Alkylalkoxypolysiloxanes. IX[1]. *Methylethoxypolysiloxanes Containing the Trimethylsiloxy Group*

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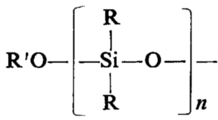
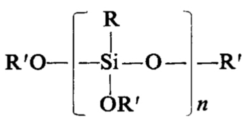
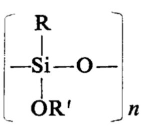
Many alkylalkoxypolysiloxanes have hitherto been synthesized. They have following general formulas, and each was prepared from only one kind of alkylchlorosilane.



$$R'O-\left[-\overset{\displaystyle R}{\underset{\displaystyle R}{Si}}-O-\right]_n-R' \qquad (A)$$



$$R'O-\left[-\overset{\displaystyle R}{\underset{\displaystyle OR'}{Si}}-O-\right]_n-R' \qquad (B)$$



$$\left[-\overset{\displaystyle R}{\underset{\displaystyle OR'}{Si}}-O-\right]_n \qquad (C)$$

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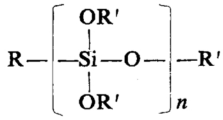
[1] Part VIII of this series, R. Okawara and M. Katayama, This Bulletin, 33, 659 (1960).



$$\mathrm{R}-\left[-\underset{\mathrm{OR'}}{\overset{\mathrm{OR'}}{\mathrm{Si}}}-\mathrm{O}-\right]_n-\mathrm{R'}$$

(D)

R, R′=alkyl group

In this paper, the syntheses and properties of the lower members of linear and branched methylethoxypolysiloxanes involving the trimethylsiloxy group $(CH_3)_3SiO$ are described.

Compounds which belong to series A to D have been synthesized by one of the following methods:

(1) partial hydrolysis of dialkyldialkoxysilane or alkyltrialkoxysilane[2]

(2) sodium hydrogen carbonate treatment of partially alcoholyzed alkylchlorosilanes[3]

(3) thermal condensation between Si-OR and Si-Cl[4]

(4) hydrolysis of partially alcoholyzed alkylchlorosilanes in wet pyridine[5].

Method 4 is different from 1 in that the former takes into account the difference in reactivity toward water between the Si-Cl and the Si-OC_2H_5 bonds. It appears that the ethoxy groups reacted quite randomly with H_2O to decrease the yield in method 1, especially when two kinds of methylethoxysilane were used. Therefore, method 1 was not examined. Also the results of some experiments showed that methods 2 and 3 were not conveniently applicable to the preparation. In consequence, method 4 was adopted. Partially ethanolyzed silicon tetrachloride, methyltrichlorosilane and dimethyldichlorosilane were mixed separately with trimethylchlorosilane and cohydrolyzed in wet pyridine in benzene containing the calculated amount of water. The products of hydrolysis were fractionally distilled. The details of the reactions are summarized in Table I. The desired products were obtained in moderate yield. This method is based on the difference of reactivity towards water between the Si-Cl and Si-OC_2H_5 bonds. As the Si-OC_2H_5 bond is also known to hydrolyze rapidly, particularly in an acidic medium, a slightly basic medium of wet pyridine in benzene was used. The properties of the compounds obtained by the fractionation through a highly efficient Stedman column are given in Table II.

The infrared spectra of these compounds give additional information about the characteristic vibrations of the ethoxy group and the methyl group attached to the silicon atom. Infrared spectra of some types of methylethoxypolysiloxanes have been reported[6]. The spectra obtained for the compounds studied here are similar to those of the methylethoxypolysiloxanes cited above in the region 1300 to 3500 cm^{-1}. The spectra in the region 700 to 1300 cm^{-1} are presented on Fig. 1. Frequencies and assignments are shown in Table III.

A sharp band near 1250 cm^{-1} is known to be characteristic of the symmetric deformation of the methyl groups attached directly to a silicon atom. The spectra in Fig. 1 show that, except in $(CH_3)_3SiOSi(CH_3)_2OC_2H_5$, this band is a doublet. The compounds $[(CH_3)_3SiO]_3SiCH_3$ and $[(CH_3)_3SiO]_4Si$ have been reported[7] to show a doublet in the same region.

