

refractions of a large number of reported organo-silicon liquids.

3. A method requiring only refractive index and density measurements has been developed

for determining the average composition of polymethylpolysiloxane systems.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY]

## Derivatives of the Methylchlorosilanes. V. Polysiloxanes from Methylchlorosilane

BY ROBERT O. SAUER, W. J. SCHEIBER AND STUART D. BREWER

In view of the ready availability<sup>1</sup> of methylchlorosilane it appeared of some interest to prepare the cyclic and linear polymethylpolysiloxanes of the general formulas  $(\text{CH}_3\text{SiHO})_n$  and  $(\text{CH}_3)_3\text{Si}[\text{OSiH}(\text{CH}_3)]_n\text{OSi}(\text{CH}_3)_3$ , analogous to those reported recently by Patnode and Wilcock<sup>2</sup> from dimethylchlorosilane. In general we have utilized the methods of preparation and of characterization already described.<sup>2</sup>

### Experimental

To obtain the cyclic compounds methylchlorosilane has been hydrolyzed in ether solution; the organic phase was then fractionally distilled. The linear polysiloxanes were prepared by "equilibration" of such a hydrolyzate with a relatively large amount of hexamethyldisiloxane.

**Starting Materials.**—The methylchlorosilane used in our experiments was prepared by the reaction of methyl chloride with copper-silicon.<sup>1</sup>

After rigorous purification by fractional distillation this substance had the following properties: b. p. 41.0° (748 mm.),  $d_{27}^{20}$  1.105, m. p. -92.5°. Analysis for hydrolyzable chlorine by hydrolysis in ice-ether mixture and titration of the liberated acid indicated that our sample was substantially pure methylchlorosilane.

*Anal.* Calcd. for  $\text{CH}_3\text{SiCl}_2$ : Cl, 61.66. Found: Cl, 61.61, 61.59, 61.60.

Stock and Somieski,<sup>3</sup> who first reported this compound, give  $d^{20}$  ca. 0.93 g./cc. and m. p. -93°.

The hexamethyldisiloxane was prepared by the hydrolysis of trimethylchlorosilane.

methylchlorosilane. The product first formed is a highly viscous oil which in a few minutes is transformed into an opalescent, sticky, rubbery gel. However, the formation of this high polymer can be obviated by employing a water-insoluble diluent which apparently increases the proportion of low-molecular weight cyclic polymers originally formed and suppresses their polymerization by reducing the concentration of hydrochloric acid.

Four moles (460 g.) of methylchlorosilane was added with vigorous stirring to a mixture of 1 liter of diethyl ether and 2 kg. of cracked ice over a half-hour period. The temperature of the hydrolyzing mixture dropped from 0 to -10°, but rose finally to 7°. After stirring an additional half hour the aqueous layer was separated and the organic phase washed repeatedly with water until neutral to methyl orange. Distillation of the ethereal solution gave: (a) 2,4,6,8-tetramethylcyclotetrasiloxane, b. p. 134.5-134.9° (755 mm.), 85.4 g. (35.6%); (b) 2,4,6,8,10-pentamethylcyclopentasiloxane, b. p. 168.6-168.9° (755 mm.), 40.1 g. (16.7%); and (c) 2,4,6,8,10,12-hexamethylcyclohexasiloxane, b. p. 92.6-93.0° (21 mm.), 10.6 g. (4.4%). Intermediate fractions totaling 34.9 g. were collected, but there was no indication of the expected 2,4,6-trimethylcyclotrisiloxane; the residue amounted to 66.5 g. Pure 2,4,6,8,10,12-hexamethylcyclohexasiloxane, b. p. 76-77° (10 mm.), was obtained from fraction (c) by redistillation in a small glass-packed column. The refractive indices, densities and melting points of these new compounds are given in Table I.

The expected composition of these compounds was confirmed by determining the percentage hydrogen attached to silicon, %H(-Si), according to the equation  $\text{Si-H} + \text{KOH} \rightarrow \text{H}_2 + \text{Si-OK}$ .

