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Abstract

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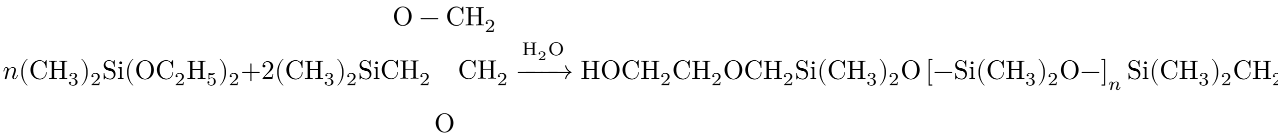
ON THE SYNTHESIS OF DIHYDRIC ALCOHOLS OF THE SILOXANE SERIES

SYNTHESIS OF BIS-(β-HYDROXYETHOXYMETHYL)-POLYDIMETHYLSILOXANES

There are rather few reports in the literature concerning the synthesis of dihydric organosilicon alcohols containing hydroxyl groups in organic radicals. Thus, the synthesis of bis-(hydroxymethyl)-tetramethyldisiloxane by the action of methanol on bis-(acetoxymethyl)-tetramethyldisiloxane ([1,2]), and the synthesis of bis-(β-hydroxyethoxymethyl)-tetramethyldisiloxane by the action of sodium glycolate on bis-(chloromethyl)-tetramethyldisiloxane ([3]), have been described.

In the present work, reactions for the synthesis of bis-(β-hydroxyethoxymethyl)-polydimethylsiloxanes of various molecular weights, from 360 to 1800, were studied. To obtain such dimethylsiloxane oligomers containing β-hydroxyethoxymethyl groups at the chain ends, the cohydrolysis reaction of dimethyldiethoxysilane with the heterocyclic derivative $(CH_3)_2SiOCH_2CH_2OCH_2$, the synthesis of which was described in a previous communication ([3]), was investigated, according to the reaction:

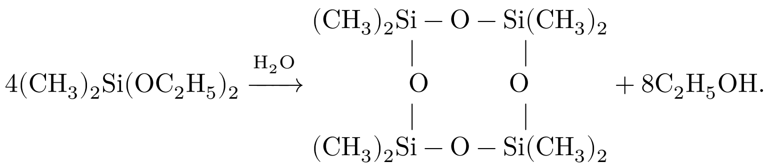


$$n(CH_3)_2Si(OC_2H_5)_2+2(CH_3)_2SiCH_2\overset{O-CH_2}{}\underset{O}{}CH_2 \xrightarrow{H_2O} HOCH_2CH_2OCH_2Si(CH_3)_2O\,[-Si(CH_3)_2O-]_n\,Si(CH_3)_2CH$$

(I)

This reaction is based on the ability, established by us, of the indicated heterocyclic derivative to undergo hydrolysis readily, converting into a disiloxane; i.e., in the present case the heterocyclic derivative plays the role of a monofunctional compound terminating the chain of the polydimethylsiloxane formed upon hydrolysis of dimethyldiethoxysilane.

The hydrolysis was carried out in an aqueous acid medium without solvent. The reaction proceeded according to the scheme indicated; however, it was accompanied by the side reaction of separate hydrolysis of dimethyldiethoxysilane and the formation of octamethylcyclotetrasiloxane according to the reaction:



$$4(CH_3)_2Si(OC_2H_5)_2 \xrightarrow{H_2O} \begin{array}{ccc} (CH_3)_2Si & - O - & Si(CH_3)_2 \\ | & & | \\ O & & O \\ | & & | \\ (CH_3)_2Si & - O - & Si(CH_3)_2 \end{array} + 8C_2H_5OH. \qquad (II)$$

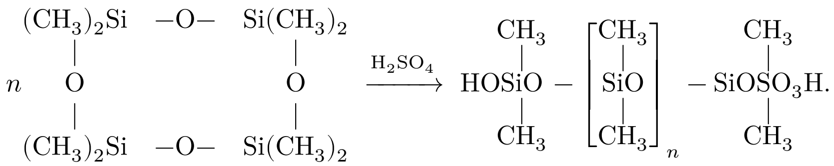
This changed the ratio between the dimethyldiethoxysilane introduced into the reaction and the chain-terminating heterocyclic derivative, which led to the formation of bis-(β-hydroxyethoxymethyl)-polydimethylsiloxanes with a number of dimethylsiloxane units approximately half as large as would follow from the ratio of the components taken for the reaction.

