# SYNTHESIS OF ORGANOSILOXANES CONTAINING

## SILACYCLOHEXANE UNITS

K. A. Andrianov, M. V. Sobolevskii, UDC 542.91:546.287
M. B. Lotarev, A. M. Lazareva, D. V. Nazarova, and A. S. Shapatin

One of the methods for the preparation of mixed cycloorganosiloxanes is the condensation of  $\omega, \omega'$ -dihydroxypolyalkyl(aryl)siloxanes with organochlorosilanes [1-4], which is accomplished by the scheme:

$$\begin{array}{c} \mathbf{R} \\ \mathbf{HO} - (\mathbf{Si} - \mathbf{O})_m \mathbf{H} + \mathbf{R'} \mathbf{R''} \mathbf{SiCl}_2 \xrightarrow{\mathbf{Rs'''N}} & \boxed{\mathbf{R} & \mathbf{R'} \\ - (\mathbf{Si} - \mathbf{O})_m - \mathbf{Si} - \mathbf{O} - + 2\mathbf{Rs'''N} + 2\mathbf{Rs'''N} + \mathbf{R''} \\ \mathbf{R} & \mathbf{R''} \end{array}$$
(A)

where m = 2-4.

In order to obtain cycloorganosiloxanes, containing organic frames composed of silicocarbon heterocycles, we made a study of the heterofunctional condensation reaction, which proceeds according to the schemes:





Fig. 1. Infrared spectra of tetramethylsilacyclohexyltrisiloxane (I) and octamethyldi(silacyclohexyl)hexacyclosiloxane (II).

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 10, pp. 2300-2303, October, 1971. Original article submitted July 13, 1970.

© 1972 Consultants Bureau, a division of Plenum Publishing Corporation, 227 West 17th Street, New York, N. Y. 10011. All rights reserved. This article cannot be reproduced for any purpose whatsoever without permission of the publisher. A copy of this article is available from the publisher for \$15.00.

1. Physicochemical Characteristics of Cycloorganosiloxanes	1, %	ŝ	32,06	32,06	33,63	
	Calculated	H	8 <sup>,</sup> 39.	8 <b>,</b> 39,	8,33	
		υ	41,22	<b>41,2</b> 2	39,29	
	Found, 7/a	S	32,60	32,05	33,68 33,75	
		H	8,67	8,25	8,39 8,41	
		υ	41,58	41,71 41,23	39,28 39,44	
	Calculated	mol. wt.	262	524	336	•
		MR	1	l	86,57	
	Found	mol. wt.	250	253	368	
		MR		I	86,06	
	$d_4^{20}$			I	1,0035	
	$D_{D}^{n}$		1	[	1,4275	
	Mp, °C		3133	62,5 63,5	l	
	Bp, °C (p, mm of Hg)		4446 (1)	I	93—95 (4)	
	Formula of compound		[(GH <sub>9</sub> ) <sub>2</sub> SiOJ <sub>2</sub>	[(GH <sub>2</sub> ) <sub>1</sub> SiO] <sub>4</sub>		
TABLE	No.		-	=	III	

Cycloorganosiloxanes
of
Characteristics
Physicochemical
<b>FABLE 1.</b>

$$\begin{array}{c|c} CH_3 & CH_3 & CH_3 \\ I & I \\ Cl-Si-O-(Si-O)_m - Si-Cl + \\ I \\ CH_3 & CH_3 \\ CH_3 & CH_3 \\ HO \\ OH \end{array} \xrightarrow{(c_6H_6N)} CH_3 \\ CH_3 \\$$

where m = 0-1.

From the products of these reactions we isolated and characterized three new cycloorganosiloxanes, the properties of which are given in Table 1. It is interesting to mention that compound (II) is formed in up to 34% yield, whereas the maximum yield of compound (I) is 13%, in which connection the selected solvent has an important effect on the direction of the reaction. Thus, for example, the formation of compound (II) in 15% yield is observed when the condensation reaction is run in ether according to scheme (B), whereas compound (I) is formed in benzene. When the reaction is run in ether according to scheme (C) the yield of compound (I) is 13% and that of compound (II) is 30%, while in benzene the yield of compound (II) is 34%.

The difficulty of forming compound (I) and the easier formation of compound (II) testify to the possible stepwise character of the condensation reaction. It is possible to postulate that the reaction proceeds according to the scheme

$$\begin{array}{c} CH_{3} & CH_{3} \\ 2HO - Si - O - Si - OH + \\ I \\ CH_{3} & CH_{3} \end{array} \xrightarrow{C_{3}H_{3}N} HO \begin{pmatrix} CH_{3} \\ -Si - O \\ -Si - O \\ CH_{3} \end{pmatrix}_{2} - Si - O \begin{pmatrix} -H_{3} \\ -Si - O \\ -Si - O \\ CH_{3} \end{pmatrix}_{2} - H$$
(D)

and then

$$\begin{array}{c} CO_{3} \\ HO\left(-\underset{CH_{3}}{\overset{j}{\underset{D}{\text{CH}_{3}}}}\right)_{2} - Si - O\left(-\underset{CH_{3}}{\overset{j}{\underset{D}{\text{CH}_{3}}}}\right)_{2} H + \underbrace{Si}_{Cl} - \underbrace{\underset{C_{8}H_{8}N}{\overset{c}{\underset{D}{\text{CH}_{3}}}} - \left(\underset{CH_{3}}{\overset{j}{\underset{D}{\text{CH}_{3}}}\right)_{4} \left(-\underset{CH_{3}}{\overset{c}{\underset{D}{\text{CH}_{3}}}}\right)_{2} \end{array} \right)$$
(E)

