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Abstract

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ORGANOSILICON COMPOUNDS WITH HYDROCARBON BRIDGES BETWEEN SILICON ATOMS

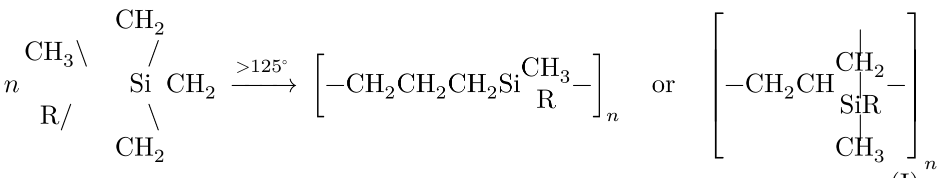
THERMAL TRANSFORMATIONS

In work (1) we studied the thermal transformations of the $Si(CH_2)_nSi$ grouping in a flow system at 600°. Under these conditions the bridging group in α,ω-hexamethyldisilylalkanes $(CH_3)_3Si(CH_2)_nSi(CH_3)_3$ is cleaved when $n \geq 2$, while at $n = 1$ it is retained, but a methyl radical or hydrogen is split off. In the present work we studied the action of elevated temperatures on bridged compounds at temperatures up to 400° in sealed ampoules. As compounds containing a bridging group, substances of the following types were tested:

$$(CH_3)_3Si-(CH_2)_n-Si(CH_3)_3 \quad \text{and} \quad R(CH_3)Si-(CH_2)_n$$

It turned out that α,ω-hexamethyldisilylalkanes with $n = 2, 3, 4$ do not change their properties at 350-360° during three hours and even longer heating; 5- and 6-membered cyclanes are no less stable under these conditions. In particular, 1,1-dimethylsilacyclopentane is stable at 390° (3 hours). In contrast to these cycles, four-membered compounds polymerized on heating—1-methyl-1-chlorosilacyclobutane beginning at 170-180°, and 1,1-dimethylsilacyclobutane at 125-130°. As a result of the reaction, solid, elastic substances were obtained, soluble in the starting monomers and also in benzene and chloroform.

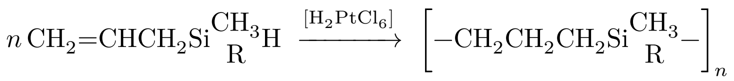
For polymers having the same elemental composition as the starting silacyclobutanes, structures (A) or (B) could be proposed:



(I)

(A) (B)

Comparison of the IR spectra* of the polymers obtained by us according to reaction (I) and by counter synthesis according to reaction (II) (3):



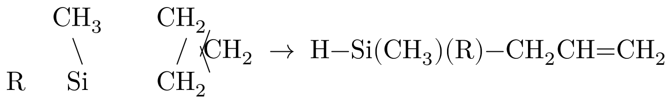
$$n\,CH_2{=}CHCH_2\overset{CH_3}{\underset{R}{Si}}H \xrightarrow{[H_2PtCl_6]} \left[-CH_2CH_2CH_2\overset{CH_3}{\underset{R}{Si}}-\right]_n$$

(II)

(A)

made it possible to establish their complete identity. At the same time the spectrum** of the polymer prepared from 1,1-dimethylsilacyclobutane was different from the spectrum of the polymer of structure (B), known from the literature (4). These data allowed us to choose structure (A) for the polymer obtained.

It is unlikely that, in reaction (I), the formation of a linear polymer is preceded by isomerization of (III) silacyclobutanes into allylsilane hydrides,



$$\begin{matrix} & CH_3 & CH_2 & \\ & \backslash & / \; \backslash & CH_2 \\ R & Si & CH_2 & \end{matrix} \rightarrow H{-}Si(CH_3)(R){-}CH_2CH{=}CH_2$$

(III)

Indeed, in a control experiment we established that $H{-}Si(CH_3)(R){-}CH_2CH{=}CH_2$ does not polymerize appreciably at 180-200°, whereas under these conditions $Cl(CH_3)Si{-}(CH_2)_3{-}$ is completely converted into a polymer. In addition, the IR spectrum of the monomer distilled from an experiment involving incomplete polymerization of $Cl(CH_3)Si{-}(CH_2)_3{-}$ showed the absence of impurities of hydride-containing compounds.