Changing the hydrolysis conditions in order to reduce the development of the side reaction showed that, if the cohydrolysis reaction is carried out with an amount of water calculated by formula (4),

$$A = \frac{n}{n-m},$$

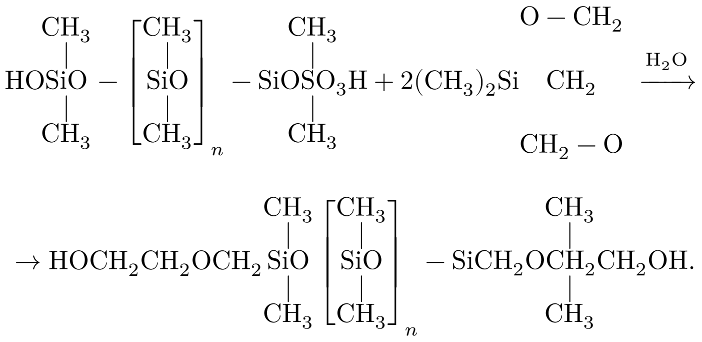
where A is the number of dimethylsiloxane units, n is the number of moles of the difunctional derivative, and m is the number of moles of water, then bis-(β-hydroxyethoxymethyl)-polydimethylsiloxanes are obtained with a number of dimethylsiloxane units close to that specified by the reaction. The yield of bis-(β-hydroxyethoxymethyl)-polydimethylsiloxanes reaches 80%, and no cyclic polydimethylsiloxanes are formed. This shows that the reaction proceeds only according to scheme (I).

For the synthesis of the indicated dihydric organosilicon alcohols we also used the reaction of catalytic rearrangement of octamethylcyclotetrasiloxane. This reaction, under the action of sulfuric acid on octamethylcyclotetrasiloxane, leads to linear polydimethylsiloxanes according to the scheme:



$$n \begin{array}{ccc} (CH_3)_2Si & -O- & Si(CH_3)_2 \\ | & & | \\ O & & O \\ | & & | \\ (CH_3)_2Si & -O- & Si(CH_3)_2 \end{array} \xrightarrow{H_2SO_4} \begin{array}{c} CH_3 \\ | \\ HOSiO \\ | \\ CH_3 \end{array} - \left[\begin{array}{c} CH_3 \\ | \\ SiO \\ | \\ CH_3 \end{array} \right]_n - \begin{array}{c} CH_3 \\ | \\ SiOSO_3H. \\ | \\ CH_3 \end{array} \qquad (III)$$

By regulating the ratio between sulfuric acid and octamethylcyclotetrasiloxane, the degree of polymerization n can be varied within the desired limits. The second phase of the reaction consisted in the cohydrolysis of the oligomer obtained according to scheme (III) with the heterocyclic derivative according to the scheme:



$$\mathrm{HO\overset{CH_3}{\underset{CH_3}{Si}}O-\left[\overset{CH_3}{\underset{CH_3}{Si}}O\right]_n-\overset{CH_3}{\underset{CH_3}{Si}}OSO_3H+2(CH_3)_2Si\begin{matrix}O-CH_2\\ CH_2\\ CH_2-O\end{matrix}}\xrightarrow{H_2O}$$

$$\rightarrow \mathrm{HOCH_2CH_2OCH_2\overset{CH_3}{\underset{CH_3}{Si}}O\left[\overset{CH_3}{\underset{CH_3}{Si}}O\right]_n-\overset{CH_3}{\underset{CH_3}{Si}}CH_2OCH_2CH_2OH.}$$

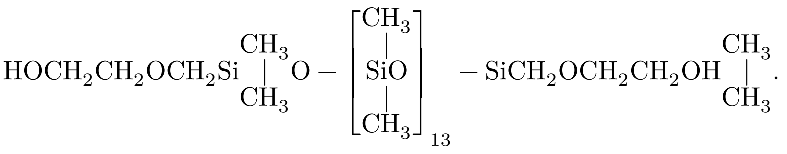
As the experimental results showed, bis-(β-hydroxyethoxymethyl)-polydimethylsiloxanes are obtained in this case; however, the degree of polymerization n in the compounds obtained is somewhat greater than would correspond to the ratio of the components taken for the reaction. With the aid of the reactions described above, dihydric organosilicon alcohols were obtained with numbers of dimethylsiloxane units equal to 1, 2, 12, 13, 20, and 21.

