Cyclopolysiloxanes from Cohydrolysis of Dimethyldichlorosilane with Methyldichlorosilane and Ethyldichlorosilane

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Recently, a series of linear and branched methylhydropolysiloxanes having the formula $\mathbf{M'D'_nM'}$[a] (n=0–6), $\mathbf{MM'}$, $\mathbf{M'DM'}$, $\mathbf{M'D'DM'}$, $\mathbf{M'D_2M'}$, $\mathbf{M'_3}$, $\mathbf{T}$ and $\mathbf{MD'_nM}$ (n=1–6) have been reported[1,2]

Now we wish to report on the preparation and properties of methylhydrocyclotetrasiloxanes; $\mathbf{D_3D'}$, $\mathbf{D_2D'_2}$ and $\mathbf{DD'_3}$, and the similar ethylmethylhydrocyclotetrasiloxanes; $\mathbf{D_3D^*}$[b], $\mathbf{D_2D^*_2}$ and $\mathbf{DD^*_3}$. These compounds were obtained from the cohydrolysis of the mixture of methyldichlorosilane(III′) (or ethyldichlorosilane (III*)) and dimethyldichlorosilane(II) in various mole ratios.

Since it has been known that the hydrolysis in an acidic medium is favourable to the formation of the lower membered rings[3] and further, the amount of Si-H split by hydrolysis is not so large even in the case of direct hydrolysis[1], the hydrolysis was carried out by adding chlorosilanes to the mixture of ether and water. Then the product was distilled and thermally rearranged under reduced pressure (10–20 mm.). Almost all the hydrolyzate distilled out as an untreated hydrolyzate and the remaining gel was also thermally rearranged completely without any residue up to the still-pot temperature of 450°C. The amount of the untreated and thermally rearranged hydrolyzates varied with the composition of the starting mixture, but their active hydrogen contents are nearly the same as is shown in Table I. Then both the hydrolyzates were united and the composition of the tetrasiloxanes was determined by fractionation through a high efficient column. About 40–50% of the hydrolyzate was found to be the tetrasiloxanes. For example, the distribution of the tetrasiloxanes $\mathbf{D_nD^*_{4-n}}$ (n=0–4), is shown in Fig. 2 with regard to the composition of the starting mixture.

Formally, $\mathbf{DD'_3}$, $\mathbf{D_2D'_2}$ and $\mathbf{D_3D'}$ are obtained by substituting one unit of $\mathbf{D'}$ in tetramethylcyclotetrasiloxane successively by $\mathbf{D}$ unit. Among them, $\mathbf{D_2D'_2}$ would consist of at least two isomers: $\underline{\mathbf{-DDD'D'-}}$ and $\underline{\mathbf{-DD'DD'-}}$. Sauer[4] has already characterized methylhydrocyclopolysiloxanes $\mathbf{D'_n}$ (n=4–6), but for comparison, $\mathbf{D'_n}$ (n=4–7) was also prepared and characterized in this paper.

Regular changes of the physical constants are read from Table II, referring to the compounds of $\mathbf{D_nD'_{4-n}}$ and $\mathbf{D_nD^*_{4-n}}$ (n=0–3). For comparison, the effect of substituting one $\mathbf{D'}$ unit successively by $\mathbf{D}$ unit in $\mathbf{D'_4}$ and $\mathbf{M'D'_2M'}$[c] is summarized in Table III. It may be seen that the effect of substituting one $\mathbf{D'}$ unit by one $\mathbf{D}$ unit is the same as the substitution of H(-Si) by one methyl group. In the linear compounds, the effect of introduction of the second methyl group does not cause such a marked increase of refractive index as that of the first methyl group but the density increases by nearly the same amount. However in the series of cyclocompounds $\mathbf{D_nD'_{4-n}}$, successive substitution of a methyl group causes the regular increase of boiling point and refractive index and the regular decrease of density.

Referring to the series of isomeric compounds $\mathbf{D_nD^*_{4-n}}$ (n=0–4), the gradual increase of boiling point, Δd_D^{20} and Δn_D^{20} are pointed out by substituting $\mathbf{D}$ unit successively by $\mathbf{D^*}$ unit. Thus the boiling point, the refractive index and the density of $\mathbf{D^*_4}$ assumed by this relation were not in accordance with that of the tetramer, but accorded well with the trimer reported

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[1] R. Ōkawara and M. Sakiyama, This Bulletin, **29**, 236 (1956).

