SYNTHESIS OF DIMETHYLCYCLOSILOXANES CONTAINING SILICON-ATTACHED FUNCTIONAL GROUPS

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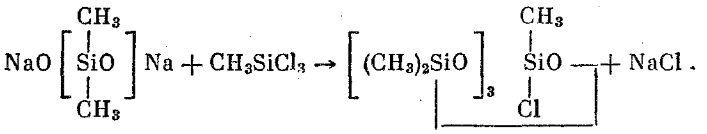
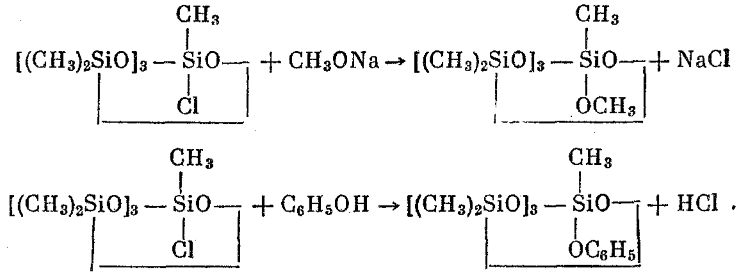
Linear polydimethylsiloxanes are inert substances, and it is difficult to bring about reactions in the chain. It is of great interest both from the theoretical and the practical points of view to develop methods of synthesizing cyclic polydimethylsiloxanes containing reactive groups in the molecular chains. These would make it possible to convert the polymers into various materials with the aid of various chemical reactions. In the present work we undertook the task of developing methods of synthesizing dimethylsiloxane cyclic compounds containing silicon-attached functional groups such as chloro, alkoxy, phenoxy, and amino groups which, being highly reactive, may serve as functional groups for further transformations. In a previous investigation it was shown that by double decomposition between the disodium salt of 1,5-dihydroxyhexamethyltrisiloxane and alkoxydichloromethylsilanes, ethoxy- and butoxy-hexamethylcyclotetrasiloxanes could be synthesized [1]. However, when this reaction was applied for the synthesis of compounds containing methoxy and phenoxy groups, satisfactory results were not obtained. In the present work we had the object of synthesizing dimethylcyclosiloxanes containing silicon-attached halogen. The successful development of such a method would open up wide possibilities for the synthesis of dimethylcyclosiloxanes containing various silicon-attached functional groups which might be prepared by the replacement of the mobile halogen by alkoxy, acyl, amino groups, etc.

For the synthesis of chloroheptamethylcyclotetrasiloxane we carried out double decomposition between the disodium derivative of 1,5-dihydroxyhexamethyltrisiloxane and trichloromethylsilane. On studying the exchange reaction between the disodium derivative of 1,5-dihydroxyhexamethyltrisiloxane and trichloromethylsilane, we showed that, with excess of trichloromethylsilane under mild conditions, it was possible to leave one silicon-attached chlorine unreplaced and ensure that reaction led to the formation of cyclic products of low molecular weight. The reaction went as follows:



