ADDITION REACTIONS OF LINEAR SILOXANES TO ALLYLAMINE*

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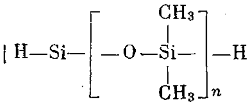
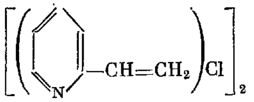
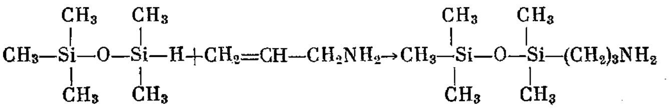
Continuing investigations begun previously on the addition of silicon hydrides of various structures to allylamine [1-2] we have studied the addition of pentamethyldisiloxane and sym-methyldisiloxane to allylamine. It might be expected that the reaction of linear siloxanes with allylamine would take place either at the double bond, giving addition products – primary organosilicon amines – or at the amino group with the liberation of hydrogen and the formation of secondary organosilicon amines.

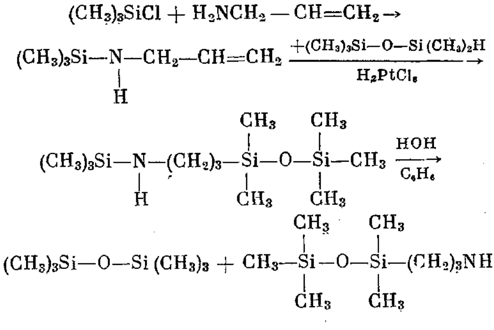
Graber and Jäger [3] isolated with yields of 15-18% products of the addition of allylamine to a siloxane of the general formula  $[H{-}Si{-}[{-}O{-}Si(CH_3)_2{-}]_n{-}H$ at 100°C in an autoclave in the presence of catalytic amounts of hexachloroplatinic acid. They also reported the formation of large amounts of substances which were not identified but, in their opinion, consisted of dehydrocondensation products. In view of this, for the synthesis of compounds containing an amino group in an organic radical attached to a silicon atom these authors [3] used the addition of siloxanes to an allylamine with a substituted amino group and subsequent hydrolysis of the compounds obtained.

We have performed the addition reaction in an atmosphere of hydrogen. As catalyst for the reaction we used a complex of bivalent platinum  and a 0.1 solution of chloroplatinic acid in absolute i-C_3H_7OH. The reaction mixture was heated at 150°C for 10 h. It was found that pentamethyldisiloxane reacts with allylamine to form an addition product – γ-aminopropylpentamethyldisiloxane – with a yield of 56.6% in the following way



$$CH_3{-}Si(CH_3)_2{-}O{-}Si(CH_3)_2{-}H + CH_2{=}CH{-}CH_2NH_2 \rightarrow CH_3{-}Si(CH_3)_2{-}O{-}Si(CH_3)_2{-}(CH_2)_3NH_2$$

The physicochemical properties of the γ-aminopropylpentamethyldisiloxane obtained were completely identical, as is shown in Table 1.



$$(CH_3)_3SiCl + H_2NCH_2-CH{=}CH_2 \rightarrow$$
$$(CH_3)_3Si{-}NH{-}CH_2{-}CH{=}CH_2 \xrightarrow[H_2PtCl_6]{+(CH_3)_3Si{-}O{-}Si(CH_3)_2H}$$
$$(CH_3)_3Si{-}NH{-}(CH_2)_3{-}Si(CH_3)_2{-}O{-}Si(CH_3)_2{-}CH_3 \xrightarrow[C_6H_6]{HOH}$$
$$(CH_3)_3Si{-}O{-}Si(CH_3)_3 + CH_3{-}Si(CH_3)_2{-}O{-}Si(CH_3)_2{-}(CH_2)_3NH_2$$

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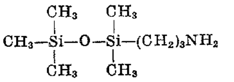
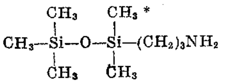
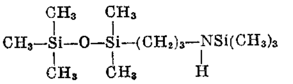
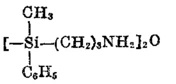
A. V. Topchiev Institute of Petrochemical Synthesis, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 5, pp. 1132-1135, May, 1969. Original article submitted October 22, 1969.

TABLE 1

Compound	Bp, °C (p, mm Hg)	n_D^{20}	d_4^{20}	MR found	MR calcu-lated	Yield, %
 $CH_3-Si(CH_3)_2-O-Si(CH_3)_2-(CH_2)_3NH_2$	67—70 (6)	1,4210	0,8430	61,66	61,65	56,6
 $CH_3-Si(CH_3)_2-O-Si(CH_3)_2-(CH_2)_3NH_2$ *	55—56 (4)	1,4220	0,8483	61,44	61,65	—
 $CH_3-Si(CH_3)_2-O-Si(CH_3)_2-(CH_2)_3-N(H)Si(CH_3)_3$	90—94 (4)	1,4200	0,8366	84,69	84,55	43
 $[-Si(CH_3)(C_6H_5)-(CH_2)_3NH_2]_2O$	178 (2)	1,5449	1,0300	114,17	114,02	53,75

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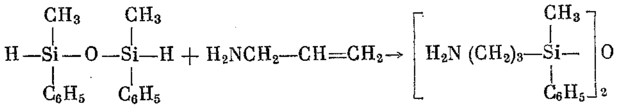
* Obtained by independent synthesis.