TABLE I

Value of n	$n^{20D}$	$d_{20}^{20}$ (vac.)	$R_D$	M. p., °C.	Mol. wt.		%H(-Si) <sup>b</sup> Found
					Calcd.	Found <sup>a</sup>	
4	1.3870	0.9912	0.2375	-69 ± 3	240.4	239, 241, 244	1.64, 1.64
5	1.3912	.9985	.2381	-108 ± 3	300.5	298, 297, 297	1.65
6	1.3944	1.006	.2380	-79 ± 2	360.6	360	1.67

<sup>a</sup> Cryoscopic in cyclohexane; maximum concentration of solute in weight per cent.: 0.56, 0.72, 0.78, respectively. Theoretical for  $\text{CH}_3\text{SiHO}$ , 1.68.

**The Cyclic Polysiloxanes,  $(\text{CH}_3\text{SiHO})_n$ .**—Although an oil of about 20-25 centistokes viscosity usually results when dimethylchlorosilane is hydrolyzed by adding it directly to water or to a mixture of ice and water, a somewhat different result is obtained under these conditions with

The samples (0.15-0.20 g.) were decomposed with 40% aqueous potassium hydroxide solution in a Zerewitinoff apparatus, modified in such a way that the reaction mixture could be vigorously agitated by means of a solenoid-actuated plunger. The results are given in Table I. The lower-than-theoretical values for %H(-Si) obtained for the more volatile members is attributed to partial evaporation of unreacted sample into the gas buret. The residue from the distillation of the lower cyclic compounds was analyzed by the same procedure giving 1.68% H(-Si).

(1) Rochow, *THIS JOURNAL*, **67**, 963 (1945).

(2) Patnode and Wilcock, *ibid.*, **68**, 358 (1946).

(3) Stock and Somieski, *Ber.*, **52**, 695 (1919).

Because of the identical elementary constitution of these compounds it was necessary to determine accurately their molecular weights in order to assign molecular formulas. Our determinations were made cryoscopically in cyclohexane with the results given in Table I.

Dow cyclohexane was distilled from sodium, and the distillate carefully refractionated in a column of about twenty theoretical plates. The heart fractions used for the molecular weight determinations had the following properties: b. p. 81.1° (761 mm.),  $n_D^{20}$  1.4263, f. p. 6.20°. The freezing point depression constant  $K$  per 100 g. of solvent was determined on five known compounds, giving an average value for  $K$  of 207 (see Table II).

TABLE II

Solute	Max. concn. (wt. %)	$K$		
Naphthalene	0.26	210	209	212 213
Triphenylmethane	.73	203	201	
Biphenyl	.48	204	205	
Dibenzyl	.54	207		
Decamethylcyclopentasiloxane	.97	207	208	

In general, the technique, both for the determination of  $K$  and later in the determination of the molecular weights, was to obtain the freezing points of the cyclohexane solutions at two or more concentrations and extrapolate to zero concentration. In all cases straight lines were obtained and, except in the case of  $(\text{CH}_3\text{SiHO})_4$ , the extrapolated freezing point agreed with the actual freezing point within the experimental error ( $\pm 0.002^\circ$ ).

Since no cyclic trimer was obtained in the above preparation and since hydrolysis of methylchlorosilane without solvent led to the formation of high polymers, an enhanced reactivity of the siloxane linkage in these substances toward acid cleavage was indicated. This conclusion was further strengthened by the discovery that  $(\text{CH}_3\text{SiHO})_4$  is converted into a high polymer by 20% aqueous hydrochloric acid, whereas  $[(\text{CH}_3)_2\text{SiO}]_4$  is essentially unchanged when subjected to the same conditions.

Ten milliliters of concentrated hydrochloric acid was added to a mixture of 10 ml. of 2,4,6,8-tetramethylcyclo-tetrasiloxane and 10 ml. of water, and the resulting mixture was shaken vigorously. After two hours the oily layer was quite viscous, and there was a slight gas pressure in the closed bottle. At the end of three hours the oil layer had been converted to an opalescent, rubbery solid. A slight gas pressure was again noted in the container.