Wright et al.[7] reported that the characteristic bands of the unit $(CH_3)_3SiO$ lie at 754~756 cm^{-1} and 841 cm^{-1}, that of $(CH_3)_2SiO$ at 800~814 cm^{-1} and that of CH_3SiO at 800 cm^{-1}. Table III shows that the same bands are observed in the spectra of our compounds containing these particular groups, except that the 800 cm^{-1} band of the $(CH_3)_2SiO$ unit is split into a doublet.

A band near 960 cm^{-1} is connected with the C–C stretching vibration of the C_2H_5O group, and those in the region 1000 to 1150 cm^{-1} are related to Si–O–Si and Si–O–C skeletal vibrations. Of the latter, the band near 1100 cm^{-1} decreases in intensity with the substitution of ethoxy groups by trimethylsiloxy groups. The C–O bond is believed to contribute greatly to this absorption band. A similar tendency in intensity is seen for the bands near 780 cm^{-1} and 1160 cm^{-1}.

Experimental

Starting Materials. — Trimethylchlorosilane (I), dimethyldichlorosilane and methyltrichlorosilane were supplied by the Shin-etsu Chem. Ind. Co. Silicon tetrachloride was obtained by the reaction of silicon with chlorine. Those chlorosilanes were partially alcoholyzed with ethanol below 5°C in a three-necked flask with an efficient stirrer, a reflux condenser and a dropping funnel. Then the mixture was warmed to 50°C to complete the reaction and it was fractionally distilled through a Stedman column of about 30 theoretical plates. Boiling points and chlorine content are shown in Table I. The experimental value for the chlorine content of triethoxychlorosilane was considerably less than the calculated value. This is thought to be due to contamination by tetraethoxysilane which has a boiling point close to that of triethoxychlorosilane. This mixture (VII) was used for the source of triethoxychlorosilane without further purification.

Sodium Hydrogen Carbonate Treatment of the Mixture of I and II.—To the refluxing mixture of

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2) H. J. Fletcher and M. J. Hunter, *J. Am. Chem. Soc.*, **71**, 2919, 2922 (1949).

3) R. Okawara et al., This Bulletin, **28**, 360, 364, 367 (1955).

4) R. Okawara et al., ibid., **27**, 428, 582 (1954).

5) R. Okawara et al., ibid., **31**, 22 (1958); **33**, 659 (1960).

6) R. Okawara, ibid., **31**, 154 (1958).

7) N. Wright and M. J. Hunter, *J. Am. Chem. Soc.*, **69**, 803 (1947).

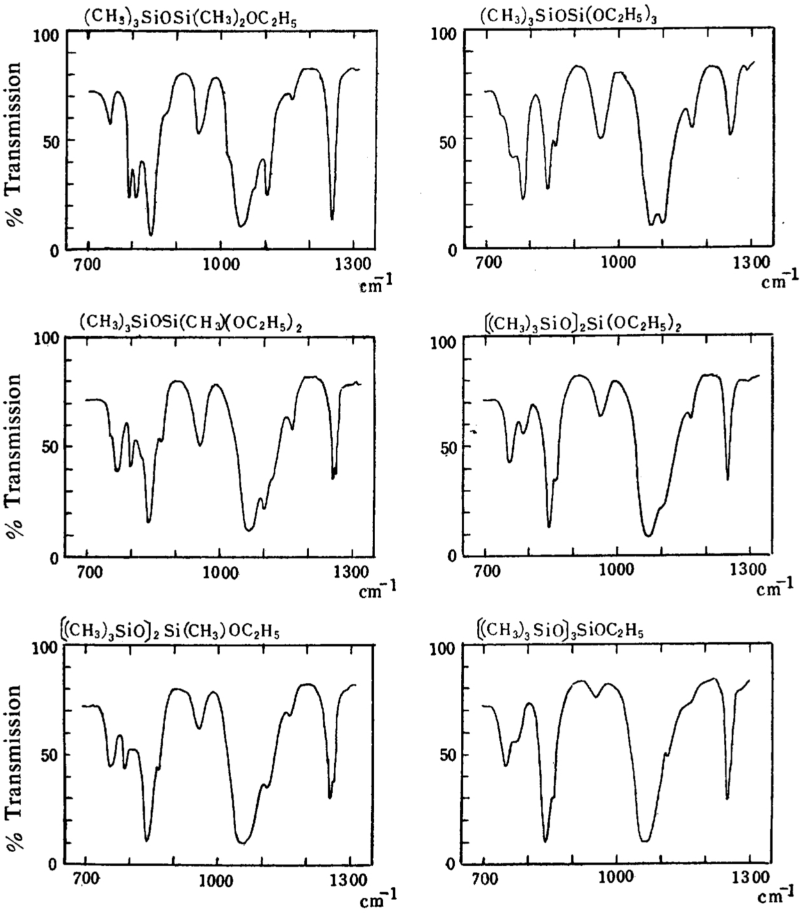

Fig. 1. Infrared spectra of methylethoxypolysiloxanes containing the trimethylsiloxy group.