[2] R. Ōkawara and M. Sakiyama, ibid., **29**, 547 (1956).

[a] The shorthand notations were indicated in the preceding papers 1) and 2).

[b] In this paper, in addition to the previous notation, $\mathbf{D^*}$ will be used to indicate C_2H_5SiHO unit.

[3] W. I. Patnode and D. F. Wilcock, *J. Am. Chem. Soc.*, **68**, 358 (1946).

[4] R. O. Sauer, S. D. Brewer and W. I. Scheiber, ibid., **68**, 962 (1946).

[c] Refractive index and density of the linear tetramers $\mathbf{M'D'_2M'}$, $\mathbf{M'D'DM'}$ and $\mathbf{M'D_2M'}$ have been reported (*loc. cit.* 1) and 2)) n_D^{20} : 1.3830, 1.3862 and 1.3875, d_4^{20} : 0.8613, 0.8623 and 0.8632, respectively.

in the previous paper⁵⁾ in which they were assigned by the determination of the molecular weight in dioxane. Here, again, the first four members of $\mathbf{D}^*_n$ were isolated from the hydrolyzate of ethyl dichlorosilane(III*). From the molecular weight determination in benzene and in dioxane, and further from the wave length of the infra-red absorption band associated with the Si-O stretching vibration, the first member of $\mathbf{D}^*_n$, though small in amount and unstable, was assigned to be cyclotrimer and the erroneous assignment in the previous paper has been corrected.

Experimental

Starting Materials. — Dimethyldichlorosilane (II) and methyldichlorosilane (III') used in these experiments were supplied from the Shin-etsu Chem. Ind. Co. Ethyldichlorosilane (III*) was prepared by the reaction of industrial ethylchloride with silicon-copper. The two isomeric chlorosilanes, II and III* have been reported to have a close boiling point 70.2°C⁶⁾ and 74.9°C⁷⁾, respectively. For fear of contamination of a small amount of II, which would be formed in the course of the direct synthesis, the fractions of III* were carefully fractionated by a Stedman column of about 30 theoretical plates. The constant boiling plateau (74°–75°C) having the constant chlorine content was used for the preparation, and especially for the preparation of $\mathbf{D}^*_n$ the back part of the plateau was taken to avoid the contamination of II.

Anal. Found: Cl, 54.8 %. Calcd. for $C_2H_6SiCl_2$ Cl, 54.9 %.

Fractionation of the Polysiloxanes. — Throughout this experiment, the hydrolyzates were fractionated through a Stedman column of about 50 theoretical plates.

Analysis of Active Hydrogen.—Active hydrogen content % H(-Si), was measured by decomposing the sample with butanolic sodium hydroxide in a Zerewitinoff's apparatus.

Hydrolyzates from the Acidic Medium.—The mixture of chlorosilanes was added to the ice-cooled mixture of ether and water with vigorous stirring. The organic layer was washed with water until it became neutral to methylorange. The oily product from the ether layer was distilled under reduced pressure at 10–20 mm., and the untreated and thermally rearranged products were collected separately in an ice-cooled receiver. The results with regard to the chlorosilane mixture of II and III* are given in Table I.

The untreated and thermally rearranged products which distilled out up to 300°C and 450°C respectively, were collected together and rigorously fractionated. For example, the result of Expt. 2 is shown in Fig. 1.

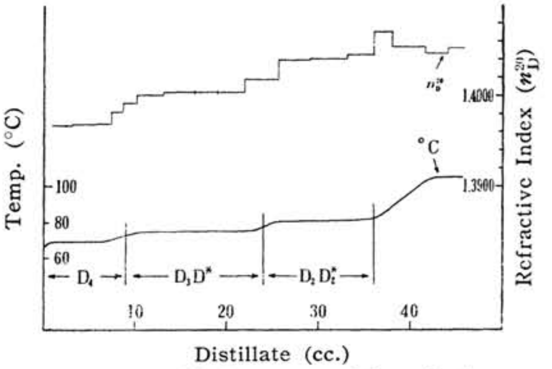

Fig. 1. Distillation curve of the cohydrolyzate (Expt. 2 of Table 1) at 18 mm.