Experimental part

I. Cohydrolysis of dimethyldiethoxysilane and the heterocyclic derivative in the presence of an excess amount of water

A mixture of 6.6 g (0.05 mole) of the heterocyclic derivative $(CH_3)_2SiCH_2OCH_2CH_2O$, 75.0 g (0.5 mole) of dimethyldiethoxysilane, and 100 ml of water acidified with HCl to a weakly acidic reaction was heated; the oily layer was extracted with sulfur ether, washed with water to neutral reaction, and dried over sodium sulfate, after which first the sulfur ether was distilled off from the oily layer at atmospheric pressure, and then, under vacuum, the volatile products of hydrolysis. The maximum vapor temperature during distillation was 200° at 3 mm. As a result of the distillation, 22.1 g of cyclic polydimethylsiloxanes and 12.8 g (25%) of polydimethylsiloxanediol were isolated. The silicon content in the volatile products.

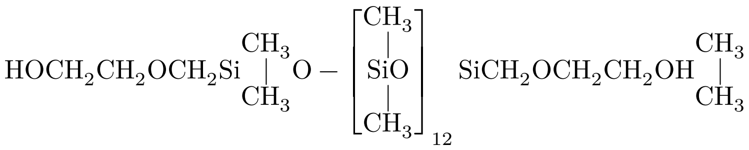
amounted to 38.05% (calculated for $-[(CH_3)_2SiO]-$, 37.85%). The distillation residue was a colorless, transparent, viscous liquid whose elemental composition corresponded to a compound of the following structure:



$$\mathrm{HOCH_2CH_2OCH_2\overset{CH_3}{\underset{CH_3}{Si}}O-\left[\overset{CH_3}{\underset{CH_3}{Si}}O\right]_{13}-\overset{CH_3}{\underset{CH_3}{Si}}CH_2OCH_2CH_2OH.}$$

$C_{36}H_{104}O_{18}Si_{15}$.	Found, %:	C	34.94;	35.10;	H	8.28;	8.38;	Si 33.92;	33.93;	OH 2.74
	Calculated, %:	C	34.70;		H	8.41;		Si 33.78;	OH 2.73	

Under analogous conditions, from 13.2 g (0.1 mole) of $(CH_3)_2SiCH_2OCH_2CH_2O$, 148.3 g (1.0 mole) of $(CH_3)_2Si(OC_2H_5)_2$, and 150 ml of water, 50.7 g of cyclic polydimethylsiloxanes and 44.9 g (44% of theory) of a dihydric alcohol of the structure

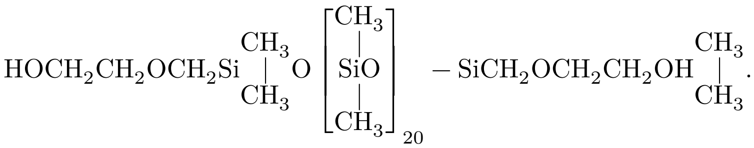


$$HOCH_2CH_2OCH_2Si\begin{array}{c}CH_3\\|\\CH_3\end{array}O-\left[\begin{array}{c}CH_3\\|\\SiO\\|\\CH_3\end{array}\right]_{12}SiCH_2OCH_2CH_2OH\begin{array}{c}CH_3\\|\\CH_3\end{array}$$

were isolated.

$C_{34}H_{102}O_{17}Si_{14}$. Found, %: C 34.75; 34.72; H 8.32; 8.31; Si 33.67; 33.96; OH 2.90
Calculated, %: C 34.87; H 8.37; Si 33.51; OH 2.91

In attempting to isolate a dihydric alcohol with 40 dimethylsiloxane units, it was possible to obtain only an alcohol corresponding to the following structure:



$$HOCH_2CH_2OCH_2Si\begin{array}{c}CH_3\\|\\CH_3\end{array}O\left[\begin{array}{c}CH_3\\|\\SiO\\|\\CH_3\end{array}\right]_{20}-SiCH_2OCH_2CH_2OH\begin{array}{c}CH_3\\|\\CH_3\end{array}.$$

The hydrolysis reaction was carried out under analogous conditions. From 13.2 g (0.1 mole) of $(CH_3)_2SiCH_2OCH_2CH_2O$, 296.5 g (2.0 moles) of $(CH_3)_2-Si-(OC_2H_5)_2$, and 300 ml of water, 90.1 g (55% yield) of cyclic polydimethylsiloxanes and 50.1 g of a dihydric alcohol containing 20 dimethylsiloxane units were isolated.