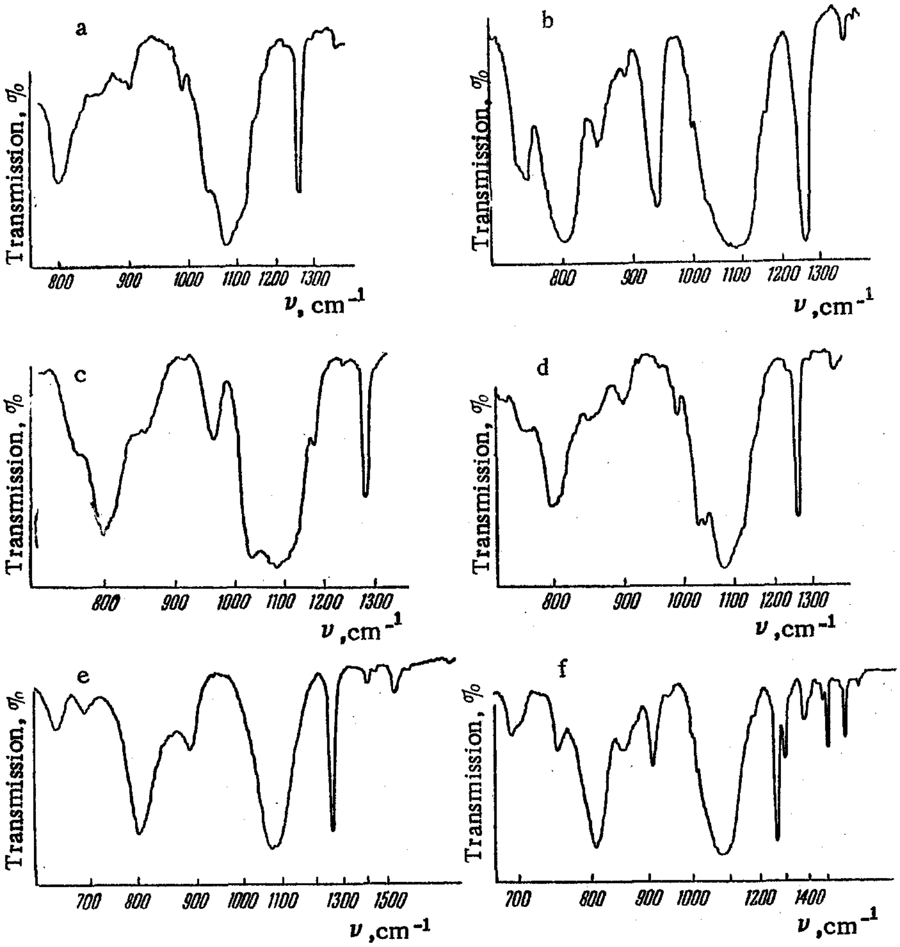
$$\mathrm{NaO}\left[\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{SiO}}}\right]\mathrm{Na} + \mathrm{CH_3SiCl_3} \rightarrow \left[(\mathrm{CH_3})_2\mathrm{SiO}\right]_3\,\underset{\mathrm{Cl}}{\overset{\mathrm{CH_3}}{\mathrm{SiO}}}\text{—} + \mathrm{NaCl}.$$

We then obtained chloroheptamethylcyclotetrasiloxane in about 30% yield together with other compounds that could not be distilled in a vacuum. A study was made of the replacement of chlorine in chloroheptamethylcyclotetrasiloxane by methoxy and by phenoxy under the action of sodium methoxide and of phenol, and it was found that reaction proceeds as below with formation of methoxyheptamethylcyclotetrasiloxane and heptamethylphenoxycyclotetrasiloxane:



$$[(\mathrm{CH_3})_2\mathrm{SiO}]_3-\underset{\mathrm{Cl}}{\overset{\mathrm{CH_3}}{\mathrm{SiO}}}\text{—} + \mathrm{CH_3ONa} \rightarrow [(\mathrm{CH_3})_2\mathrm{SiO}]_3-\underset{\mathrm{OCH_3}}{\overset{\mathrm{CH_3}}{\mathrm{SiO}}}\text{—} + \mathrm{NaCl}$$

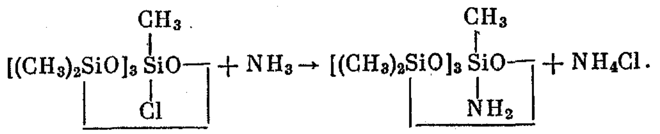
$$[(\mathrm{CH_3})_2\mathrm{SiO}]_3-\underset{\mathrm{Cl}}{\overset{\mathrm{CH_3}}{\mathrm{SiO}}}\text{—} + \mathrm{C_6H_5OH} \rightarrow [(\mathrm{CH_3})_2\mathrm{SiO}]_3-\underset{\mathrm{OC_6H_5}}{\overset{\mathrm{CH_3}}{\mathrm{SiO}}}\text{—} + \mathrm{HCl}.$$



Infrared spectra of organoalkoxycyclotetrasiloxanes: a) methoxyhexamethylcyclotetrasiloxane; b) heptamethylphenoxycyclotetrasiloxane; c) diethoxyhexamethylcyclotetrasiloxane; d) dibutoxyhexamethylcyclotetrasiloxane; e) aminoheptamethylcyclotetrasiloxane; f) anilinoheptamethylcyclotetrasiloxane.

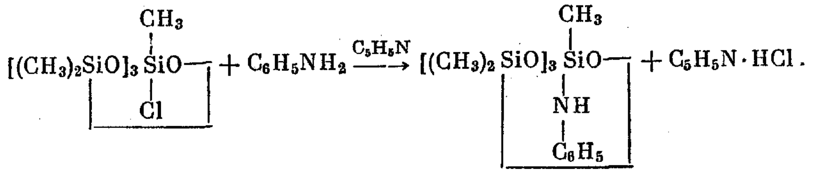
However, these reactions were accompanied by other processes, which probably involved ring opening and polymerization. This is confirmed by the fact that in the isolation of methoxyheptamethylcyclotetrasiloxane and heptamethylphenoxycyclotetrasiloxane there were also obtained polymeric substances which could not be distilled in a vacuum.

