SYNTHESIS AND POLYMERIZATION OF SOME ORGANO-1-OXA-3,5-DICARBACYCLOHEXASILANES

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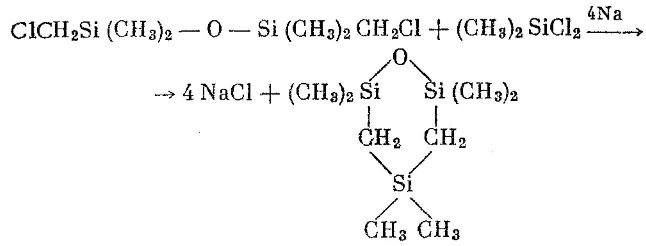
As is well known, one method of preparing macromolecular organosiloxanes is provided by the catalytic polymerization of organocyclosiloxanes in presence of acidic or basic catalysts. The tendency for organocyclosiloxanes to undergo polymerization depends, on the one hand, on the strain in the ring, and on the other, on the sizes of the groups around the silicon atoms. Among the dimethylcyclosiloxanes the most highly strained is the six-membered hexamethylcyclotrisiloxane, which has a strain energy of 3-4 kcal/mole. The four-membered tetramethylcyclodisiloxane has not been isolated at all. Recently some five-membered cyclic paraffin-siloxanes of general formula $RR'Si-CH_2-CH_2-SiRR'-O$ [1] (R = alkyl, R' = aryl) have been prepared. The strain energy of such rings, determined from the heat of polymerization, is 8-12 kcal/mole, and a phenyl substituent on silicon does not affect the value of the strain energy of the ring. Catalytic amounts of a base bring about cleavage of the siloxane bond with formation of a linear polymer of high molecular weight [2]. The polymerization of 1,1-dimethylsilacyclopentane was studied [3], and it was shown that it polymerizes with formation of a viscous oil of mol. wt. 1930 only in presence of 2.5 moles per cent of $AlBr_3$; but in presence of small amounts of $AlBr_3$ or $AlCl_3$ polymerization does not go even after boiling for 5-8 hr.

In the present investigation we synthesized six-membered oxadicarbacyclohexasilanes of structure $(CH_3)_2Si-O-Si(CH_3)_2CH_2-Si(CH_3)R-CH_2$, in which R = methyl, ethyl, or phenyl; and we studied their tendency to polymerize in the presence of potassium hydroxide and of aluminum chloride. Such compounds were synthesized by the reaction of bischloromethyltetramethyldisiloxane and a dialkyl(or aryl)dichlorosilane with sodium in toluene in accordance with the scheme:

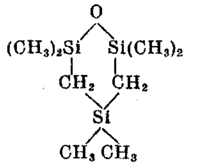
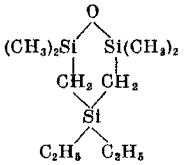
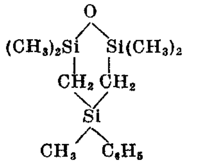


$$ClCH_2Si(CH_3)_2-O-Si(CH_3)_2CH_2Cl + (CH_3)_2SiCl_2 \xrightarrow{4Na} 4\,NaCl + \ldots$$

In this way we synthesized three six-membered cyclic compounds, which were characterized by elementary composition, molecular weight, and infrared spectrum (Figs. 1, 2, and 3). The properties of the compounds are given in the table.

In the infrared spectra of all three compounds lines were found that corresponded to the frequency of Si – O in a six-membered ring, namely 800, 1000-1040 cm^{-1}. For the $Si-CH_3$ bond we found intense lines in the regions of 1250 and 1350 cm^{-1} and a weak line at 1400 cm^{-1}. For the six-membered cycle $(CH_3)_2Si-O-Si(CH_3)_2-CH_2-Si(C_2H_5)_2-CH_2$ we found further lines at 1460 and 1407 cm^{-1}, characteristic for the vibration of the group $C_2H_5(\gamma Si)$. For $(CH_3)_2Si-O-Si(CH_3)_2CH_2-Si(CH_3)C_6H_5CH_2$ we found an intense line at 1250 cm^{-1}, characteristic for the vibrations of the group $CH_3(\gamma Si)$ and a line at 1429 cm^{-1}, characteristic for the vibrations of the group $C_6H_5(\gamma Si)$. In the study of the tendency for such cycles to undergo polymerization we used potassium hydroxide and aluminum chloride as catalysts. The experiments showed that the polymeriza-

