of trimethylsilylbenzene, *p*-fluoro- and *p*-chlorotrimethylsilylbenzenes were determined in benzene solution at 25°. The results are given in Table I.

TABLE I

MOLAR REFRACTIONS, POLARIZATIONS AND DIPOLE MOMENTS

Substance	MR_D	P_∞ (25°)[a]	μ (Debye)
Trimethylsilylbenzene	49.87	53.9	0.44
p-Fluorotrimethylsilylbenzene	49.76	108.0	1.69[b]
p-Chlorotrimethylsilylbenzene	54.87	114.0	1.70[c]

[a] The data used for the calculation of P_∞ are given in Table II. [b] The average value of the moments obtained by five investigators for fluorobenzene in benzene solution near 25° is 1.44*D*. [c] The average value of the moments obtained by eighteen investigators for chlorobenzene in benzene solution near 25° is 1.57*D*.

Our value for the moment of trimethylsilylbenzene is in reasonable agreement with that obtained by Malatesta and Pizzotti[5a] (0.7*D*) for triethylsilylbenzene in carbon tetrachloride solutions. However, the interpretation by Malatesta[4b] of

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(1) Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940, pp. 58-70.

(2) Whitmore and Sommer, THIS JOURNAL, **68**, 483 (1946)

(3) Swain, Esteve and Jones, *ibid.*, **71**, 965 (1949).

(4) (a) Mulliken, Rieke and Brown, *ibid.*, **63**, 41 (1941); (b) Berliner and Bondhus, *ibid.*, **68**, 2355 (1946); **70**, 854 (1948); (c) Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944.

(5) (a) Malatesta and Pizzotti, *Gazz. chim. ital.*, **72**, 491 (1942); (b) **73**, 143 (1943).