The reason for the different behavior of silacyclobutanes as compared with 5- or 6-membered silacycloalkanes at elevated temperatures apparently should be sought in the strain of the 4-membered ring (5,6). It is known, for example, that under the action of alcoholic alkali or concentrated sulfuric acid (with subsequent treatment with water) silacyclobutanes undergo ring opening, forming sym-dipropyltetraalkyldisiloxanes considerably more readily than 5- or 6-membered rings (6).

It should be noted that, in contrast to the known (3,4,7,8) methods for obtaining linear polymers of the type

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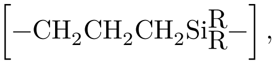
* The IR spectra were recorded on a double-beam IKS-10 instrument in the regions 400-2400 and 2750-3100 cm^{-1}.

** In it, the frequency in the 2000-2200 cm^{-1} region, attributable to the $\equiv Si{-}H$ bond and usually very intense, is completely absent.



$$\left[-CH_2CH_2CH_2Si\overset{R}{\underset{R}{}}-\right],$$

the method of thermal polymerization of silacyclobutanes makes it possible to prepare products of the highest molecular weight.

The 5- and 6-membered cyclanes were obtained by known methods ([9,10]).

1-Methyl-1-chlorosilacyclobutane. 212 g of $ClCH_2CH_2CH_2SiCl_2(CH_3)$, 30 g of Mg in 500 ml of ether were boiled with stirring for 12 h. After separation of the magnesium precipitate, the filtrate was distilled. 151 g of trichloride was recovered, and 26 g of crude $Cl(CH_3)Si{-}(CH_2)_3{-}$ was obtained, b.p. 105-109°. Yield 68% based on the trichloride used. After distillation on a column of 10 t.t., the analytically pure substance had the following properties: b.p. 106°/738 mm; n_D^{20} 1.4490; d_4^{20} 0.9858. MR_D found–32.8, calculated 32.4. Found Cl 21.13%, calculated Cl 21.09%.

Raman spectrum*: 151 (3), 177 (7 sh), 203 (8 v.sh), 241 (7 sh), 394 (10), 433 (8 sh), 553 (2), 639 (5 sh), 678 (4 sh), 721 (3 sh), 771 (1), 825 (1), 874 (4), 901 (9), 925 (3), 1128 (5), 1217 (1), 1260 (0), 2936 (9 sh), 2985 (10 sh).

1,1-Dimethylsilacyclobutane was obtained in the usual way from CH_3MgBr (9 g Mg) and 31 g of $Cl(CH_3)Si{-}(CH_2)_3{-}$ in 100 ml of ether, in an amount of 17 g. Yield 65%, b.p. 82-83°/740 mm; n_D^{20} 1.4260; d_4^{20} 0.7702; MR_D found 32.6; calculated 32.8.

Raman spectrum: 151 (2); 189 (6 sh); 217 (7); 239 (5); 450 (10 r); 614 (9 sh); 649 (5); 690 (2); 706 (3); 728 (4); 810 (5 sh); 886 (5 sh); 908 (8 sh); 931 (4); 1066 (0); 1125 (4); 1195 (2); 1219 (2); 1255 (2); 1327 (1); 1417 (6 v.sh); 1454 (1); 2860 (0); 2908 (10 sh); 2934 (4); 2971 (1 r.sh).

Literature data ([11]): b.p. 81°/730 mm; n_D^{20} 1.4270, d_4^{20} 0.7746. MR_D found 32.2.

In the spectra of both of the above-described silacyclobutanes, no frequencies characteristic of Si—H or C=C bonds were observed. In these spectra, as well as in the Raman spectrum of $C_2H_5(CH_3)Si{-}(CH_2)_3{-}$, synthesized in work ([12]), a stable set of frequencies was observed: a very intense line in the region 430-450 cm^{-1}, as well as lines in the region 725, 815, 878, 903, 927, 1125 cm^{-1}, which apparently characterize the silacyclobutane grouping.

