Cyclopolysiloxanes from Ethyldichlorosilane

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From the hydrolysis product of ethyldichlorosilane and from its pyrolysis product, cyclic polyethylpolysiloxanes of the general formula $(C_2H_5SiHO)_n$ were obtained analogous to those reported by Sauer(1) and Brewer(2) from methyldichlorosilane.

Experimental

Starting Materials. — The ethyldichlorosilane used in our experiments was prepared by the reaction of ethyl chloride with copper-silicon and was purified by fractionation through a 75 cm. helices packed column. The fraction having the boiling point 75.5°—76°C. (760 mm.) was taken as starting material. Analysis for hydrolyzable chlorine by hydrolysis in water-methanol solution and titration of the liberated acid indicated that our sample was pure ethyldichlorosilane(3). *Anal.* Calcd. for $C_2H_6SiCl_2$:Cl, 54.96. Found: Cl, 54.5.

Hydrolysis.—To obtain the cyclic compounds ethyldichlorosilane has been hydrolyzed in ether solution according to Sauer's direction; e. g., two moles (258 g.) of ethyldichlorosilane was added to a mixture of 0.5 liter of diethyl ether and 1 kg. of cracked ice, which was vigorously stirred, over a half-hour period, some rubbery gel being produced. To avoid the gellation, ethyldichlorosilane was diluted with the same weight of diethyl ether and this solution was added to hydrolyzing mixture. Two typical experimental results are given in Table 1.

During the addition of ethyldichlorosilane, the temperature of the hydrolyzing mixture dropped from 0° to −8°C. As soon as the addition was completed the etherlayer was separated. Then the ice-cold water (the same weight as was used in the hydrolyzing mixture) was added and vigorous stirring was continued during an additional 15 minutes. The ether layer was washed repeatedly with water until it got neutral to methylorange and dried over dehydrated sodium sulphate.

Hydrolyzates

(a) **Untreated Hydrolyzate.** — The hydrolysis products were distilled by means of a Claisen flask containing a bundle of glass wool to prevent bumping. After ether was driven off at 760mm, the distillate was collected under 20 mm. The temperature of the oil bath was gradually raised to 220°C.

The temperature ranges and the amounts of distillate collected are given in Table I. Practically no distillate was given when the residue was further heated up to 240°C.

(b) **Thermally Rearranged Hydrolyzate.** — When the untreated hydrolyzate was distilled off, transparent sticky rubbery gel remained as the residue. By means of the pyrolysis of the residue under high vacuum using a rotary pump, the liquid distillate was acquired (Table 1) and there remained a small amount of transparent thin film stuck on the upper part of the flask. It may be seen from Table 1 that the ratio of untreated hydrolyzate to thermally rearranged hydrolyzate (Exp. 1, 11.2 g.: 21.3 g., Exp. 2, 40.7 g.: 34.8 g.) was greatly influenced by the hydrolyzing condition.

Cyclopolysiloxanes from (a) and (b). — The hydrolyzate (a) and (b) were rigorously fractionated through a 40 pair packed modified Stedman

Table 1

Exp. No.	$C_2H_5SiHCl_2$ diluted with (ether)	Hydrolyzing mixture		Hydrolyzate					
				Untreated			Thermally rearranged		
				Distillate		Still	Distillate		Still
		Ice	Ether	Temp. (20 mm.)	Yield	Temp.	Temp. (high vac.)	Yield	Temp.
	g.	g.	g.	°C.	g.	°C.	°C.	g.	°C.
1	100	500	200	100—130	11.2	—180	100—130	14.2	250—310
	(100)				0	180—220	130—170	7.1	310—400
2	250	1000	400	100—110	31.7	—140	100—140	19	250—310
	(250)			110—140	9	140—220	140—180	15.8	310—400

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(1) Sauer, Scheiber and Brewer, *J. Am. Chem. Soc.*, **68**, 962 (1946).

(2) Brewer, *J. Am. Chem. Soc.*, **70**, 3962 (1948).

(3) Meals, *J. Am. Chem. Soc.*, **68**, 1880 (1946).

Table 2

Hydrolyzate	Fraction No.	n_D^{20} After days 1	3	8	60	d_4^{20} After days 1	3	60
Untreated	I (a)	—	1.4139	—	1.4139	0.9834	—	0.9838
	II (a)	—	1.4176	—	1.4176	0.9922	—	0.9918
Thermally rearranged	I (b)	1.4127	—	1.4138	1.4136	—	0.9820	0.9821
	II (b)	1.4179	—	1.4176	1.4175	—	0.9920	0.9922
	III (b)	1.4201	—	1.4201	1.4198	—	1.0025	1.0022

Table 3

Mol. Formula	Mol. Wt. calcd.	Mol. Wt. found	Mol. Refn. calcd.	Mol. Refn. found	Si-H%(c) found	C %(d) found	H %(e) found	b. p. °C (20mm.Hg.)
I $(C_2H_5SiHO)_3$	223	223	56.70(a)	56.63(b)	1.33	32.00	8.01	106
II $(C_2H_5SiHO)_4$	297	294	75.60	75.39	1.28	32.63	8.07	135
III $(C_2H_5SiHO)_5$	371	362	94.50	93.68	—	32.38	7.97	165

(a) Warrick: *J. Am. Chem. Soc.*, **68**, 2455 (1946).

