## Hydrolysis of Methylethoxydisilylmethanes

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Because of their outstanding thermal and dielectric properties, silicones are now a class of polymers of ever-increasing importance. However, the silicon-oxygen bonds contained in this type of polymer are susceptible to fission and rearrangements by the action of acids and alkalies. Improvements in this respect have attracted the attention of many chemists.

It has been established that silicon-carbon bonds are more resistant than silicon-oxygen bonds to chemical and thermal attacks. The substitution of oxygen atoms in the skeleton of polysiloxane by carbon atoms, either wholly or partially, would give polymers with higher chemical and thermal stabilities.

Among the many possibilities, the polymers possessing a skeleton of  $(-Si-C-Si-O)_n$ , for which we coined the name "polysilmethosiloxanes" by adopting the name "silmethylene" suggested by Sommer,<sup>1</sup> seem to be very tempting, since it appears that this type of polymer may not be very difficult to synthesize.

Goodwin et al.<sup>2</sup> has prepared a class of compounds which might be termed oligomers of this type by stepwise Grignard synthesis. This method would, of course, be rather difficult to extend to the preparation of high polymers.

Hexachlorodisilylmethane can now be easily obtained by "direct" synthesis from methylene chloride and silicon,<sup>3</sup> or as a by-product in other cases.<sup>4</sup> It would be convenient to prepare polymers of the required type by hydrolyzing alkyl halo- or alkoxy-disilylmethanes derived from this hexachloro compound. Bluestein<sup>5</sup> obtained polytetramethylsilmethosiloxane from the diffuoro-monomer.

While our work on methylethoxydisilylmethanes was going on, Hizawa and Nojimoto<sup>6</sup> published their work on the similar line. They obtained polymers of oily, elastic, and rigid forms by the hydrolysis of the chloro and methoxy monomers.

Our experiments on the ethoxy monomer gave quite different results. Only the pentafunctional monomer — methylpentaethoxydisilylmethane gave a crosslinked, infusible, and insoluble polymer; all the others gave, either exclusively or in part, definite simple compounds. Tetramethyldiethoxydisilylmethane gave, on hydrolysis, a cyclic compound, cyclobissilmethosiloxane, which resisted attempts to open the ring. Trimethyltriethoxydisilylmethane gave a part of a low polymer with rings connected by oxygen atoms and a part of a simple compound with a fused ring structure. Dimethyltetraethoxydisilylmethane gave a nearly theoretical yield of a high-melting solid with a caged structure.

Studies were also made by co-hydrolyzing two monomers together, and in these cases, definite simple compounds were also obtained instead of cross linked polymers.

We prefer to use the ethoxy monomers for two reasons: first, unlike the chlorosilanes which make the medium increasingly acidic during hydrolysis, the alkoxy silanes can be hydrolyzed at a definite pH from the beginning to the end; secondly, the consecutive members of the methylethoxydisilylmethane series have boiling points some 15° apart, so that they can be obtained in a highly pure form easily.

The monomers were prepared by the action of methylmagnesium bromide on hexaethoxydisilylmethane, which was, in turn, obtained by the alcoholysis of hexachlorodisilylmethane. In the alcoholysis, the use of a theoretical quantity of absolute ethanol gave a quantitative yield of the ethoxy compound.<sup>7</sup>

By using stoichiometric quantities of the Grignard reagents, the yields obtained of the even-numbered symmetrically-substituted monomers were decisively higher than those of the odd-numbered ones. In the preparation of the pentamethylethoxydisilylmethane, the use of five moles of the Grignard reagent gave a low yield of the desirable product, and only when the molar ratio was raised to 1:6.7 was a satisfactory result obtained. The properties of the monomers are listed in Table I.

The hydrolysis of the monomer were done by the procedure<sup>8</sup> recommended for the preparation of octamethylcyclotetrasiloxane (D4) and is briefly as follows:

One part of the monomer or a mixture of two monomers was dropped slowly into a well-stirred and ice-cooled mixture of 2 parts of 6N hydrochloric acid and two parts ether. Stirring was continued for 3 hours at room temperature, and the etheral layer was separated and worked as usual.

The products obtained by the hydrolysis of the different monomers are listed in Table II. The proposed formulas are given in Table III.

