IR spectroscopic study of the reaction of dihydroxyorganocyclosiloxanes with 2,2-dimethyl-1-oxa-2-silacyclohexane

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The reaction of various mono- and dihydroxyorganocyclosiloxanes with 2,2-dimethyl-1-oxa-2-silacyclohexane was studied by IR spectroscopy. A series of new bis[dimethyl(hydroxybutyl)siloxy]organocyclosiloxanes were obtained.

Key words: 2,6-bis[dimethyl(hydroxybutyl)siloxy]-2,4,4,6,8,8-hexamethylcyclo-2,4,6,8-tetrasiloxane, 2,6-bis[dimethyl(hydroxybutyl)siloxy]-2,4,4,6,8,8-hexaethylcyclo-2,4,6,8-tetrasiloxane, 2,8-bis[dimethyl(hydroxybutyl)siloxy]-2,4,4,6,6,8,10,10,12,12-decamethylcyclo-2,4,6,8,10,12-hexasiloxane, 2,8-bis[dimethyl(hydroxybutyl)siloxy]-2,8-diphenyl-4,4,6,6,10,10,12,12-octamethylcyclo-2,4,6,8,10,12-hexasiloxane, 2,2-dimethyl-1-oxa-2-silacyclohexane, dihydroxyorganocyclosiloxanes, IR and NMR spectra.

Organosilicon compounds containing hydroxy groups in the organic moiety are of interest for obtaining carbosiloxane block-copolymers. The reactions of hydroxysilanes with silaoxacyclohexanes is a convenient method for synthesizing these alcohols.[1—3]

In the present work we studied the reaction of dihydroxyorganocyclosiloxanes with 2,2-dimethyl-1-oxa-2-silacyclohexane (SOCH) according to Scheme 1.

The course of the reaction was monitored by IR spectroscopy. Since the frequencies of the stretching vibrations of hydroxy groups in aliphatic alcohols and silanols are within the 3640—3620 and 3700—3680 cm^{-1} regions, respectively,[2] the completeness of the reactions can be determined from changes in the relative intensities of the ν(Si—OH) and ν(COH) bands in the spectra of dilute solutions (CCl_4, $C = 0.002 \div 0.0001$ mol L^{-1}) of reaction mixtures.

To establish the structure of the reaction products, we studied the IR spectra of the starting dihydroxyorganocyclosiloxanes (**1**—**10**) and of model organosilicon alcohols, $Me_2EtSiC_4H_8OH$ and $[HOC_4H_8SiMe_2]_2O$. The IR spectrum of a dilute solution (CCl_4, $C = 0.002$ mol L^{-1}) of monofunctional ethyldimethyl(hydroxybutyl)silane incorporating a hydroxybutyl moiety, which is also contained in the organosilicon alcohols synthesized by us, displays only one absorption band of the "free" OH group at 3632 cm^{-1}. Di(hydroxybutyl)tetramethyldisiloxane, which contains two hydroxy groups and one siloxane group, can form both intra- and intermolecular hydrogen bonds. The IR spectrum of this compound recorded without a solvent contains a very intense ν(OH) absorption band at 3300 cm^{-1}. Three absorption bands in the region of OH stretching vibrations are observed in a CCl_4 solution, namely, those at 3632, 3495, and 3347 cm^{-1}. The band at 3347 cm^{-1}, which can be attributed to intermolecular hydrogen bonds, disappears in strongly diluted solutions. The remaining bands correspond to ν(OH) of the free OH group and to intramolecular chelates, C—OH...O, formed either through two hydroxyls or through one hydroxyl and the oxygen atom of the siloxane bond. It was reported previously that the closure of a 14-membered ring through two hydroxyls is less probable than the formation of an eight-membered chelate.[4] It can therefore be assumed that the absorption band at 3495 cm^{-1} observed in a dilute solution is due to intramolecular bonding of an OH group with the oxygen atom of the siloxane bond.

