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SILANE DERIVATIVES WITH HYDROCARBON BRIDGES BETWEEN SILICON ATOMS

ON THE POLYMERIZATION OF 1,1-DIMETHYLSILICACYCLOPENTANE

In papers (^{1,2}) three of us described a polycondensation reaction, specific to the chemistry of organosilicon compounds, of disilanes with hydrocarbon bridges between silicon atoms, occurring under the action of aluminum halides. Thus, in the case of compounds of the type $(CH_3)_3Si(CH_2)_kSi(CH_3)_3$, where $k = 1, 2, 3, 6$, the reaction proceeded with formation of tetramethylsilane and polymeric silicon hydrocarbons consisting of repeating groupings $\equiv Si(CH_2)_kSi\equiv$; depending on the reaction conditions and on the value of k, cyclic polymers (of the type $[-(CH_3)_2Si(CH_2)_k-]_n$), linear polymers (of the type $CH_3[Si(CH_3)_2CH_2)_k]_nSi(CH_3)_3$), or three-dimensional polymers were obtained. This reaction is evidently general for compounds of the $(CH_3)_3Si-R-Si(CH_3)_3$ type; we have established, in particular, that when $-R-$ is arylene, the condensation reaction of these silicon hydrocarbons likewise occurs under the action of aluminum halides. In our opinion, the reason for this direction of the reaction lies in the unequal stability of the $\equiv Si-CH_3$ and $\equiv Si-R-$ bonds (the latter being less stable) under the action of aluminum halides.

In the present work we studied the action of aluminum halides on 1,1-dimethylsilicacyclopentane. Considering this silicon hydrocarbon as a kind of bridged compound in which the radical $-R-$ is bonded to one and the same silicon atom, we assumed that here too the $\equiv Si-(CH_2)_4$ bond would be more active under the action of AlX_3 than the $\equiv Si-CH_3$ bond. In this case one could expect formation of the reactive radical $-Si(CH_3)_2CH_2CH_2CH_2CH_2-$. The experimental data confirmed our assumption. It turned out that in the presence of $AlCl_3$ and $AlBr_3$ a specific polymerization reaction occurs, which may be represented by scheme (A):

$$(CH_3)_2Si(CH_2)_4 \xrightarrow{Al_2X_6} [(CH_3)_2Si(CH_2)_4]\cdot Al_2X_6 \rightarrow$$

Fig. 1. IR spectra of the starting and polymeric compounds. I —polymer of 1,1-dimethylsilacyclopentane; II —polymer of 1,4-hexamethyldisilylbutane; III —1,4-hexamethyldisilylbutane; IV —1,1-dimethylsilacyclopentane

Figure 1: Fig. 1. IR spectra of the starting and polymeric compounds. I —polymer of 1,1-dimethylsilacyclopentane; II —polymer of 1,4-hexamethyldisilylbutane; III —1,4-hexamethyldisilylbutane; IV —1,1-dimethylsilacyclopentane

$$\rightarrow [-(CH_3)_2Si(CH_2)_4-]\cdot Al_2X_6 \rightarrow -[Si(CH_3)_2CH_2CH_2CH_2CH_2]_n - + Al_2X_6. \tag{A}$$

The transformation proceeds very vigorously upon brief heating of the silane with the catalyst*. To prove the structure of the product obtained, we carried out a counter synthesis of the polymer, consisting of analogous fragments, according to scheme (B):

$$(CH_3)_3SiCH_2CH_2CH_2CH_2Si(CH_3)_3 \xrightarrow{Al_2Br_6} -[SiCH_2CH_2CH_2CH_2]_n - + Si(CH_3)_4. \tag{B}$$

(in the polymer)

* In contrast to this, when 1,1-dimethylsilicacyclopentane is treated with conc. H_2SO_4, as was shown earlier (^{3}), quantitative cleavage of the $\equiv Si - CH_3$ bond occurs, while the $\equiv Si - (CH_2)_4-$ bond in the ring is not affected.

The IR spectra of the polymers* (see Fig. 1), prepared according to schemes A (spectrum I) and B (spectrum II), are identical, which gives grounds for considering the structure of the elementary units forming these polymers to be identical. Judging from the spectrum of 1,4-hexamethyldisilylbutane (spectrum III), the structure of the elementary

Fig. 1. IR spectra of the starting and polymeric compounds. *I* —polymer of 1,1-dimethylsilacyclopentane; *II* —polymer of 1,4-hexamethyldisilylbutane; *III* —1,4-hexamethyldisilylbutane; *IV* —1,1-dimethylsilacyclopentane.

unit of the polymers is the same as in this monomeric compound; spectra I and II contain the bands characteristic of III at 740, 1005, 1060, 1075, and 1195 cm^{-1}. At the same time, the spectrum of 1,1-dimethylsilacyclopentane (IV) differs markedly from spectrum I.

It may be noted that in the region of the stretching vibrations of C—C bonds, the spectra of monomer III and polymers I and II contain bands at 1060 and

1075 cm^{-1}, with different relative intensity distributions in each of these spectra. This difference is possibly explained by the spatial arrangement (rotational isomerism) of the C—C—C chains in the monomers and polymers.