When chloroheptamethylcyclotetrasiloxane was treated with liquid ammonia, reaction readily went as follows:



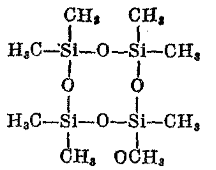
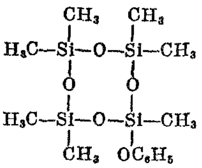
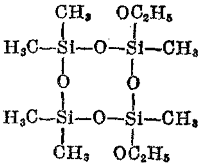
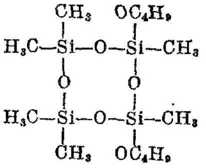
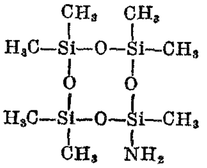
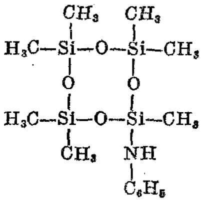
$$[(CH_3)_2SiO]_3\underset{Cl}{\overset{CH_3}{Si}}O + NH_3 \rightarrow [(CH_3)_2SiO]_3\underset{NH_2}{\overset{CH_3}{Si}}O + NH_4Cl.$$

We then obtained aminoheptamethylcyclotetrasiloxane in 60.4% yield. When chloroheptamethylcyclotetrasiloxane was treated with aniline, we obtained anilinoheptamethylcyclotetrasiloxane in about 40% yield. Reaction went as follows:



$$[(CH_3)_2SiO]_3\underset{Cl}{\overset{CH_3}{Si}}O + C_6H_5NH_2 \xrightarrow{C_5H_5N} [(CH_3)_2SiO]_3\underset{\substack{NH\\ C_6H_5}}{\overset{CH_3}{Si}}O + C_5H_5N\cdot HCl.$$

Physical Properties of Compounds Synthesized

Cyclosiloxane	Formula	B.p. in °C (p in mm)	d_4^{20}	n_D^{20}	MR	
					found	cal-culated
Methoxyhexa-methylcyclo-tetrasiloxane		75—77 (1)	0,9916	1,3992	76,13	75,62
Heptamethyl-phenoxycyclo tetrasiloxane		119—123 (1,5)	1,0378	1,4442	95,73	95,05
Diethoxy-hexamethyl-cyclotetra-siloxane		162—186 (4)	1,0100	1,4029	85,98	85,69
Dibutoxyhexa-methylcyclo-tetrasiloxane*		96—114 (1)	0,9804	1,4103	104,25	104,24
Aminohepta-methylcyclo-tetrasiloxane		40,5 (1)	1,0208	1,4065	72,90	72,91
Anilinohepta-methylcyclo-tetrasiloxane		136—139 (5)	0,9711	1,4482	96,23	97,23

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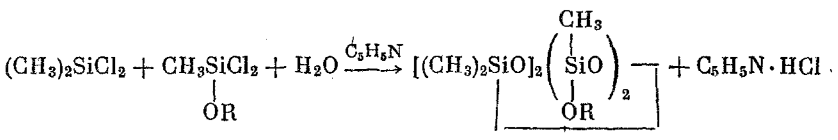
*The positions of the alkoxy groups were not established.

These reactions show that, by the replacement of the mobile chlorine in chloroheptamethylcyclotetrasiloxane, it is possible to prepare cyclic compounds containing various silicon-attached functional groups.

Apart from the compounds described, diethoxyhexamethylcyclotetrasiloxane was prepared by the cohydrolysis of dichlorodimethylsilane with dichloroethoxymethylsilane, and dibutoxyhexamethylcyclotetrasiloxane by the cohydrolysis of dichlorodimethylsilane with butoxydichloromethylsilane:



$$(CH_3)_2SiCl_2 + \underset{OR}{CH_3SiCl_2} + H_2O \xrightarrow{C_5H_5N} [(CH_3)_2SiO]_2\left(\underset{OR}{\overset{CH_3}{SiO}}\right)_2 + C_5H_5N\cdot HCl$$

All the compounds synthesized are clear, colorless liquids, readily soluble in benzene, toluene, ether, and acetone. Their physical properties are given in the table. The structures of the products were determined from their infrared spectra and elementary compositions. As will be seen from the figure, for all the compounds synthesized an intense SiO absorption band was observed in the region of about 1080 cm^{-1}, which corresponds to the SiO vibration in an eight-membered ring; absorption bands in the regions of 800 and 1260 cm^{-1} are characteristic for the $Si-CH_3$ bond.