We found that the ability of the starting dihydroxyorganocyclosiloxanes **1**—**10** to form intramolecular hydrogen bonds markedly depends on the size of the cyclosiloxane ring. The IR spectra of dilute solutions (CCl_4, $C = 0.002 \div 0.0001$ mol L^{-1}) of compounds **1**—**4** contain only absorption bands of the free OH group at 3695 cm^{-1} for methyl derivatives and at 3689 cm^{-1} for phenyl-substituted organocyclosiloxanes. Under the same conditions, the spectrum of 2,6-dihydroxyoctaethylcyclopentasiloxane (**5**) contains not only a band of the free OH group, but also a very weak absorption band at 3550 cm^{-1}, which is probably caused by intramolecular hydrogen bonds. Two conformations are possible for 2,8-dihydroxyoctaethylcyclohexasiloxane (**6**), namely, *cis* (boat conformation) and *trans* (folded conformation).[5] The IR spectrum of the *trans* conformer without a

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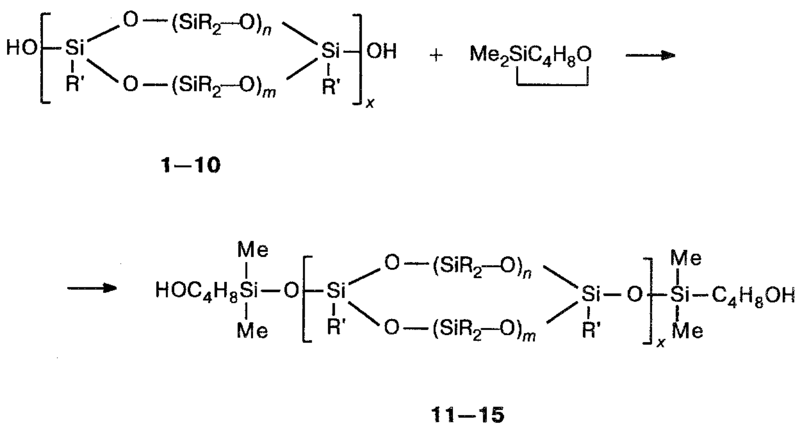
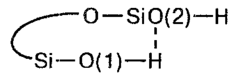
Scheme 1



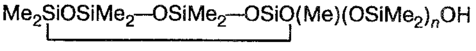
1,11: R, R' = Me (*n*, *m* = 1)
2,12: R, R' = Et (*n*, *m* = 1)
3: R = Me; R' = C_6H_5 (*n*, *m* = 1)
4: R, R' = Ph (*n*, *m* = 1)
5: R, R' = Et (*n* = 1, *m* = 2)
6, 13: R, R' = Me (*n*, *m* = 2)
7, 14: R = Me, R' = Ph (*n*, *m* = 2)
8, 15: R = Me, R' = Ph (*n*, *m* = 2)
9: R, R' = Me (*n* = 2, *m* = 3)
10: R, R' = Me (*n*, *m* = 3)
1—7, 9—14 (*x* = 1)
8, 15 (*x* = 5)

solvent contains one broad band at 3267 cm^{-1} due to intermolecular hydrogen bonds. The spectrum of its solution contains a band of the free OH group at 3695 cm^{-1} and a band at 3555 cm^{-1}, which probably corresponds to intramolecular hydrogen bonds. The IR spectrum of *cis*-**6** recorded without a solvent contains one absorption band at 3276 cm^{-1}. In a CCl_4 solution (C = 0.002 mol L^{-1}), several absorption bands are observed: one at 3277 cm^{-1}, which disappears after dilution to C = 0.0001 mol L^{-1} and corresponds to intermolecular hydrogen bonds; one at 3481 cm^{-1} with a shoulder at 3575 cm^{-1}, which probably originates from intramolecular hydrogen bonds, and a band of free OH groups consisting of two components at 3690 and 3678 cm^{-1}. It is possible that the band at 3690 cm^{-1} belongs to the free OH group, while that at 3678 cm^{-1} corresponds to the OH group whose oxygen atom participates in hydrogen bond formation as an electron donor.[5,6]

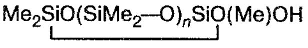


The IR spectrum of a solution of 2,6-dihydroxydiphenyloctamethylcyclohexasiloxane (**7**) contains bands at 3689 and 3560 cm^{-1} (ν(OH) of the free and intramolecular bonds) along with an absorption band at 3624 cm^{-1} attributable to the intramolecular interaction of the Si—OH group with π-electrons of the phenyl ring. Such interaction has been observed previously for α,ω-dihydroxydiphenylsiloxanes.[7—9] The intensity of the band of "bonded" OH groups in the spectra of dihydroxymethylcyclohepta- and dihydroxymethyloctasiloxanes (**9**, **10**) is much stronger than the band of free OH groups. Hence, the degree of association increases with increase in the siloxane ring size, although the strength of intramolecular hydrogen bonds increases, as judged by the displacement of ν(OH).

