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SILOXANE DERIVATIVES OF SILACYCLOALKANES AND THEIR POLYMERIZATION

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We have previously [1] described carbon-chain oligomers containing silacyclobutane groups in framing groups, as well as di- and poly-silazane compounds of the type $[RSi(CH_2)_{n-1}CH_2]NH$ or $[HNSi(CH_2)_{n-1}CH_2]_x$, where n = 3, 4 [2].

The present communication deals with the synthesis of individual oligomeric and polymeric siloxane compounds, with silacycloalkane groups framing the polysiloxane chain. They were all obtained by hydrolysis or cohydrolysis of silacyclanes of the type $RClSi(CH_2)_{n-1}CH_2$ (n = 3, 4, 5; R = Me, Ph, Cl) with alkylchlorosilanes having OH, ONa, or AcO groups at the silicon atom. Magnesium carbonate is a convenient acceptor for the hydrogen chloride formed in the hydrolysis of chlorosilacyclobutanes, silacyclobutane compounds being very sensitive to hydrogen chloride. In this way there were obtained, for example: $(CH_3)_3SiO(CH_3)SiCH_2CH_2CH_2$. Bp 63–65° (44 mm); d_4^{20} 0.8431; n_D^{20} 1.4161. Found: MR_D 51.91; Br number 92 . Calculated for MR_D 51.92; Br number 92.

$[(CH_3)_3SiO]_2SiCH_2CH_2CH_2$. Bp 68–70° (10 mm); d_4^{20} 0.8738; n_D^{20} 1.4089. Found: MR_D 7031. Calculated: MR_D 70.56.

$CH_2{=}CH(CH_3)_2SiO(CH_3)SiCH_2CH_2CH_2$. Bp 51–53° (18 mm); d_4^{20} 0.8633; n_D^{20} 1.4318. Found: MR_D 55.96; 168; Br number 15.8%.* Calculated: MR_D 56.08; 172, Br number 15.8%.

$(CH_3)_2Si[OSi(CH_3)_2]_2OSiCH_2CH_2CH_2$. Bp 83–86° (10 mm); d_4^{20} 1.0018; n_D^{20} 1.4185. Found: MR_D 77.45; 52; Br number 17.1%. Calculated: MR_D 77.56; 52; Br number 17.1%. Also obtained were oligomers and polymers of the type $CH_2CH_2CH_2Si(CH_3)O[Si(CH_3)_2O]_nSi(CH_3)CH_2CH_2CH_2$ where n = 0, 58, 243, 378, etc.

In all cases, the elementary analyses corresponded to the theoretical values for Si, C, and H. The presence of functional groups was checked by IR spectra (absorption bands at 915, 1123, and 1179 cm^{-1}), by quantitative functional analysis, and by the same method of bromine numbers.

The compounds prepared are polyfunctional highly reactive compounds, and can be caused to participate in various polymerization reactions involving one of the functional groups. Using peroxide initiators, 1,3,3-trimethyl-1,1-(trimethylene)-3-vinyldisiloxane can be polymerized and copolymerized with multi-bond conjugated olefins, and the resultant polymers contain unchanged silacyclobutane groups. At 100° C in the presence of nitrogeneous basic catalysts (e.g., Me_4NOH), hexamethyl-1,1-(trimethylene) cyclotetrasiloxane is polymerized, and copolymerized with cyclosiloxanes, to give high-molecular polysiloxanes, also containing silacyclobutane groups.

Silacyclobutane derivatives of polysiloxanes can be polymerized with scission of the Si–C link, of the silacyclobutane groups, either by means of anionic catalysts (alkalies, silanolates, organometallic compounds, and alkali metals), or else thermally, without a catalyst, at 120–250° C.

Compounds containing two or more silacyclobutane groups, are of potential interest as cross-linking agents, and some of them as thermosetting oligomers.

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* Addition of Br to the Si–C bond in a ring gives a S–Br link, and alkali titration of this gives the Br content [3].

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PMR SPECTRA OF SOME MORPHOLINE DERIVATIVES

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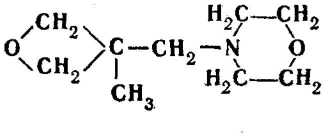
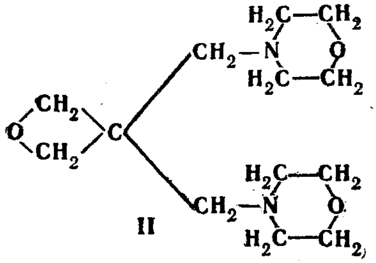
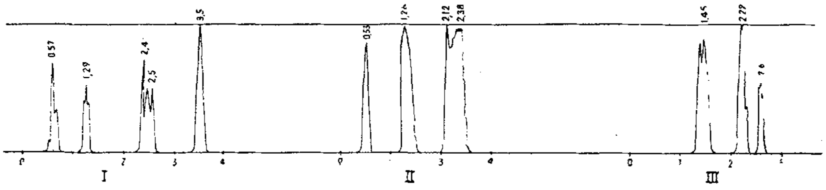
Figure 1 shows experimental PMR spectra* for two morpholine derivatives which we recently synthesized, 3, methyl-3-morpholinomethyloxacyclobutane, bp 244° C (I) [1], and 3,3-bis(morpholinomethyl) oxacyclobutane, bp 72° C (II) [2].



I



II



PMR spectra of morpholine derivatives (for explanation see text).

For comparison the PMR spectrum of morpholine (III) itself, determined under the same conditions, is given. Compound II was dissolved in CCl_4. The measurements were made with a JNM-3 instrument, frequency 40 mcps, resolution 5×10^{-8}. With increase in the magnetic field, the ppm values increase, too. The proton resonance chemical shifts are measured relative to water, used as an external standard.

According to the literature, the proton spectrum of morpholine [3, 4] consists of two very intense signals from protons of the CH_2 groups, amounting to 2.3 and 1.1 ppm. The first of these signals belongs to the methylene group α to the nitrogen atom, and the second to the β methylene group. Our proton resonance chemical shift values for the α and β methylene groups of the morpholine ring are quite close to those for all three compounds considered (table).

According to [4], it is correct that the PMR spectrum of morpholine (III) should also contain a signal from the NH group, value 4.3 ppm. However, our morpholine PMR spectrum had a third signal due to a proton, and equal to only 2.6 ppm.

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