Starting substances. The synthesis of 1,1-dimethylsilacyclopentane and 1,4-hexamethyldisilylbutane was carried out by the described methods (^{4,5}), starting from 1,4-dibromobutane. 1,4-Hexamethyldisilylbutane was obtained as follows. To 60 g of $(CH_3)_3SiCH_2CH_2CH = CH_2$ (^{6}) and 2 drops of a 0.1 N solution of H_2PtCl_6 in isopropyl alcohol, 40 g of methyldichlorosilane was slowly added while the mixture was boiling. After the temperature of the mixture reached 125°, a further 14 g of methyldichlorosilane was added, and then boiling was continued the mixture for 4 hours. Distillation gave 65.5 g (63% of theory) of 1-trimethylsilyl-4-methyldichlorosilylbutane, b.p. 220-223°, n_D^{20} 1.4445; d_4^{20} 0.9625. MR_D found 67.2, calculated 67.0. Found, %: Cl 29.4; 29.5. Calculated for $Si_2C_8H_{20}Cl_2$ 29.2%.

By the reaction of methylmagnesium chloride (from 30 g Mg) with 82 g of $(CH_3)_3SiCH_2CH_2CH_2CH_2SiCl_2CH_3$ in 800 ml of abs. ether, 1,4-hexamethyldisilylbutane with b.p. 193-200° was obtained. Distillation of the crude product on a 20-theoretical-plate column gave 80 g (95% of theory) of disilylbutane with b.p. 196-7° (atm.), n_D^{20} 1.4270; d_4^{20} 0.7655. The properties and spectra of the preparation obtained by this method and by method (5) are identical.

Polymerization of 1,1-dimethylsilacyclopentane. 5.16 g of $(CH_3)_2Si(CH_2)_4$ and 0.34 g (2.6 mol. %) of $AlBr_3$ were heated for 2 min at 120-130° in a flask with a reflux condenser, with vigorous stirring of the mixture by a magnetic stirrer. In this process the contents of the flask, without boiling, turned into a light-yellow transparent and very viscous mass. The weight of the reaction mixture after polymerization was 5.47 g. The polymer was dissolved in 50 ml of ether; the ether solution was washed several times with distilled water and dried over $CaCl_2$. After removal of the ether and vacuum treatment of the residue at 70-80°/3 mm for one hour, a polymer was obtained (4.1 g—80% of theory), a very viscous, almost glass-like, transparent, colorless substance, soluble in benzene, acetone, and ether. Mol. wt. (average) 1930 (cryoscopically in benzene). Elemental analysis:

$-Si(CH_3)_2CH_2CH_2CH_2CH_2-$.	Found, %:	Si 24.6; 24.6;	C 63.1; 62.7;	H 12.2; 12.1
	Calculated, %:	Si 24.6;	C 63.1;	H 12.3

When small amounts of $AlBr_3$ were used (up to 0.3 mol. %) or $(C_2H_5)_3Br_3Al_2$

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* The IR spectra were recorded on an IKS-12 instrument in the 700-1300 cm^{-1} region in a thin layer between glasses and in the 1300-1500 cm^{-1} region in a 0.1-mm layer; NaCl prism.

(up to 15.0 mol. %), polymerization did not proceed even upon boiling the mixture for 4-8 hours. The use of 2-5 mol. % $AlCl_3$ in the indicated reaction leads to the formation of an analogous polymer. More prolonged heating of the reaction mixture at a temperature above 120–130° probably leads to structuring of the linear polymer, similarly to what we observed earlier (2). Thus, when the reaction was carried out between 4.15 g of $(CH_3)_2Si(CH_2)_4$ and 0.17 g of $AlCl_3$ at 150–160°, a rubber-like polymer was formed. The latter, after grinding, dissolved only partly in boiling benzene. After the usual treatment of the benzene extract and vacuum treatment of the soluble polymer at 110–120° (5 mm), 0.8 g of a yellow viscous substance was obtained. Mol. wt. 950 (cryoscopically in benzene).

Found, %: Si 24.3; 24.4; C 63.6; 63.8; H 12.2; 12.4
SiC_6H_{14}. Calculated, %: Si 24.6; C 63.1; H 12.3

The remaining polymer was a rubber-like insoluble substance.

Polycondensation of 1,4-hexamethyldisilylbutane. Into a flask with a descending condenser were placed 26 g of $(CH_3)_3SiCH_2CH_2CH_2CH_2Si(CH_3)_3$, and $AlBr_3$ (10 mol. %) was added; the temperature of the mixture rose by 5–6°. On heating the mixture (80–83° in the pot), tetramethylsilane was distilled off (b.p. 26–27°; n_D^{20} 1.3600). After the weight of the condensate had reached 10.9 g, the reaction mixture was instantly transformed from a mobile liquid into a transparent rubber-like substance, and heating was stopped. The weight of the substance remaining in the flask was 18.7 g. The ground polymer was treated with hot ether and then with water. After the usual treatment of the ether extract, 3.5 g of a viscous light-yellow polymer was obtained. Mol. wt. 850 (cryoscopically in benzene).

Found, %: Si 25.2; C 62.6; H 12.2
SiC_6H_{14}. Calculated, %: Si 24.6; C 63.1; H 12.3

The remaining portion was a colorless rubber-like insoluble polymer.

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Note: Figure translations are in progress. See original paper for figures.