I (21.8 g., 0.2 mol.) and II (27.8 g., 0.2 mol.), sodium hydrogen carbonate (16.8 g., 0.2 mol.) was added in portions. A reaction occurred violently with the evolution of hydrogen chloride and carbon dioxide. After completion of the reaction, the mixture (20 g.) was fractionally distilled. No plateau was found corresponding to $(CH_3)_3SiOSi(CH_3)_2$-OC_2H_5. It was thought from the distillation curve that the product was a complex mixture of methylethoxysilanes and -polysiloxanes.

Attempts to Condense I and Tetraethoxysilane Thermally.—A mixture of I (11 g., 0.1 mol.) and tetraethoxysilane (52 g., 0.25 mol.) was refluxed at 124°C for 20 hr., but no reaction occurred. The starting materials were recovered by the fractional distillation of the reaction mixture.

A mixture of I (22 g., 0.2 mol.) and tetraethoxysilane (21 g., 0.1 mol.) was passed through an electrically-heated quartz tube of 40 cm. length and 5 cm. diameter at 300°C for 4.5 hr. The condensate (40 g.) was fractionally distilled. Unreacted tetraethoxysilane was obtained, along with hexaethoxydisiloxane, which could be produced from the partial hydrolysis of tetraethoxysilane by a small amount of water remaining in the reaction tube or formed by oxidation of the ethoxy groups. Between the plateaus of these two compounds, a small plateau having a high refractive index (n_D^{20} 1.3862. reported[8] for $(C_2H_5O)_4Si$: n_D^{20} 1.3837) was found. The thermal condensation : $Si\text{-}Cl + C_2H_5O\text{-}Si \rightarrow Si\text{-}O\text{-}Si + C_2H_5Cl$ might have occurred in this experiment, but the yield was too low to apply this method to the synthesis.

Hydrolysis of Chlorosilane Mixture in Wet Pyridine.—The details of each experiment are given in Table I.

The typical operation was as follows. The hydrolyzing mixture consisting of benzene and the calculated amount of pyridine and water was placed in a three-necked flask with an efficient stirrer, a reflux condenser and a dropping funnel. The mixture of I and II to VII was added to the hydrolyzing mixture which was cooled with an ice-bath. The rate of addition was controlled, so that the white smoke of the chlorosilane-pyridine adduct would not be evolved from the top of the reflux condenser. After addition, the mixture was stirred for 1 hr. at room temperature. Whenever

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[8] D. F. Peppard et al., ibid., 68, 77 (1946).

TABLE I. HYDROLYSIS OF CHLOROSILANE MIXTURE IN WET PYRIDINE

Exp. No	Chlorosilane mixture		Benzene as diluent ml.	Yield of condensate (% theory)	Main product $R=(CH_3)_3SiO$	Yield g.
	$(CH_3)_3SiCl$ g. (mol.)	Ethoxychlorosilane g. (mol.)				
1	43.6 (0.4)	II* 55.5 (0.4)	100	46 (60)	$RSi(CH_3)_2(OC_2H_5)$	14
2	65.4 (0.6)	III 47.7 (0.3)	100	63 (79)	$R_2Si(CH_3)(OC_2H_5)$	26
3	43.6 (0.4)	III 63.6 (0.4)	80	47 (64)	$R_2Si(CH_3)(OC_2H_5)$	15
4	27.3 (0.25)	IV 53.4 (0.25)	100	35 (66)	$RSi(CH_3)(OC_2H_5)_2$	18
5	59.9 (0.55)	V 29.9 (0.17)	50	30 (52)	$R_3Si(OC_2H_5)$	9
6	54.4 (0.5)	VI 47.3 (0.25)	100	57 (69)	$R_2Si(OC_2H_5)_2$	31
7	19.0 (0.17)	VII 50.0 (—)	25	38 (—)	$RSi(OC_2H_5)_3$	20