Properties of Organo-1-oxa-3,5-dicarbacyclohexasilanes

Formula	B.p., °C (p, mm)	n_D^{20}	d_4^{20}	MR	
				found	calculated
	90—93 (45)	1,4385	0,8846	64,97	65,67
	97—100 (15)	1,4524	0,8930	74,96	74,26
	134—138 (8)	1,5112	0,9607	85,39	85,29

tion of such organo-1-oxa-3,5-dicarbacyclohexasilanes proceeds with much more difficulty than that of six- and eight-membered dimethylcyclosiloxanes. In polymerization under given conditions, i.e., at 120° in presence of 1.3% of KOH, in the course of 4 hr hexamethylcyclotrisiloxane forms a polymer in 46.3% yield; mol. wt. 169800.

The cyclic compound $(CH_3)_2Si—O—Si(CH_3)_2—CH_2—Si(CH_3)_2CH_2$ does not change in viscosity in the course of 4 hr, and only after 33 hr does it form a liquid polymer in 19% yield.

Replacement of methyl by phenyl to give $Si(CH_3)_2—O—Si(CH_3)_2—CH_2SiCH_3(C_6H_5)CH_2$ raises the activity of the compound with respect to polymerization in presence of bases. After only 3 hr of heating at 120° with 1% of KOH we obtained 6% of polymer of mol. wt. 1490. In this case the electronegative phenyl substituent on the silicon atom makes the Si – O – Si link more sensitive to nucleophilic attack by potassium hydroxide.

As in the polymerization of $Si(CH_3)_2—O—Si(CH_3)_2—CH_2—Si(CH_3)_2CH_2$ in presence of alkali, in the polymerization of this compound in presence of aluminum chloride it was very inert. When it was heated for 20 hr at 120° in presence of 5.9% by weight of $AlCl_3$, about 70% was recovered unchanged, and about 30% remained as a nondistilling residue, n^{20}_D 1.4420.

EXPERIMENTAL

A mixture of 0.1 mole of bischloromethyltetramethyldisiloxane and 0.1 mole of dichlorodimethylsilane was added with stirring to a suspension of 0.4 mole of sodium in toluene at 108-109°. After the addition of the chloro compounds, the mixture was heated further for 3 hr at the same temperature, after which it was cooled, the precipitate of sodium chloride was filtered off, and the filtrate was fractionated. First toluene was distilled off, and then the reaction products of low molecular weight were driven off in a vacuum. A 25.9% yield was obtained of a fraction having: b.p. 90-92° (45 mm); n^{20}_D 1.4385; d_4^{20} 0.8844. $(CH_3)_2Si—O—Si(CH_3)_2—CH_2—Si(CH_3)_2CH_2$ has a mol. wt. of 218, and the value found cryoscopically in benzene was 206. Found: C 43.65, 43.76; H 10.08, 9.88; Si 37.74, 37.91%; MR 64.97. $C_8Si_3OH_{23}$. Calculated: C 44.03; H 10.09; Si 38.53%; MR 65.67.

From 0.1 mole of bischloromethyltetramethyldisiloxane and 0.1 mole of dichloromethylphenylsilane with 0.4 mole of sodium, reacting under the conditions of the preceding experiment, we obtained $Si(CH_3)_2—O—Si(CH_3)_2—CH_2—Si(CH_3)C_6H_5—CH_2$; yield 10.52%; b.p. 134-138° (8 mm); n^{20}_D 1.5112; d_4^{20} 0.9594. Found: C 56.17, 56.28; H 8.67, 8.78; Si 29.21, 29.14%; MR 85.39. $C_{13}Si_3OH_{24}$. Calculated: C 55.71; H 8.57; Si 30.07%; MR 85.29.