EXPERIMENTAL

Dichloromethoxymethylsilane and the disodium derivative of 1,5-dihydroxyhexamethyltrisiloxane were synthesized by known methods [2,3].

Dichloromethylphenoxysilane. A four-necked flask fitted with oil-sealed stirrer, dropping funnel, thermometer, and reflux condenser protected by a calcium chloride tube was charged with 75 g (0.5 mole) of trichloromethylsilane. With vigorous stirring a solution of 47 g (0.5 mole) of phenol in 70 g of dry benzene was added dropwise from the dropping funnel, and the mixture was heated at 80° for 6 hr. Benzene was distilled from the reaction product. By repeated fractionation we isolated dichloromethylphenoxysilane, b.p. 198.5° (740 mm), in 22.1% yield; d^{20}_4 1.2063; $n^{20}D$ 1.4922. Found: Cl 40.00; Si 13.45; H 3.80; Cl 34.31%. $C_7H_8OSiCl_2$. Calculated: C 50.57; Si 13.52; H 3.36; Cl 34.29%.

Chloroheptamethylcyclotetrasiloxane. A four-necked flask fitted with oil-sealed stirrer, thermometer, and reflux condenser protected by a calcium chloride tube was charged with 28.4 g (0.1 mole) of the disodium derivative of 1,5-dihydroxyhexamethyltrisiloxane and 45 g of dry benzene. With vigorous stirring 14.9 g of trichloromethylsilane was added gradually. The temperature of the reaction mixture then rose to 70-80°. Stirring was continued further for 1 hr. The cooled mixture was filtered, and benzene was distilled from the liquid part. As a result of fractionation we isolated chloroheptamethylcyclotetrasiloxane, b.p. 79-81° (14 mm). Found: Cl 11.6%. $C_7H_{21}O_4Si_4Cl$. Calculated: Cl 11.2%.

Methoxyheptamethylcyclotetrasiloxane. A suspension of 1.15 g (0.05 mole) of sodium in 11 g of dry ether was prepared in a four-necked flask fitted with oil-sealed stirrer, thermometer, dropping funnel protected by a calcium chloride tube, and reflux condenser protected by a calcium chloride tube. With vigorous stirring, 1.62 g (0.05 mole) of chloroheptamethylcyclotetrasiloxane was added to the suspension.* The reaction mixture was stirred further for 3 hr; sodium chloride was then filtered off, and ether was distilled off. As a result of repeated fractionation we isolated methoxyheptamethylcyclotetrasiloxane, b.p. 75-77° (1 mm); yield 26.1%. Found: C 30.13, 30.26; Si 35.2, 35.41; H 7.72, 7.80%. $C_8H_{24}O_5Si_4$. Calculated: C 30.76; Si 35.90; H 7.69%.

Heptamethylphenoxycyclotetrasiloxane. A four-necked flask fitted with oil-sealed stirrer, thermometer, reflux condenser protected by a calcium chloride tube, and tube for the passage of nitrogen was charged with 17.6 g (0.2 mole) of chloroheptamethylcyclotetrasiloxane and 5.7 g (0.22 mole) of phenol. The reaction mixture was heated in an oil bath at 120° for 8 hr, and then nitrogen was passed through the cooled reaction mixture for 18 hr to remove HCl. Phenol was distilled from the reaction product, and the residue was vacuum-fractionated. As a result of repeated fractionation we isolated heptamethylphenoxycyclotetrasiloxane, b.p. 119-123° (1.5 mm); yield 41.4%. Found: C 42.3, 42.40; Si 30.19, 30.50; H 6.53, 6.66%. $C_{13}H_{28}O_5Si_4$. Calculated: C 41.47; Si 29.54; H 6.94%.

Aminoheptamethylcyclotetrasiloxane. A four-necked flask fitted with oil-sealed stirrer, condenser protected by a calcium chloride tube, and thermometer was cooled with a mixture of solid carbon dioxide and acetone and charged with 20 g of liquid ammonia. Slow dropwise addition was made of 15.8 g (0.05 mole) of chloroheptamethylcyclotetrasiloxane. The reaction mixture was stirred for 1 hr; ammonia was then evaporated off, and 20 ml of ether was added. Ammonium chloride was filtered off, and ether was distilled off. As a result of fractionation we isolated aminoheptamethylcyclotetrasiloxane, b.p. 40.5° (1 mm); yield 60.4%. Found: C 28.37, 28.60; Si 36.90, 36.54; H 7.65, 7.98; N 3.95, 3.24%. $C_7H_{23}O_4N$. Calculated: C 28.20; Si 37.70; H 7.76; N 4.7%.