* II $(CH_3)_2Si(OC_2H_5)Cl$ b. p. 95°C, Calcd. for II: Cl, 25.6. Found: Cl, 25.9%.
III $CH_3Si(OC_2H_5)Cl_2$ b. p. 100°C, Calcd. for III: Cl, 44.6. Found: Cl, 44.1%.
IV $CH_3Si(OC_2H_5)_2Cl$ b. p. 126°C, Calcd. for IV: Cl, 19.9. Found: Cl, 20.2%.
V $Si(OC_2H_5)Cl_3$ b. p. 102°C, Calcd. for V: Cl, 59.2. Found: Cl, 58.2%.
VI $Si(OC_2H_5)_2Cl_2$ b. p. 136°C, Calcd. for VI: Cl, 37.6. Found: Cl, 38.0%.
VII A mixture of $Si(OC_2H_5)_3Cl$ with $Si(OC_2H_5)_4$ b. p. 156°C, Calcd. for $Si(OC_2H_5)_3Cl$: Cl, 17.5. Found: Cl, 10.3%.

TABLE II. METHYLETHOXYPOLYSILOXANES
$R=(CH_3)_3SiO$

Methylethoxy-polysiloxanes	B. p. °C/mmHg	Refractive index n_D^{20}	Density d_D^{20}	Molar refr. Found (Calcd.)*	% Si Found (Calcd.)
$RSi(CH_3)_2(OC_2H_5)$	129.6/760	1.3844	0.8324	54.08 (54.31)	29.5 (29.20)
$RSi(CH_3)(OC_2H_5)_2$	154.9/760	1.3870	0.8766	59.72 (59.70)	25.5 (25.26)
$RSi(OC_2H_5)_3$	177.3/760	1.3868	0.9110	65.13 (65.09)	22.1 (22.25)
$R_2Si(CH_3)(OC_2H_5)$	170.0/760	1.3880	0.8623	72.95 (72.95)	31.9 (31.62)
$R_2Si(OC_2H_5)_2$	182.8/760	1.3880	0.8915	78.50 (78.34)	29.2 (28.41)
$R_3Si(OC_2H_5)$	194.5/760	1.3888	0.8803	91.48 (91.59)	33.2 (32.98)

* Calculated from bond refractivities by E. L. Warrick, *J. Am. Chem. Soc.*, **68**, 2455 (1946).

TABLE III. INFRARED SPECTRA OF TRIMETHYLSILOXYETHOXYSILOXANES: POSITIONS OF BANDS (IN cm^{-1})
$R=(CH_3)_3SiO$

$RSi(CH_3)_2$-OC_2H_5	$RSi(CH_3)$-$(OC_2H_5)_2$	$R_2Si(CH_3)$-OC_2H_5	$RSi(OC_2H_5)_3$	$R_2Si(OC_2H_5)_2$	$R_3Si(OC_2H_5)$	Assignment
749	751	757	757	753	751	$(CH_3)_3SiO_{1/2}$
	768		783	786	771	
791 809	798	788				$(CH_3)_2SiO$, $CH_3SiO_{3/2}$
842	841	841	840	842	842	$(CH_3)_3SiO_{1/2}$
875	867	867	856	859	860	
950	956	956	961	959	955	C-C str.
1022						
1054	1067	1061	1073	1067	1065	SiOSi
1082	1100	1112	1098	1098	1114	
1106	1117					
1162	1164	1162	1164	1164	1163	
1255	1254	1254	1252	1252	1251	$CH_3(-Si)$
	1263	1261	1260	1260	1259	

the chlorosilane odor still remained, several drops of wet pyridine were added. The mixture was washed with cold water, and then dried with sodium sulfate. Benzene was removed by distillation, followed by a fractionation through a Stedman type column of about 50 theoretical plates.

Determination of Silicon Content.—It is known that when methylpolysiloxanes containing the trimethylsiloxy group are decomposed by the action of concentrated sulfuric acid, volatile decomposition products are evolved. Therefore this method cannot be applied to the determination of silicon content in these compounds. In this study, about 0.5 g. of the sample was decomposed by sodium peroxide in a Paar bomb.

Infrared Spectra.—A Hilger H800 spectrometer with a sodium chloride prism was used. Spectra were taken in carbon disulfide solution in the region 700 to 1400 cm^{-1} and in carbon tetrachloride solution in the region 1300 to 3500 cm^{-1}. The concentrations were 3% in both cases.

Summary

(1) Methylethoxypolysiloxanes containing the trimethylsiloxy group have been prepared.

(2) The infrared spectra of these compounds are discussed.

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