In studying the hydrolysis of dichlorosilacyclohexane it was shown by a number of authors [5-7] that dichlorosilacycloalkanes are little inclined to undergo cycloformation, probably due to the spatial configuration of the silicocarbon heterocycles.

The formation of compound (II) was also proved by examining the IR spectra of compounds (I) and (II), which are shown in Fig. 1. As can be seen from an examination of the frequencies of the vibrations attributed to the Si-O bond, in the case of compound (I) this frequency, namely at 1028 cm<sup>-1</sup>, lies in the region of the characteristic Si-O frequencies for cyclic trimers  $(1010-1030 \text{ cm}^{-1})$ , whereas in the spectrum of compound (II) this band lies in the 1068 cm<sup>-1</sup> region, which is characteristic for cyclic siloxanes containing a number of silicon atoms equal to four or greater. The 912 cm<sup>-1</sup> band, attributed to the vibrations of the silacyclohexane ring [8] in compound (II), has a high intensity, which can be regarded as proof that a large amount of silacyclohexane units is present.

In contrast to compounds (I) and (II), compound (III) is formed in high yield (65%) when the reaction is carried out according to scheme (C) if the synthesis is run in 1,2-dimethoxyethane, using an equimolar ratio of the components (simultaneous addition of the reactants in pyridine solution at 50°C).

### EXPERIMENTAL METHOD

The  $\omega, \omega'$ -dichlorodimethylsiloxanes and  $\omega, \omega'$ -dihydroxydimethylsiloxanes were obtained as described in [9].

Condensation according to schemes (B) and (C) was accomplished in the following manner: in a fournecked flask, equipped with a sealed stirrer, two dropping funnels and a reflux condenser, was placed a solution of 17.4 g of pyridine in 150 ml of absolute ether. From the dropping funnels were added in drops 13.2 g of dihydroxysilacyclohexane in 130 ml of absolute ether and 20.3 g of tetramethyldichlorodisiloxane in 130 ml of absolute ether. The flask was cooled in cold water during the addition of the reactants. At the end of addition the reaction mixture was heated at  $35^{\circ}$  for 1 h, after which the obtained precipitate was dissolved in water, and the ether layer was separated and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Then the solvent was distilled off, while the residue (30 g) was fractionally distilled in vacuo.

The following fractions were isolated: with bp  $59-60^{\circ}$  (5 mm), 4 g (13%), which represented tetramethylsilacyclohexylcyclotrisiloxane (it crystallized in the refrigerator), and with bp  $89-167^{\circ}$  (5 mm), 9 g (30%), which represented octamethyldi(silacyclohexyl)cyclohexasiloxane (the fraction crystallized at room temperature, and was recrystallized from methanol).

#### CONCLUSIONS

1. A study was made of the heterofunctional condensation of  $\omega, \omega'$ -dichloro(dihydroxy)dimethylsiloxane with dihydroxy(dichloro)silacyclohexane.

2. Three new cycloorganosiloxanes, containing silacyclohexane groups in the chain, were synthesized.

3. It was shown that the silacyclohexane difunctional derivatives are specific in the cycloformation reaction.

#### LITERATURE CITED

- 1. US Patent No. 3358009, Cl. 260-448, 2, 12/12/1967; Offic. Gaz., 845, 717 (1967).
- 2. US Patent No. 3340289, Cl. 260-448, 2, 5/9/1967; Offic. Gaz., 842, 323 (1967).

3. Belgian Patent No. 635646 (US priority as of 18/12/1961); Chem. Abstrs., 61, 13452 (1964).

- 4. US Patent No. 3367955, Cl. 260-448, 2, 18/12/1961; Chem. Abstrs., 65, 900 (1966).
- 5. F. Bayer and H. Post, J. Org. Chem., 28, 1941 (1963).
- 6. N. S. Nametkin, V. M. Vdovin, É. D. Babich, and T. N. Arkhipova, Dokl. Akad. Nauk SSSR, <u>171</u>, 1345 (1967).
- 7. G. Oshesky and F. Bentley, J. Am. Chem. Soc., 79, 2057 (1957).
- 8. T. Takiguchi, J. Am. Chem. Soc., 81, 2359 (1959).
- 9. W. Patnode and D. Wilcock, J. Am. Chem. Soc., 68, 358 (1946).