Alkylalkoxypolysiloxanes. VIII.[1] *Lower Members of Cyclic Methyl- and Ethyl-isopropoxypolysiloxanes*

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Cyclic trisiloxane, the first member of the cyclic polysiloxanes, has been known. While there were found stable compounds such as dialkyl cyclotrisiloxanes and $(C_2H_5Si(OC_2H_5)O)_3$[2], a group of unstable compounds was also known. Spontaneous changes of physical constants were reported with those unstable cyclotrisiloxanes; $((CH_3)HSiO)_3$[3], $((C_2H_5)HSiO)_3$[4], $(CH_3Si(OC_2H_5)O)_3$[2] and $((C_2H_5O)_2SiO)_3$[5].

In this paper, the preparation and properties of cyclic polysiloxanes as indicated by the following formula will be described.

$(RSi(OC_3H_7\text{-}i)O)_n$ $R=CH_3$ and C_2H_5; $n=3$ and 4

One of the objects of this paper is to assure that the rapid hydrolysis method[2,5] developed by the author is applicable for the preparation of cyclotrimers, and the other is to obtain some knowledge of their stability.

The results showed that the cyclic trimer together with the tetramer were formed by using a considerable dropping rate. Comparing the yield of cyclotrimers, the ethyl compound is formed more easily than the methyl compound in those conditions. The infrared absorption spectra of those cyclotrimers showed, as in the case of $(CH_3Si(OC_2H_5)O)_3$[2,6] and $(C_2H_5Si(OC_2H_5)O)_3$[2], a strong absorption at 1023 cm^{-1} which would likely be attributed to the vibration of Si-O bond in cyclotrisiloxane ring. Though a measurable strain[7] would be expected in the cyclotrisiloxane ring of those compounds, no increase of the refractive index,

TABLE I. RESULTS OF THE HYDROLYSIS

Dichlorosilane (1 mol.) was added to the ice-cooled hydrolyzing mixture which consisted of pyridine (2 mols.), water (1 mol.) and 250 g. of benzene.

Expt.	Dichlorosilane	Droppping rate g./min.	Hydrolyzate: Total yield (%)	Composition (%): C_3**	C_4**	Residue
1	I*	15	57	13	16***	71
2	I	30	65	13	20	67
3	II*	20	75	32	10	58

* I: $CH_3(i\text{-}C_3H_7O)SiCl_2$,
II: $C_2H_5(i\text{-}C_3H_7O)SiCl_2$

** C_3: Cyclic trimer
C_4: Cyclic tetramer

*** Gelation occurred in still-pot after 16% of C_4 has distilled out.

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3) S. D. Brewer, *J. Am. Chem. Soc.*, 70, 3962 (1948).
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6) R. Okawara, ibid., 31, 154 (1958).
7) T. Tanaka, ibid., 34, 282 (1960).

TABLE II. CYCLIC POLYSILOXANES

Polymer size n	Boiling point °C/mmHg	Refractive index n_D^{20}	Density d_D^{20}	Molar refraction found (calcd.)*	Molecular weight found (calcd.)**	Anal. Si, % found*** (calcd.)
	$(C_2H_3Si(OC_3H_7\text{-}i)O)_n$					
3	67/1	1.3973	0.9912	86.23	348	23.80
				(85.98)	(354.6)	(23.76)
4	97/1	1.4023	1.0009	115.09	—	23.77
				(114.64)	(472.8)	(23.76)
	$(C_2H_5Si(OC_3H_7\text{-}i)O)_n$					
3	92/1	1.4129	0.9817	100.74	407	21.22
				(99.87)	(396.7)	(21.24)
4	125/1	1.4177	—	—	—	21.22
						(21.24)

* Calculated from bond refractivities by E. L. Warrick, *J. Am. Chem. Soc.*, **68**, 2455 (1946).
** Cryoscopic measurement in benzene.
*** Silicon was determined by decomposing the sample with concentrated suluric acid.

due to a spontaneous decomposition, was observed with the samples sealed in a soft glass ampule within one year.

Experimental

Starting Materials. — Methyltrichlorosilane used in these experiments was supplied from the Shin-etsu Chem. Ind. Co. Ethyltrichlorosilane was obtained from the product of silicon-ethylchloride reaction. Methylisopropoxydichlorosilane (I) and ethylisopropoxydichlorosilane (II) were prepared by adding 1 mol. of isopropanol to 1 mol. of those trichlorosilanes, respectively. After the addition, the mixture was aerated with stirring to drive off the hydrogen chloride at room temperature. Then the mixture was fractionated through a Stedman column of about 20 theoretical plates. Redistilled dichlorosilanes were taken for the starting materials.

Methylisopropoxydichlorosilane (I) b. p. 112.5°~113°C (Reported[8]: b. p. 110°~111°C)

Found: Cl, 41.1. Calcd. for (I): Cl, 41.0%.

Ethylisopropoxydichlorosilane (II) b. p. 137°~8°C (Reported[9]: b. p. 67°C/60 mmHg)

Found: Cl, 37.5. Calcd. for (II): Cl, 37.9%.

Hydrolysis and Fractionation of the Hydrolyzate.—Hydrolysis was carried out as described in the preceding papers.[2,5] The results are summarized in Table I.

The composition of the hydrolyzate was determined by fractionation through a Stedman column of about 50 theoretical plates. In Expt. 1, gelation occurred in a still-pot after 16% of C_4 distilled out; accordingly the fractionation of the other runs were carried out with the distillable fraction which was obtained from the hydrolyzate through a simple distillation. Comparing the yield of C_3, the ethyl compound is more easy to be formed than the methyl compound.

The fractions which exhibited constant boiling points and refractive indicies were taken for the samples and their physical constants are given in Table II.

Infrared Spectra and Stability. — Infrared absorption spectra were obtained with a Hilger H-800 infrared spectrophotometer with a rock salt prism. In the range 700~1300 cm^{-1}, samples were observed as solution in carbon disulfide. The positions of the strong bands which appeared in the range 1000~1100 cm^{-1} are shown in Table III.

TABLE III

Compound	Absorption Spectra (in cm^{-1})		
$(CH_3Si(OC_3H_7\text{-}i)O)_3$	1023	1044	—
(〃)$_4$	—	1044	1086
$(C_2H_5Si(OC_3H_7\text{-}i)O)_3$	1024	1045	—
(〃)$_4$	—	1043	1087

All the samples shown in Table II, which were sealed in a glass ampule, gave no changes of refractive index within one year.

Summary

1) Methyl- and ethyl-isopropoxydichlorosilane were hydrolyzed with considerable dropping rate using pyridine as an acid acceptor.

2) Methyl- and ethyl-isopropoxycyclotrisiloxane have been prepared and characterized. Those compounds were found to be stable.

3) Methyl- and ethyl-isopropoxycyclotetrasiloxane have been prepared and characterized.

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