Allylmethylchlorohydrosilane. To 50 g of Mg in 1 liter of ether, 2 ml of allyl bromide was added, and after the reaction had started a mixture of 120 g of allyl bromide and 172 g of methyldichlorosilane was added in such a way that vigorous boiling of the ether did not cease. After separation of the precipitate, double

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* In all cases the Raman spectra were recorded on an ISP-51 instrument with a medium camera; intensities are given on a 10-point visual scale.

distillation (on a 20-theoretical-plate column) gave $CH_2{=}CHCH_2SiClH(CH_3)$ in a yield of 13% based on the CH_3SiCl_2H taken; b.p. 94-95°/755, n_D^{20} 1.4310, d_4^{20} 0.9175. MR_D found 34.0, calculated 34.5.

IR spectrum: 198(3 sh); 210(3); 240(1); 280(0); 407(3 sh); 496(7 sh); 588(4 sh); 656(1); 688(3); 722(1); 742(2); 769(1); 797(0); 851(vs); 907(2); 940(1); 995(1); 1165(6 sh); 1190(2 sh); 1239(w); 1253(0); 1301(8 r); 1392(3); 1419(3); 1635(10); 2175(9 sh); 2890(2 sh); 2908(9); 2974(5); 3003(6); 3080(4).

The frequencies 407, 940, 995, 1165, 1300, 1392, 1635, 3003, and 3080 cm^{-1} characterize the allyl group bonded to silicon, and the line at 2175 cm^{-1} characterizes the $\equiv$Si–H bond (13).

Polymer $-[Cl(CH_3)SiCH_2CH_2CH_2]_n-$. On heating 6 g of $CH_2{=}CHCH_2SiCl(CH_3)H$ with 1 drop of a 0.1 N solution of H_2PtCl_6 in isopropyl alcohol to 80°, the reaction proceeded exothermically, after which the mixture was heated for 1 h at 140-150°C. The polymer was evacuated at 100°/2 mm for 2 h. The yield of polymer was ~60%; it was a brittle paraffin-like mass with m.p. 60-65°, readily soluble in benzene and CCl_4.

Thermal tests were carried out in ampoules*, into which a sample of the substance (1.5-2 ml) was charged; the air was then displaced with dry nitrogen and the ampoule was sealed. Thermal stability was established in cases where the appearance, specific gravity, and n_D^{20} of the substance remained practically unchanged.

A sample of $(CH_3)_2Si(CH_2)_3$, heated for 3 h at 230°, was converted into a solid polymer. To obtain a 1-2% solution of this polymer in benzene, 24-36 h were required for the polymer to swell, and after brief shaking it dissolved completely. The polymer was precipitated by a double volume of methanol as a sticky lump. After evacuation at 100°/2 mm for 3 h, the yield was >85%. When the polymer was heated in air to 70° it became completely transparent, and at 160-180° it was converted into a very viscous liquid. Films of this substance, obtained by removing the solvent from benzene solutions of the polymer, resembled polyethylene films in appearance but were more elastic. They were used for recording IR spectra, which were compared with the spectra of the polymer $-[(CH_3)_2SiCH_2CH_2CH_2]_n-$published in (4). The reprecipitated polymer was analyzed:

SiC_5H_{12}. Found, %: C 60.39; 60.15; H 11.99; 11.83; Si 27.90; 28.19
Calculated, %: C 59.90; H 12.06; Si 28.02

The polymer of 1-methyl-2-chlorosilacyclobutane, obtained at 230°, was a transparent rubber-like substance that hydrolyzes in air.

SiC_4H_9Cl. Found, %: Si 23.54; 24.02
Calculated, %: Si 23.25

If polymerization of silacyclobutanes is carried out at temperatures close to the initial polymerization temperatures for 5-20 min, the contents of the ampoules constitute a very viscous liquid, consisting

* Pyrex glass.

mainly of unreacted monomer and a small amount of polymer, whose appearance was similar to those described above.

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