To determine the nature of intramolecular interactions, we studied the IR spectra of four monohydroxycyclosiloxanes:


$Me_2SiOSiMe_2—OSiMe_2—OSiO(Me)(OSiMe_2)_nOH$

(**16**: n = 1; **17**: n = 3) and


$Me_2SiO(SiMe_2—O)_nSiO(Me)OH$ (**18**: n = 3; **19**: n = 4).

Compound **16** displays one absorption band of the free OH group, and compounds **17—19** display additional absorption bands of bonded OH groups. A comparison of mono- and 2,6-dihydroxycyclohexasiloxanes (**19** and **6**) shows that their solutions in CCl_4 display quite similar bands of the free and bonded OH groups at 3695 and 3555 cm^{-1}. Only one variant of SiOH...OSi intramolecular interaction is possible in the case of compounds **17**—**19**. Hence, one can assume that the intramolecular hydrogen bond in compounds **7**—**10** is formed through an oxygen atom of the siloxane ring rather than through two hydroxy groups. Hence, the ring size and the length of the hydroxysiloxane chain alter the flexibility of the molecule and thus affect the possibility of formation of intramolecular chelate bonds. Chelate structures are formed starting from the ring of cyclopentasiloxane, and the degree of association increases with increasing ring size.

It has been shown previously that hydroxysilanes react with silaoxacyclohexanes in the presence of a catalyst.[1—3] Taking into account the known lability of the cyclosiloxane bond and the possible polymerization of the cyclosiloxane moiety, we carried out a series of experiments in the absence of a catalyst. The mixture of 2,8-dihydroxydiphenyloctamethylcyclohexasiloxane with SOCH is heterogeneous at room temperature, and the reaction hardly proceeds at all over a period of two days, both without a solvent and in solution. At 50—60 °C, a ν(COH) absorption band appears, whose intensity increases over time, while the intensity of ν(SiOH) decreases until its complete disappearance. Compounds **1**, **2**, and **6** behave similarly. Owing to the high molecular mass of **8** and the low concentration of hydroxy groups in it, this compound reacts with SOCH much less readily. When equimolar amounts of the reagents are heated for 9 h at 50—60 °C, the reaction does not occur, and the ν(SiOH) absorption band totally disappears after some time only if a significant excess of SOCH is used. Compounds **9**, **10**, and **19** react with difficulty: according to the IR spectra, the completeness of the reaction after 15 h at 80 °C was as low as 40—50 %. The participation of silanol groups in the formation of intramolecular hydrogen bonds is likely to hinder the completion of the reaction.

The physicochemical constants of the compounds obtained are presented in Table 1. Their structures were confirmed by elemental analyses and NMR spectra.

Experimental

IR spectra were recorded on a Specord M-82 spectrophotometer. Spectra of dilute solutions were measured in mountable cells with a 1—2 cm thickness. NMR spectra were obtained on a Bruker WP-200SY spectrometer at a working frequency of 200.13 MHz in CCl_4 using $SiMe_4$ as the internal standard. The starting hydroxycyclosiloxanes and SOCH were obtained according to known procedures.[9—12]

Synthesis of compound 14. A mixture of compound **7** (0.203 g) and SOCH (0.12 g) was heated for 5 h at 55—60 °C until complete disappearance of the band at 3689 cm^{-1}. The warm solution was evacuated at 2 Torr until a constant weight was attained to remove the SOCH. This procedure gave 0.3 g of compound **14**. In the ^1H NMR spectrum, $\delta(CH_2O) = 3.41$. The intensity ratios are $H_{CH_3} : H_{C_6H_5} = 3.4$, $H_{CH_3} : H_{C_2H_4} = 4.3$; calculated: 3.6 and 4.5, respectively.

Compounds **11**—**15** were obtained similarly.

Table 1. Properties of bis[dimethyl(hydroxybutyl)siloxy]-organocyclosiloxanes

Compound	n_D^{20}	Found / Calculated (%)			Molecular formula
		C	H	Si	
11	1.4421	38.61	8.60	29.83	$C_{18}H_{48}O_8Si_6$
		38.53	8.62	30.04	
12	1.4545	44.44	9.14	25.55	$C_{24}H_{60}O_8Si_6$
		44.67	9.37	26.11	
13	1.4258	37.60	8.34	31.13	$C_{22}H_{60}O_{10}Si_8$
		37.25	8.52	31.67	
14	1.4788	46.04	7.68	26.90	$C_{32}H_{64}O_{10}Si_8$
		46.11	7.74	26.96	
15	1.4782	44.80	6.72	28.70	$C_{112}H_{200}O_{38}Si_{32}$
		44.05	6.60	29.44	

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