In Fig. 1, the complete plateaus of $\mathbf{D}_4$, $\mathbf{D}_3\mathbf{D}^*$ $\mathbf{D}_2\mathbf{D}^*_2$ were found and it was easy to calculate the percentage composition of them by cutting on the distillation curve. The plateau of $\mathbf{DD}^*_3$ was not found, but from the refractive index, which was higher than the neighboring fractions at the next portion of $\mathbf{D}_2\mathbf{D}^*_2$, it was supposed to be present in this portion, although small in amount. The distribution of the tetrasiloxanes thus determined is shown in Fig. 2.

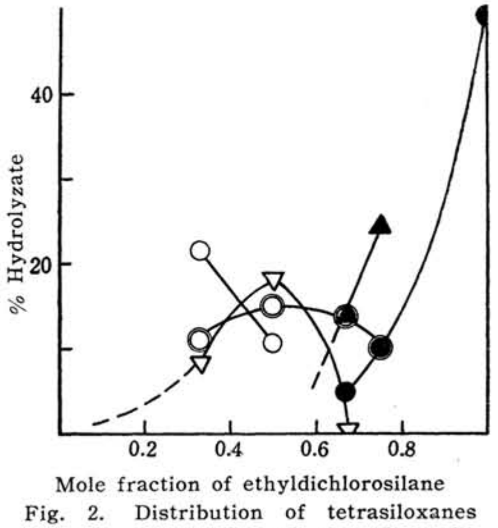

Fig. 2. Distribution of tetrasiloxanes $\mathbf{D}_n\mathbf{D}^*_{4-n}$ $(n=0-4)$ with regard to the mole fraction of ethyldichlorosilane (III*/II+III*).

○ $\mathbf{D}_4$	▽ $\mathbf{D}_3\mathbf{D}^*$
◎ $\mathbf{D}_2\mathbf{D}^*_2$	▲ $\mathbf{DD}^*_3$
● $\mathbf{D}^*_4$	

Fractionation of the hydrolyzate of III* (Expt. 5 of Table I) gave the first plateau at 67°C/20 mm., which amounted to 9 % of the hydrolyzate. The succeeding plateaus amounting to 48, 25 and 6 % of the hydrolyzate, were found to be those of

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5) R Ōkawara, E. Asada and T. Watase, This Bulletin, **26**, 141 (1953).

6) W. F. Gilliam, E. M. Hadsell, H. A. Liebhafsky and M. M. Sprung, *J. Am. Chem. Soc.*, **73**. 4252 (1951).

7) R. N. Meals, ibid., **68**, 1880 (1946).

TABLE I

COHYDROLYZATES FROM THE MIXTURE OF DIMETHYLDICHLOROSILANE(II) AND ETHYLDICHLOROSILANE(III*)

In each experiment, the mixture of the starting materials was added to the hydrolyzing medium which consisted of 500 cc. of ether and 1 l. of water.

Expt. No.	Starting Materials		Hydrolyzate		%H(−Si)		
		mol.	Total (T) % theory	Untreated % T	Untreated	(Calcd.)	Thermally Rearranged
1	III* II	0.5 1.0	84	82	—	(0.45)	—
2	III* II	0.76 0.76	80	73	—	(0.68)	0.67
3	III* II	1.0 0.5	83	63	0.90	(0.90)	0.80
4	III* II	1.2 0.4	83	71	1.00	(0.98)	0.94
5	III*	0.83	84	50	1.35	(1.35)	1.32