The structures of the products from pentamethylethoxydisilylmethane and tetramethyldiethoxydisilylmethane need no comment. They are, obviously, decamethylbissilmethosiloxane (formula I,  $(Mc_2)$  Table III) and octamethylcyclobissilmethosiloxane (formula II,  $Dc_2$ ), respectively. Contrary to expectation, the latter compound, although closely resembling D4 in structure, resisted attempts to open the ring by the usual methods.

Hydrolysis of trimethyltriethoxydisilylmethane gave nearly a theoretical yield of an oily product, which, on vacuum distillation, was separated into a volatile liquid and a nondistillable oil. Analysis and molecular weight determination showed the molecular formula of the volatile liquid to be  $C_{16}H_{44}O_6Si_8$ . Judging from the ease with which the  $Dc_2$  ring system form,

				Physical C	TAI ontents and /	BLE I Analysis of	the Mon	omersa					
							R	$IR_D$		Si, 9	20	Yield.	
	Mo	nomer		o.p., °C. mm.	$n_{ m D}^{20}$	$d_4^{20}$	Cale.	Found	Ca	lc.	Found	%	Reference
Pc'	Me(EtO) <sub>3</sub>	SiCH <sub>2</sub> Si(C	)Et)3	132 - 134/25	1.4104	0.9519	80.75	80.8	7 18.	-07	18.23	42.9	1
0°)	Me(EtO)	SiCH_Si((	OFt) <sub>2</sub> Me	123 - 124/25.5	1.4127	0.9292	75.36	75.3(	6 20.	.28	20.01	45.9	1
$T_{c}'$	Me <sub>s</sub> (EtO)	SiCH <sub>2</sub> Si(C	)Ft) <sub>2</sub> Me	104 - 106/25	1.4144	0.8974	69.97	69.7	4 22	.45	22.69	23.7	×
				(112/25)	(1.4148) (	(0.8914)							
D°,	Me <sub>2</sub> (EtO)	SiCH <sub>2</sub> Si(O	)Et)Me <sub>2</sub>	88-90/28	1.4152	0.8600	64.58	64.1	<u>مر</u>	I	j	71.6	4
	•			(186.5/760)	(1.4159) (	(0.8615)							
Mc'	Me <sub>s</sub> SiCH,	si(OEt)M	le <sub>2</sub>	161 - 163 / 760	1.4160	0.8159	59.19	58.51	1	ı	-	56.8	67
	Monomer						l	Si,	%	Mol.	wt.	Yield.	
-	hydrolyzed	Product	m.p., °C.	b.p., °C. mm.	$n_{ m D}^{20}$	$d_4^2$	8.4	Calc.	Found	Calc.	Found	%	Reference
	Mc′	$Mc_2$		123-4/20	1.4340	0.843	-	]	l	1		95.6	13
				(233/360)	1.4340)	(0.8359	(6						
	Sc'	$Dc_2$	28.6 - 29.0	$213-4_1368$	1.4328(25°)	0.903	$5(25^{\circ})$	1	]			95	14
	-	I		(213-3.5)	(1.4341)	(0.9035	(6	00		2	001	00	
-	$T_{c}$	$\mathbf{T}_{\mathbf{C}_4}$	]	125-6/2.5	1.4509	1.035(	0	40.30	40.25	556	490	20	
		$\mathrm{Tc}_{2n}$		Undistillable	1.4566	1,0434		40.30	40.57	ļ	1530	60	
-	Qe'	Qc3	203.5 - 204.2	ļ			,	42.43	42.40	396	392	92.4	ļ
	Pc'	Pc,	Infusible		ļ	1	1	44.83	44.27		ļ	96	
	Dc' + Qc'	$Dc_2Qc$	42.2 - 54.8	120 - 1/8	]	ł	ı	39.63	40.05	424	419	31	]

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Table III Possible Formulas of the Products from Hydrolysis

the most probable structure might be dodecamethyltricyclotetrakissilmethosiloxane (formula III, Tc<sub>4</sub>). An alternative formula might be III-A. Because of the ease with which the ethoxy groups hydrolyze, and the reactivity of the intermediate hydroxy groups, formula III is to be preferred. It consists of two Dc<sub>2</sub> rings fused with a D4 ring. The structure is closely analogous with that of the compounds obtained by Scott *et al.*<sup>10</sup> in the thermal degradation of polymethylsiloxanes.