$C_{50}H_{146}O_{25}Si_{22}$. Found, %: C 33.81; 33.59; H 8.34; 8.25; Si 34.93; 34.83; OH 1.95
Calculated, %: C 34.02; H 8.34; Si 34.98; OH 1.93

II. **Hydrolysis with the calculated amount of water.** To a mixture of 7.4 g (0.05 mole) of dimethyldiethoxysilane and 13.2 g (0.1 mole) of the cyclic derivative, placed in a flask with a stirrer and an attachment for distilling off alcohol, a 3% aqueous solution of hydrochloric acid (1.8 g–0.1 mole) was added dropwise. After the addition of the water, the reaction mixture was heated with simultaneous distillation of ethyl alcohol. The maximum temperature in the vapors was 100°, and in the flask 120°. A total of 5.4 g (n_D^{20} 1.3680) of C_2H_5OH was distilled off (calculated 4.6 g), which is apparently explained by partial distillation of dimethyldiethoxysilane, since during distillation of the distilled product the major portion of it (4.4 g) distilled in the range 70–80°, after which a fraction of 80–120° (0.6 g) was isolated.

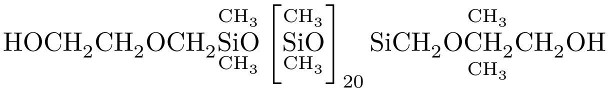
The hydrolysis product was distilled under vacuum. As a result of distillation, 5.4 g of bis-(β-hydroxyethoxymethyl)-hexamethyltrisiloxane were isolated, boiling at 150–151° at 1 mm (n_D^{20} 1.4395; d_4^{20} 1.020; MR found 92.29, calculated 92.75),

$C_{12}H_{32}O_6Si_3$.	Found, %:	C	40.55;	40.32;	H	8.96;	9.13;	Si 22.29;	22.34;	OH 9.68;	9.77
	Calculated, %:	C	40.42;		H	9.04;		Si 23.59;	OH 9.54		

and 3.8 g of bis-(β-hydroxyethoxymethyl)-octamethyltetrasiloxane, b.p. 180° at 1 mm (n_D^{20} 1.4335; d_4^{20} 1.015; MR found 110.7; calculated 111.44).

Found, %: C 38.63; 38.86; H 8.58; 8.76; Si 26.28; 25.66; OH 7.04; 7.36. $C_{14}H_{38}O_7Si_4$. Calculated, %: C 39.04; H 8.89; Si 26.06; OH 7.89.

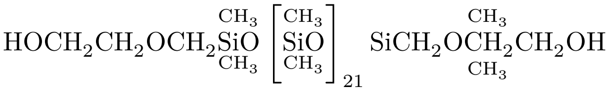
In an analogous manner, upon hydrolysis of 6.6 g (0.05 mole) of the cyclic derivative and 74.1 g (0.5 mole) of dimethyldiethoxysilane in the presence of 9.9 ml of water, 31.3 g of polydimethylsiloxanediol of the following composition was isolated (as the distillation residue after removal of the alcohol and volatile hydrolysis products):



$$\mathrm{HOCH_2CH_2OCH_2}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Si}}}\mathrm{O}\left[\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Si}}}\mathrm{O}\right]_{20}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Si}}}\mathrm{CH_2OCH_2CH_2OH}$$

Found, %: C 33.58; 33.45; H 8.34; 8.30; Si 35.49; 35.74; OH 1.98; 2.19. $C_{50}H_{146}O_{25}Si_{22}$. Calculated, %: C 34.02; H 8.34; Si 34.98; OH 1.93.

III. **Synthesis of polydimethylsiloxanediols by cohydrolysis of the cyclic derivative and of the products of cleavage of octamethylcyclotetrasiloxane by sulfuric acid.** 14.8 g (0.05 mole) of octamethylcyclotetrasiloxane and 2.45 g (0.025 mole) of conc. H_2SO_4 were heated for 3 hours at 90° in a flask equipped with a stirrer, condenser, and thermometer. To the mixture, cooled to 30°, 13.2 g (0.1 mole) of the cyclic derivative was added; the mixture thereby became more viscous and warmed up to 45°, after which water (30 ml) was added dropwise to the resulting mixture. After the introduction of water, the reaction mixture was heated at 90° for 2 hours, then, after cooling, extracted with ether, washed to neutral reaction, and dried over sodium sulfate. After removal of the ether, the hydrolysis product was evacuated to a temperature of 100° at 1 mm. 1.6 g was distilled off; the distillation residue was a light, transparent liquid of the following composition:



$$\mathrm{HOCH_2CH_2OCH_2}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Si}}}\mathrm{O}\left[\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Si}}}\mathrm{O}\right]_{21}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Si}}}\mathrm{CH_2OCH_2CH_2OH}$$

Found, %: C 33.88; 33.83; H 8.24; 8.36; Si 35.26; 35.35; OH 1.70; 1.68. $C_{52}H_{152}O_{26}Si_{23}$. Calculated, %: C 33.96; H 8.33; Si 35.09; OH 1.84.

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Note: Figure translations are in progress. See original paper for figures.

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