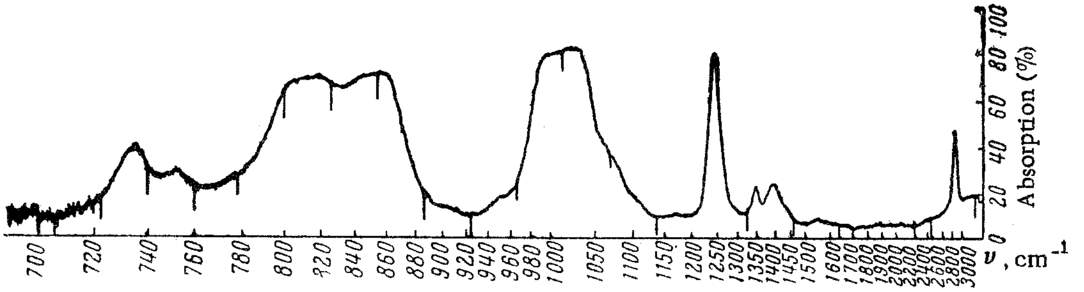


Fig. 1. Infrared spectrum of $(CH_3)_2—Si—O—Si—O—Si(CH_3)_2CH_2—Si(CH_3)_2C_2H_2$

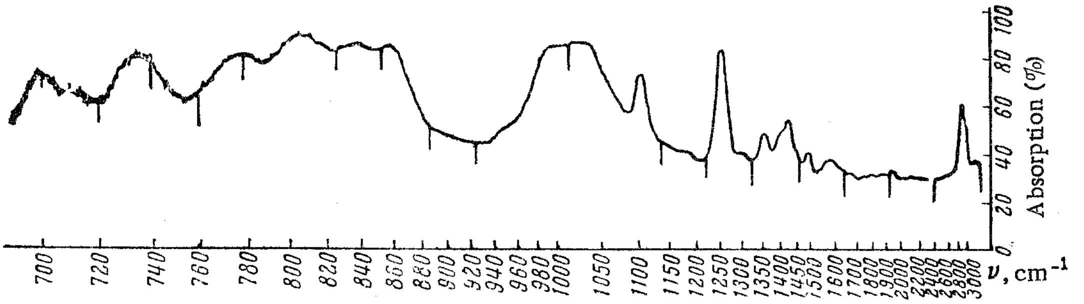


Fig. 2. Infrared spectrum of $(CH_3)_2Si—O—Si—O—Si(CH_3)_2CH_2SiCH_3C_6H_5CH_2$

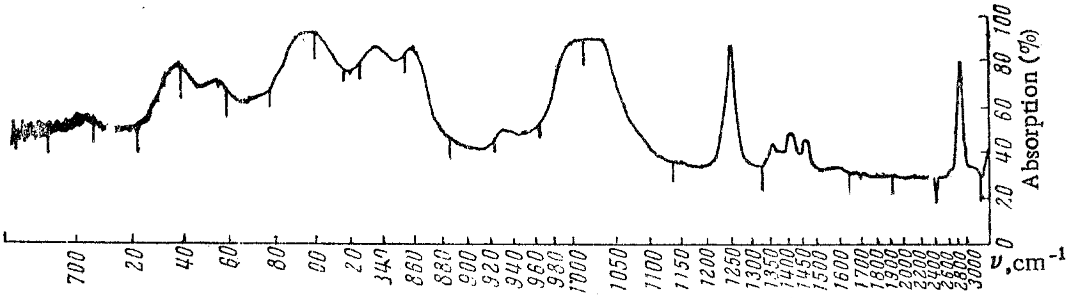


Fig. 3. Infrared spectrum of $(CH_3)_2Si—O—Si(CH_3)_2CH_2Si(C_2H_5)_2CH_2$

In an analogous way from 0.1 mole of bischloromethyltetramethyldisiloxane, 0.1 mole of dichlorodiethylsilane, and 0.4 mole of sodium in toluene we obtained a 29.9% yield of the six-membered cyclic compound $Si(CH_3)_2—O—Si(_3)_2CH—CH_2—Si(C_2H_5)_2CH_2$; b.p. 97-100° (15 mm); n^{20}_D 1.4524; d_4^{20} 0.8930. Found: C 49.26, 49.14; H 10.39, 10.49; Si 32.68, 32.46%; MR 74.96; mol. wt. 246 (cryoscopically in benzene). $C_{10}Si_3OH_{26}$. Calculated: C 48.78; H 10.56; Si 34.23; MR 74.25; mol. wt. 238.