The nondistillable oily residue possessed a molecular weight of about 1500. Its structure is presumably suggested as shown by formula IV  $(Tc_{2n})$ . An alternative formula, IV-A, is also possible, but by the same considerations as above, IV is to be preferred. It consists of  $Dc_2$  rings connected with oxygen-atoms to form a chain, with an average n of about 6 to 7. Experiments on the temperature coefficient of viscosity which gave a value for the activation energy near 10,000, also supports this view.

The hydrolysis of the tetrafunctional monomer, dimethyl tetraethoxydisilylmethane, gave very interesting results. A nearly quantitative yield of a crystalline compound melting at 203° was obtained. Its molecular formula was found to be  $C_9H_{24}O_6Si_6$ , and it was obviously formed from three monomer units. It is very stable and readily sublimable. In view of the stability of the Dc<sub>2</sub> ring system, its structure is tentatively put as hexamethyl tetracyclotrissilmethosiloxane (formula V, Qc3). An alternative formula might be proposed as V-A but is rather unlikely. Qc3 consists of a caged structure with three  $Dc_2$  rings as sides and two D3 rings as the top and bottom. It closely resembles the caged compound "methyl T6" of Sprung and Guenther.<sup>11</sup> Both are thermal stable, sublime easily, and have m. p.'s close to each other (Sprung and Guenther's compound, m. p. 210-211°). In a patent Clark<sup>12</sup> has reported a compound which might be identical with Qc<sub>3</sub>, but the structure of his compound has not been fully elucidated.

The hydrolysis of methylpentaethoxydisilylmethane gave a hard, granular polymer which was transparent under microscope. It was found to be infusible and insoluble in common organic solvents. It did not swell in chloroform and toluene, and was thermally very stable. No appreciable change was observed when it was heated to boiling with concentrated sulfuric acid. An insight into the structure of the polymer is of course impossible, but it might be inferred that it consists of  $Qc_3$  cages incorporated into the three dimensional net work,.

The co-hydrolysis of tetramethyldiethoxydisilylmethane and dimethyltetraethoxydisilylmethane is a typical example. When these two monomers were mixed in molar ratio of 2:1 and hydrolyzed as above, there was obtained, in addition to the cyclo  $Dc_2$  and the caged  $Qc_3$ , a copolymer in more than 30% yield. It crystallized readily during distillation and formed large plates from ether. It dissolves easily in common organic solvents, less in petroleum ether and is insoluble in water. From the results of analysis and molecular weight determinations its structure formula is proposed as VI, decamethylbicyclotrissilmethosiloxane ( $Dc_2Qc$ ). An alternative formula, VI-A, seems to be unlikely, judging from such physical constants as m.p., sublimability, etc. Formula  $Dc_2Qc$  consists of a fused-ring structure with a tetrafunctional unit as the central bridge and two diffunctional units as sides.

From above, it is apparent that the strong tendency of ring formation reduces the functionality of the monomers and there is more chance to form simple compounds than to form polymers of linear and crosslinked structure.

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## **Synopsis**

Hydrolysis of monomers of the type (I) should give polymers with the skeleton -Si-C-Si-O-, which might possess better properties than siloxanes. The monomers were prepared by the action of methylmagnesium bromide on hexaethoxydisilylmethane. From mono- up to pentamethylethoxydisilylmethanes were obtained, the symmetrically substituted and even-numbered methyl compounds being obtained in preferential yields.

Hydrolysis of these five monomers gave interesting results. The strong tendency of ring formation reduced their functionality and thus gave less chance to form crosslinks. While pentamethylmonoethoxydisilylmethane gave the normal product (II), tetramethyldiethoxydisilylmethane gave a ring dimer (III), which, although closely analogous to cyclosiloxane D4, resisted all attempts at ring opening to give a linear polymer. The trifunctional trimethyl compound gave an oil of the type (IV), consisting of rings connected into a chain by oxygen atoms. Dimethyltetraethoxydisilylmethane, although tetrafunctional, gave, on hydrolysis, a highly crystalline compound with a cage structure (V). Only the pentafunctional monomer, monomethylpentaethoxydisilylmethane, gave an insoluble infusible powder of high stability.

Co-hydrolysis of the monomers gave fused ring compounds; dimethyltetraethoxydi-

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silylmethane and tetramethyldiethoxydisilylmethane, when hydrolyzed together, gave a compound of formula (VI).