TABLE III

Value of $n$	$n_D^{20}$	$d_4^{20}$ (vac.)	% H(-Si)		Caled.	% C	% H	
			Caled.	Found			Caled.	Found
1	1.3818	0.8194	0.45	0.46, 0.46	37.80	37.4, 37.8	9.97	10.1, 9.7
2	1.3854	.8559	.71	.70, .72	34.01	33.5, 33.7	9.27	9.2, 9.2
3	1.3878	.8806	.88	0.88, 0.90	31.55	31.8, 31.6	8.82	8.8, 8.9
4	1.3895	.8991	1.00	0.94, 0.96	29.82	29.7, 29.6	8.51	8.5, 8.4

A further example of the enhanced reactivity of the siloxane linkage in these materials was provided by the observation that a sample of what was originally fairly pure 2,4,6,8,10-pentamethylcyclopentasiloxane, b. p. 56° (10 mm.),  $n_D^{20}$  1.3913, had polymerized slowly to a heavy oil on standing for eight months in a soft glass bottle. Analysis of the heavy oil gave a hydrogen-silicon ratio of 0.99. After nine months

this oil had gelled to a soft, rubbery solid.

**The Linear Polysiloxanes,  $(\text{CH}_3)_3\text{Si}[\text{OSiH}(\text{CH}_3)]_n\text{OSi}(\text{CH}_3)_3$ .**—A slurry of ice in a solution of 4625 g. (28.6 moles) of hexamethyldisiloxane and 1400 g. of mixed hexanes was prepared in a 10-gallon crock. A propeller-type stirrer was arranged to agitate vigorously the contents of the crock. Two kilograms (17.4 moles) of methylchlorosilane was added slowly to the vortex formed by the stirrer. The ice was continually replenished, and the addition of the chlorosilane was interrupted whenever it became necessary to siphon out some of the water layer to avoid overflow. When the addition was complete, the oily layer was separated, washed with water, and filtered to remove emulsified water.

The oil was then stirred vigorously with 360 ml. of concentrated sulfuric acid for two hours at room temperature. The acid layer was separated and discarded; a slight odor of sulfur dioxide was noted. The oil remaining was washed three times with half its volume of water and then distilled in a column of about fifteen theoretical plates. Careful fractionation yielded: hexanes, 1235 g.; hexamethyldisiloxane, 2370 g.; heptamethyltrisiloxane, 1390 g.; octamethyltetrasiloxane, 328 g.; residue, 1115 g. Distillation was stopped before the octamethyltetrasiloxane had been distilled completely.

The hexamethyldisiloxane and the residue from the above distillation were combined and treated with sulfuric acid as before. Fractionation of the resulting "equilibration" product gave more hexamethyldisiloxane, heptamethyltrisiloxane, and octamethyltetrasiloxane. In addition, the following materials were isolated: heptamethyl-3-trimethylsiloxytrisiloxane, b. p. 183.6–190.6° (760 mm.),  $n_D^{20}$  1.3872,  $d_4^{20}$  0.8533, 31 ml.; nonamethylpentasiloxane, b. p. 85.6° (10 mm.), 101 ml.; decamethylhexasiloxane, b. p. 106.5–107.6° (10 mm.), 21 ml. Certain additional substances were separated in an impure state, but their structures have not been elucidated at the present time. Presumably these latter materials contain  $\text{CH}_3\text{SiO}_{3/2}$  units as the result of either hydrolytic or oxidative attack on  $\text{CH}_3\text{SiHO}$  units by the concentrated sulfuric acid used to rearrange the siloxane linkages.

The physical constants and the analytical data on the purified samples of the new linear polymethylpolysiloxanes are given in Table III. The values of % H(-Si) reported were obtained using alcoholic potassium hydroxide; this change in technique eliminated the necessity for the thorough and protracted stirring required when aqueous alkaline solutions are employed. Because of the small amount of decamethylhexasiloxane ( $n = 4$ ) obtained and the low values of % H(-Si) found, it is inadvisable to claim high purity for our sample.

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### Summary

1. Polymethylpolysiloxanes of the types  $(\text{CH}_3\text{SiHO})_n$  and  $(\text{CH}_3)_3\text{Si}[\text{OSiH}(\text{CH}_3)]_n\text{OSi}(\text{CH}_3)_3$  have been prepared and characterized.

2. The reactivity of the siloxane (Si-O-Si) linkage in the  $(\text{CH}_3\text{SiHO})_n$  compounds toward acid cleavage appears to be enhanced over that exhibited by the  $[(\text{CH}_3)_2\text{SiO}]_n$  compounds.

SCHENECTADY, N. Y.

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