TABLE II

CYCLIC POLYSILOXANES

Compound[a]	Boiling point °C/mm.	Refractive index n_D^{20}	Density n_D^{20}	Molar refraction Found (Calcd.)[c]	Molecular weight Found[d] (Calcd.)	% H(-Si) Found (Calcd.)
D'$_4$	133/760 ((134.5))[b]	1.3870 ((1.3870))	0.9913 ((0.9912))	57.22 (57.08)	— (240.5)	1.67 (1.68)
D'$_3$D	143/760	1.3900	0.9809	61.51 (61.45)	— (254.6)	1.19 (1.19)
D'$_2$D$_2$	154/760	1.3927	0.9709	65.96 (65.82)	— (268.6)	0.75 (0.75)
D'D$_3$	165/760	1.3950	0.9620	70.55 (70.19)	— (282.6)	0.35 (0.36)
D'$_5$	60/14 ((168.7))	1.3918 ((1.3912))	0.9986 ((0.9985))	71.66 (71.35)	— (300.7)	1.67 (1.68)
D'$_6$	83/14 ((92.8/21))	1.3943 ((1.3944))	1.003 ((1.006))	86.10 (85.62)	359 (360.8)	1.66 (1.68)
D'$_7$	102/14	1.3958	—	—	411 (420.9)	1.65 (1.68)
D*$_3$	67/20	1.4078	0.9673	56.71 (56.70)	218 (222.5)	1.38 (1.36)
D*D$_3$	180/760, 75/18	1.4003	0.9598	74.97 (74.82)	— (296.6)	0.34 (0.34)
D*$_2$D$_2$	188/760, 82/19	1.4042	0.9658	75.14 (75.08)	292 (296.6)	0.67 (0.68)
D*$_3$D	201/760, 88/16	1.4090	0.9727	75.39 (75.34)	— (296.6)	1.01 (1.02)
D*$_4$	208/760, 105/20 ((106/20))	1.4141 ((1.4138))	0.9808 ((0.9836))	75.39 (75.60)	294[e] (296.6)	1.36 (1.36)
D*$_5$	80/2 ((135/20))	1.4187 ((1.4176))	0.9899 ((0.9920))	94.53 (94.50)	— (370.8)	1.37 (1.36)
D*$_6$	101/2 ((165/20))	1.4215 ((1.4200))	0.9942 ((1.0023))	113.6 (113.4)	— (445.0)	1.35 (1.36)

a) **D'**=CH_3SiHO, **D**=$(CH_3)_2SiO$, **D***=C_2H_5SiHO.

b) Reported values are indicated in brackets, (( )). The data of **D'**$_n$ and **D***$_n$ are those reported in 4) and 5) (*loc. cit.*), respectively, but for **D***$_n$, only the polymer size has been corrected.

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

d) Cryoscopic measurements in benzene.

e) The values of 293 and 295 were obtained at the concentration of 1.1 g. and 2.3 g. per 100 g. of benzene. Also, from the depression of 0.220° and 0.421°C at the concentration of 1.32 g. and 2.54 g. of the sample in 100g. of dioxane (b. p. 101°C, m. p. 11.67°C, molecular depression 4.95) the molecular weight 298 and 299 were obtained.

succeeding polymers as shown in Table II. The following small plateau at 120°C/2 mm. was also found, but it was too small in amount to be characterized accurately.

Tetrasiloxanes $\mathbf{D}_n\mathbf{D}'_{4-n}$ $(n=0-3)$ were prepared as above from the hydrolyzate (yield: 83-87% theory) of the mixture of II and III′ in various molar ratios. In the case of smaller molar ratios, x' (III′/II), the gel formed above 300°C was completely pyrolyzed until 400°C, but with increasing molar ratios, almost all the hydrolyzate came out below 300°C without any perceptible gelation in a still-pot. In tetrasiloxanes, the elevation of the boilng point at 760 mm. was found to be about 10°C when one unit of **D′** is substituted by one unit of **D**, but it required repeated distillation to obtain satisfactorily pure compounds.

To obtain a series of polymers $\mathbf{D}'_n$, the hydrolyzate(Found: H(-Si), 1.65%. Calcd. for$(CH_3SiHO)_n$: H(-Si), 1.67%) of III′, which distilled out below 300°C at 10-20 mm., was fractionated. A complete plateau was not found at the boiling point of the cyclotrimer (Reported[8]: b. p. 93.7°C) but a knick point. The succeeding plateau amounting to 40, 23, 8, 4 and 3% of the hydrolyzate, were found to be those of $\mathbf{D}'_4$ to $\mathbf{D}'_8$. Since the plateau of $\mathbf{D}'_8$ gradually rose from 114° to 118°C at 15 mm., and its active hydrogen content was somewhat lower (Found: H(-Si), 1.63%), polymers until $\mathbf{D}'_7$ are shown in Table II. The active hydrogen content of those polymers decreased slowly and regularly with increasing polymer size. The H(-Si) of the residue was 1.48%, from which it may be enough to suppose the contamination of compounds other than $\mathbf{D}'_n$.