## Résumé

L'hydrolyse de monomères du type (I) devrait donner des polymères avec le squelette —Si—C—Si—O—, qui pourraient, posséder des qualités supérieures aux siloxanes. Les monomères ont été préparés par l'action du bromure de méthylmagnésium sur l'hexaéthoxydisilylméthane. Depuis les mono jusqu'aux pentaméthyléthoxydisilylméthanes les dérivés ont été obtenus, les composés symétriquement substitués et à nombre paire de groupes méthyles étant obtenus aux rendements les meilleurs.

L'hydrolyse de ces cinqs monomères donne des résultats intéressants. La forte tendance à la formation de cycle diminue leur fonctionalité et en conséquence les empèche de former des ponts intermoléculaires. Alors que le pentaméthylmonoéthoxydisilylméthane donne le produit normal (II), le tétraméthyldiéthoxydisilylméthane donne un cycle dimérique (II) lequel, quoique très proche au cyclosiloxane  $D_{44}$ , résistait à tous les essais d'ouverture de cycle en vue d'obtenir un polymère linéaire. Le composé triméthylique trifonctionel donne une huile du type (IV), formée de cycles reliés en chaîne par les atomes d'oxygène. Le diméthyltétraéthoxydisilylméthane, quoique tétrafonctionel, donne par hydrolyse, un composé fortement cristallin avec une structure en cage (V). Seul le monomère pentafonctionel, le monométhyl-penta-éthoxydisilylméthane, donne une poudré insoluble et infusible de stabilité élevée.

Une co-hydrolyse des monomères engendre des composés à cycles condensées; lorsque le diméthyltétraéthoxydisilylméthane est hydrolysé en présence de tétraméthyldiéthoxydisilylméthane, on obtient un composé dont la formule (VI).

### Zusammenfassung

Hydrolyse von Monomeren vom Typ (I) sollte Polymere mit dem Skelett —Si—C— Si—O— liefern, die bessere Eigenschaften wie Siloxane besitzen könnten. Die Monomeren wurden durch Einwirkung von Methylmagnesiumbromid auf Hexaäthoxydisilylmethan dargestellt. Die Methylverbindungen vom Mono- bis zum Pentamethyläthoxydisilylmethan wurden erhalten, wobei die symmetrisch substituierten und geradzahligen Methylverbindungen mit bevorzugter Ausbeute entstanden.

Hydrolyse dieser fünf Monomeren ergab interessante Resultate. Die starke Ringbildungstendenz setzte ihre Funktionalität herab und ergab daher eine geringere Wahrscheinlichkeit für die Bildung von Vernetzungen. Während Pentamethylmonoäthoxydisilylmethan das normale Produkt (II) lieferte, gab Tetramethyldiäthoxydisilylmethan ein cyklisches Dimeres (III), das obgleich dem Cyklosiloxan D4 weitgehend analog, allen Versuchen, es durch Ringöffnung in ein lineares Polymeres umzuwandeln, widerstand. Die trifunktionelle Trimethylverbindung lieferte ein Öl vom Typ (IV), das aus Ringen bestand, die durch Sauerstoffatome zu einer Kette verknüpft sind. Dimethyltetraäthoxydisilylmethan lieferte, obwohl es tetrafunktionell ist, bei der Hydrolyse eine hochkristalline Verbindung mit Käfigstruktur (V). Nur das pentafunktionelle Monomere, Monomethylpentaäthoxydisilylmethan, lieferte ein unlösliches und unschmelzbares Pulver von hoher Stabilität.

Co-hydrolyse der Monomeren lieferte Verbindungen mit kondensierten Ringen; Dimethyltetraäthoxydisilylmethan und Tetramethyldiäthoxydisilylmethan ergaben bei bei gemeinsamer Hydrolyse eine Verbindung der Formel (VI).

#### Discussion

**E. Thilo** (*Berlin-Adlershof*): Lässt sich eine Erklärung dafür geben, wieso die (Si—O—Si)-Bindungen in den beschriebenen Verbindungen so extrem beständig gegen Hydrolyse sind?

Wang Pao-Jen (*Peking*): It is very interesting that the ring system of cyclo-bisoctamethyl disilomethoxysiloxane is very stable while the analogous D4 can be opened rather easily. We have tried to open the  $Dc_2$  ring with  $H_2SO_4 \cdot SO_3$ ,  $H_2SO_4$  (70%), NaOH-CH<sub>3</sub>OH, and KOH-isoPrOH complex without success. The reason why this ring system is so stable remains obscure.