(b) The values d_4^{20}: 0.9836, 0.9920, 1.0023; n_D^{20}: 1.4138, 1.4176, 1.4200 (cf. Table 2) are used for the calculation of I, II, and III respectively.

(c), (d), (e): Calculated values are 1.35, 32.43, and 8.16 respectively.

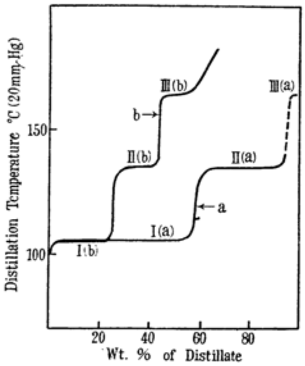

Fig. 1.—Distillation curve under 20 mm. Hg. (a) untreated hydrolyzate, (b) thermally rearranged hydrolyzate.

Distillation was performed in a course of about 7 hours.

Curve a: The fraction I(a) and II(a) were distilled out between the still-temperature of 140°—175°C. By stronger heating, between 270°—285°C the dotted curve was obtained.

Curve b: The fraction I(b) and II(b) were distilled out between the still-temperature of 170°—250°C, while III(b) was obtained between 250°—320°C.

column(4) respectively. The results are illustrated in Fig. 1.

Untreated hydrolyzate of several runs including Exp. 1 and 2 amounted to 68 g. By the rigorous fractionation, the two following fractions e. g. I(a) 40 g. and II(a) 19 g. were obtained and there remained some liquid and transparent gel. There must have occurred a partial thermal rearrangement of a lower boiling fraction to a transparent gel during a course of distillation. By stronger heating the fraction indicated by the dotted line was obtained but this fraction III(a) was not examined (Fig. 1).

Thermally rearranged hydrolyzate of several runs amounted to 97 g. By the rigorous fractionation, the three following fractions: I(b) 21 g., II(b) 14 g., and III(b) 7 g. were obtained. As shown in Fig. 1 (Curve b), above 165°C. no plateau was found. There remained some transparent rubbery gel in the still as was the case in the untreated hydrolyzate. It may be seen from these facts that a part of the lower boiling hydrolyzates polymerised to the gel.

Density and refractive index of these fractions are summarized in Table. 2.

From these data II(a) and II(b) may be regarded as the same compound. This conclusion was further supported by the molecular weight determination. The fraction I(b) which was assigned to cyclotriethyltrisiloxane by the molecular weight determination in dioxane, changed slightly its density and refractive index after a few days. But the marked changes such as Brewer(2) noted with the cyclotrimethyltrisiloxane were not found. As the molecular weight and other analytical data of this compound were the same as I(a), these may be regarded as the same compound.

The expected composition of these compounds was confirmed by determining the percentage hydrogen attached to silicon, % H(—Si), according to the equation

$$\mathrm{Si{-}H + KOH \rightarrow H_2 + Si{-}OK}$$

The samples (0.15—0.20 g.) were decomposed with 40% aqueous pottasium hydroxide solution in a Zerewitinoff apparatus. The results are given in Table 3.

Because of the identical elementary constitution of these compounds it was necessary to determine

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(4) John and Rehberg, *Ind. Eng. Chem.*, **41**, 1056 (1949).

accurately their molecular weight in order to assign molecular formulas. Our determinations were made cryoscopically in dioxane with the results given in Fig. 2.

It may be seen from the figure that the association of cyclopolysiloxanes occurred in the solution. These observed values were extrapolated to zero concentration. The molecular weights thus obtained at zero concentration are listed in Table 3, together with the other analytical data.

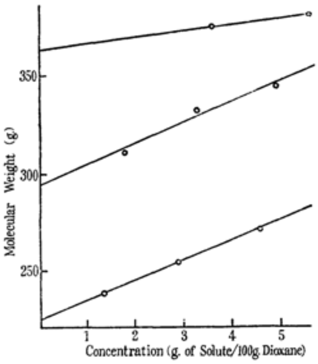

Fig. 2.—Cryoscopic molecular weight determanation in dioxane. Fisher's dioxane was distilled from sodium and the molar freezing depression constant $K=4.66$⁽⁵⁾ was used.

Since cyclic trimer was obtained in the untreated hydrolyzate, an enhanced reactivity of the siloxane linkage in these substances toward acid cleavage was not so distinct as Brewer indicated in the cyclopolymethylpolysiloxanes. This conclusion was further strengthened by the discovery that $(C_2H_5SiHO)_4$ is not readily converted in a short time into a high polymer by 20% aqueous hydrochloric acid as was the case with methyl analogue.

Summary

1. From the untreated hydrolyzate of ethyldichlorosilane, cyclic trimer $(C_2H_5SiHO)_3$ and tetramer $(C_2H_6SiHO)_4$, and from the pyrolyzed hydrolyzate cyclic trimer, tetramer and pentamer $(C_2H_5SiHO)_5$ have been acquired and characterized.

2. The reactivity of the siloxane (Si—O—Si) linkage in the $(C_2H_5SiHO)_n$ compounds toward acid cleavage appears to be not so enhanced as that exhibited by the $(CH_3SiHO)_n$ compounds.

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(5) Landolt, Tabellen. Erg. II. b. 1468.