TABLE III

CHANGES OF PHYSICAL CONSTANTS DUE TO SUCCESSIVE SUBSTITUTION OF **D′** BY **D** UNIT IN TETRASILOXANES

Compound	Numbers of **D** unit substituted	Increase of		
		Boiling point at 760 mm. Δ°C	Refractive index $\Delta n_D^{20}\times10^4$	Density $\Delta d_D^{20}\times10^3$
$\mathbf{M}'\mathbf{D}'_2\mathbf{M}'$	1	—	32	1
	2	—	13	1
$\mathbf{D}'_4$	1	10	30	−10
	2	11	27	−10
	3	11	23	− 9
	4[d]	10	18	− 6

Infra-red Spectra of $\mathbf{D}^*_n$.—The contamination of **D** unit in $\mathbf{D}^*_n$ can easily be detected by determining the active hydrogen content and also by the apearance of a sharp band in the infra-red spectra near 1260 cm^{-1}, which has been attributed to the methyl grouping in CH_3-(Si). In this experiment, the absorption spectra were obtained with a Hilger H-800 infra-red spectrophotometer with a rock salt prism. Samples were observed as solution, 3% in carbon disulfide being used in the range of 650-1300 cm^{-1}.

In the region 1200-1300 cm^{-1} two bands were found in the figure of $\mathbf{D}_n\mathbf{D}^*_{4-n}$ $(n=1-3)$: the one near 1260 and the other near 1240 cm^{-1}, which can be attributable to CH_3CH_2-(Si) group[9]. But the figure of $\mathbf{D}^*_n$ showed only the latter band. The band associated with the stretching of Si-O bond was found at 1023, 1085, 1089 and 1086 cm^{-1} for the first four members of $\mathbf{D}^*_n$, respectively. Since the cyclic trisiloxanes[9] have been reported to have the characteristic absorption band at 1010-1020 cm^{-1} and the higher cyclic polysiloxanes near 1080-1090 and 1050-1080 cm^{-1} respectively, it may be natural to suppose that the first member of $\mathbf{D}^*_n$ obtained in this experiment is cyclic trimer. The result accorded well with the molecular weight determination in benzene as shown in Table II.

The measurement of the physical properties of cyclotrimer $\mathbf{D}_3^*$ was carried out immediately after the fractionation and the infra-red spectra were measured after four days. During the measurement, only a slight change of refractive index was observed by the samples which were reserved in an ice box. All the samples which were sealed in glass ampoules became viscous fluid or gel in summer (room temperature of over 30°C) after three months, but there was found no perceptible increase of pressure in the ampoules. Infra-red spectra of the viscous fluid, after four months, gave rise to a strong band at 1094 cm^{-1} and the intensity of the band at 1023 cm^{-1}, characteristic to the cyclotrisiloxane ring, decreased. But the other compounds sealed in soft glass ampoules showed no change of refractive index.

Summary

1) Cyclotetrasiloxanes having **D′** and **D**, and **D*** and **D** units have been prepared and characterized.

2) Methylhydrocyclopolysiloxanes $\mathbf{D}'_n$ $(n=4-7)$ and ethylhydrocyclopolysiloxanes $\mathbf{D}^*_n$ $(n=3-6)$ have also been prepared and characterized. The erroneous assignment given to the latter compounds have been corrected.

3) Triethylcyclotrisiloxane $\mathbf{D}^*_3$, the first member of $\mathbf{D}^*_n$ was found to be an unstable compound.

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[8] S. D. Brewer, ibid., **70**, 3962 (1948).

[d] For $\mathbf{D}_4$, the reported values (*loc. cit.* 3)), n_D^{20} 1.3968 and d_4^{20} 0.9558 were used.

[9] C. W. Young, P. C. Servais, C. C. Currie and M. J. Hunter, ibid., **70**, 3758 (1948).