Anilinoheptamethylcyclotetrasiloxane. A four-necked flask fitted with oil-sealed stirrer, condenser protected by a calcium chloride tube, and thermometer was charged with 4.65 g (0.05 mole) of aniline and 5.5 g

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* The lack of mention of an essential reactant, methanol, is not due to an error in translation; there is no mention of methanol in the original. – Publisher.

(0.7 mole) of pyridine. To the mixture dropwise addition was made of 1.98 g (0.05 mole) of chloroheptamethylcyclotetrasiloxane, and the reaction mixture was then heated to 60° and stirred for 6 hr. Pyridine hydrochloride was filtered off. As a result of repeated fractionation we isolated anilinoheptamethylcyclotetrasiloxane, b.p. 136 to 139° (5 mm); yield 39.2%. Found: C 38.48, 38.42; Si 29.64, 29.68; H 7.53, 7.49; N 3.59, 3.46%. $C_{13}H_{28}O_4N$. Calculated: C 41.8; Si 30.00; H 7.23; N 3.76%.

Diethoxyhexamethylcyclotetrasiloxane. A four-necked flask fitted with oil-sealed stirrer, reflux condenser protected by a calcium chloride tube, dropping funnel protected by a calcium chloride tube, and thermometer was charged with 142 g of pyridine, 156 g of benzene, and 14.9 g of water. From the dropping funnel with vigorous stirring we added a mixture of 63.6 g (0.4 mole) of dichlorodimethylsilane.....* Stirring was continued further for 1 hr. Pyridine hydrochloride was filtered from the cooled mixture; the liquid part was washed four times with water and dried over anhydrous sodium sulfate. Benzene and pyridine were distilled from the liquid part. As a result of repeated fractionation we isolated diethoxyhexamethylcyclotetrasiloxane, b.p. 172-186° (4 mm); yield 7.3%. Found: C 33.68, 33.40; Si 30.67, 30.56; H 8.14, 7.95%. $C_{10}H_{28}O_6Si_4$. Calculated: C 33.70; Si 31.46; H 7.86%.

Dibutoxyhexamethylcyclotetrasiloxane. By a procedure analogous to that used for the preparation of diethoxyhexamethylcyclotetrasiloxane, after repeated fractionation we obtained dibutoxyhexamethylcyclotetrasiloxane, b.p. 92-114° (1 mm); yield 6.7%. Found: C 40.97, 41.00; Si 26.44, 25.95; H 8.85, 8.86%. $C_{14}H_{36}O_6Si_4$. Calculated: C 40.77; Si 27.18; H 8.73%.

L. Tartakovskaya, a student of the M. V. Lomonosov Moscow Institute of Fine Chemical Technology, took part in the experimental work.

SUMMARY

1. Double decomposition between the sodium derivative of 1,5-dihydroxyhexamethyltrisiloxane and trichloromethylsilane with excess of the latter, proceeds in the direction of the formation of cyclic products of low molecular weight.

2. The replacement of chlorine in chloroheptamethylcyclotetrasiloxane by the methoxy or phenoxy group proceeds in a complex manner, and in addition to methoxy- or phenoxy-heptamethylcyclotetrasiloxane, polymeric products are also formed.

3. The replacement of chlorine in chloroheptamethylcyclotetrasiloxane by the amino or anilino group occurs readily with formation of amino- or anilino-heptamethylcyclotetrasiloxane.

4. Cohydrolysis reactions of dichlorodimethylsilane with dichloroethoxymethylsilane and with butoxydichloromethylsilane were investigated, and new cyclic compounds were synthesized, namely, diethoxyhexamethylcyclotetrasiloxane and dibutoxyhexamethylcyclotetrasiloxane.

LITERATURE CITED

1. K. A. Andrianov and Lora M. Volkova, Vysokomolek. soed. 3, 1580 (1961).
2. K. A. Andrianov and A. A. Zhdanov, Dokl. AN SSSR 114, 1005 (1957).
3. K. A. Andrianov and A. A. Kazakova, Zh. obshch. khimii 29, 3754 (1959).

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*This sentence is incomplete in the original; the second component of the mixture is clearly dichloroethoxymethylsilane. – Publisher.