Reaction of $(CH_3)_2Si—O—Si(CH_3)_2—CH_2—Si(CH_3)_2—CH_2$ with KOH. 6 g of the cyclic compound was placed in an ampoule, which had been previously cooled with solid carbon dioxide. 1.4% by weight of solid KOH was introduced, and the ampoule was sealed and placed in a thermostat, where it was kept at 120° for 33.5 hr. The ampoule was again cooled, and the contents were filtered from KOH into a Favorskii flask. 4.91 g (81.8%) of a fraction of b.p. 60-64° (15 mm) and n^{20}_D 1.4379 was distilled off (the temperature in the flask reached 110°). The molecular weight of the fraction (determined cryoscopically in benzene) was 214. The residue in the flask amounted to 18.2%; it was a viscous liquid having n^{20}_D 1.4400.

Reaction of $(CH_3)_2Si—O—Si(CH_3)_2—CH_2—Si(CH_2)C_6H_5CH_2$ with KOH. 6 g of the cyclic compound was placed in an ampoule cooled with solid carbon dioxide, and 1.3% of solid KOH was added. After 3 hr at 120° the ampoule was cooled, and the liquid was filtered and vacuum-fractionated. 5.64 g (94%) of monomer was distilled off at 110-117° (2 mm). The temperature in the flask reached 200° at 2 mm. The residue in the flask, which amounted to 0.3 g (6%), was a viscous liquid of molecular weight 1436 (determined cryoscopically in benzene); n^{20}_D 1.4950.

Reaction of $(CH_3)_2Si-O-Si(CH_3)_2-CH_2-Si(CH_3)_2-CH_2$ with $AlCl_3$. 5.74 g of the cyclic compound was placed in an ampoule cooled with solid carbon dioxide, and 0.33 g of anhydrous $AlCl_3$ was added. The ampoule was sealed and placed in a thermostat at 120°. Heating was continued for 20 hr, after which the ampoule was cooled and the contents were filtered from $AlCl_3$ and fractionated. 3.43 g of monomer was distilled off at 170-175°; n^{20}_D 1.4370 (the temperature in the flask reached 200°). The molecular weight (determined cryoscopically in benzene) was 223. The residue in the flask amounted to 1.6 g (27.8%); it was a viscous liquid, n^{20}_D 1.4420.

Reaction of $(CH_3)_2Si-O-Si(CH_3)_2-O-Si(CH_3)_2-O$ with KOH. 2.37 g of hexamethylcyclotrisiloxane was introduced into an ampoule, and 0.033 g of solid KOH was added. The ampoule was sealed and placed in a thermostat, where it was kept for 4 hr at 120°. The resulting polymer was dissolved in benzene; the benzene solution was washed with water and then dried over $CaCl_2$. The yield of polymer was 46.3%. Molecular weight (determined viscometrically in benzene) 169800.

SUMMARY

1. 1-oxa-3,5-dicarbacyclohexasilanes of the following structures were synthesized:

$$(CH_3)_2Si-O-Si(CH_3)_2-CH_2-Si(CH_3)_2CH_2,$$

$$(CH_3)_2Si-O-Si(CH_3)_2-CH_2-Si(CH_3)C_6H_5CH_2 \text{ and}$$

$$(CH_3)_2Si-O-Si(CH_3)_2-CH_2-Si(C_2H_5)_2CH_2.$$

2. An investigation was made of the tendency for the cyclic compounds synthesized to polymerize in presence of potassium hydroxide and of aluminum chloride. These cyclic compounds polymerize with much greater difficulty than the six-membered hexamethylcyclotrisiloxane.

LITERATURE CITED

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