The physicochemical properties of the γ-aminopropylpentamethyldisiloxanes obtained were completely identical, as is shown in Table 1.

Under similar conditions, sym-methylphenyldisiloxane reacts with allylamine (using a molar ratio 1:2) to give condensation products at both Si – H bonds with a yield of 53.75%.


$$H-Si(CH_3)(C_6H_5)-O-Si(CH_3)(C_6H_5)-H + H_2NCH_2-CH=CH_2 \rightarrow [H_2N(CH_2)_3-Si(CH_3)(C_6H_5)-]_2O$$

In neither case was the formation of secondary organosilicon amines or polymeric products observed. The IR absorption spectra of the compounds obtained were recorded (Fig. 1). The following absorption bands were noted: 1060-1070 cm^{-1} (Si – O – Si), 1260 cm^{-1} (Si – CH_3). In the 3300-3400 cm^{-1} region there are two absorption bands characteristic for primary organosilicon amines [stretching vibrations of NH (in NH_2)]. An analysis of the NMR spectra (Fig. 2) of the addition products showed the absence of chemical shifts characteristic for methine and methyl protons (CH, CH_3) and the presence of chemical shifts of α-, β-, and γ-methylene protons.

EXPERIMENTAL

The linear siloxanes were obtained by the cohydrolysis and hydrolysis of difunctional monomers. Their purity was checked chromatographically.

The complex catalyst of bivalent platinum was obtained by a method similar to that for the preparation of cis-dichlorodipyridineplatinum [4].

γ-Aminopropylpentamethyldisiloxane. In the presence of 0.02 g of the complex catalyst, 5.7 g of allylamine was added in drops to 14.8 g of pentamethyldisiloxane. The reaction mixture was heated at 150°C for 10 h. Fractionation gave 11.6 g (yield 56.6%) of γ-aminopropylpentamethyldisiloxane, bp 67-70°C (6 mm); n_D^{20} 1.4210; d_4^{20} 0.8430. Found: Si 27.57; 27.78; C 46.88; H 10.95; 10.74; N 7.01; 7.15%; MR 61.66. $C_8H_{23}Si_2ON$. Calculated: Si 27.31; C 46.77; H 11.28; N 6.81%; MR 61.65.

Independent Synthesis of γ-aminopropylpentamethyldisiloxane. Preparation of Allyltrimethylallylamine. With stirring, 54.25 g of chlorotrimethylsilane was added dropwise to a mixture of 57 g of allylamine and 50 ml of absolute ether, the flask being cooled with running water. The reaction mixture was kept for 5 h. The precipitate of allylammonium chloride was filtered off. This gave 56.17 g (yield 87.08%) of allyltrimethylsilylamine, bp 111-115°C; n_d^{20} 1.4112. According to the literature [5]: bp 109.5°C (731 mm); n_D^{20} 1.4112.

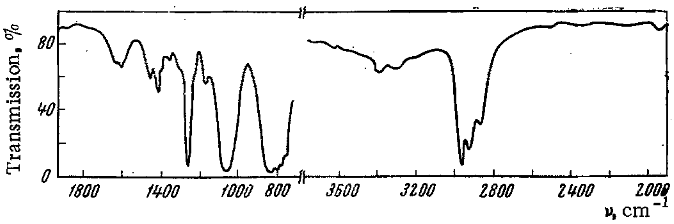


Fig. 1. IR absorption spectrum of γ-aminopropylpentamethyldisiloxane.

Preparation of Trimethylsilyl-γ-(pentamethyldisiloxanyl)propylamine. To 17 g of allyltrimethylsilylamine and 0.5 ml of a 0.1 M solution of $H_2PtCl_6 \cdot 6H_2O$ in absolute $i\text{-}C_3H_7OH$ was added 9.24 g of pentamethyldisiloxane. The reaction mixture was heated at 96°C for 6 h. This gave 16 g (43%) of trimethylsilyl-γ-(pentamethyldisiloxanyl)propylamine, bp 90-94°C (4 mm); n_D^{20} 1.4200; d_4^{20} 0.8366; Found: MR 84.69; Calculated: MR 84.55.

Hydrolysis of trimethylsilyl-γ-(pentamethyldisilanoxyl)propylamine. A mixture of 16 g of trimethylsilyl-γ-(pentamethyldisilanoxyl)propylamine, 30 ml of benzene, and 20 ml of H_2O was boiled for 2 h. The organic layer was separated off and dried with $CaCl_2$. This gave γ-aminopropylpentamethyldisiloxane, bp 55-56°C (4 mm); n_D^{20} 1.4220; d_4^{20} 0.8483; Found MR 61.44; Calculated MR 61.65.

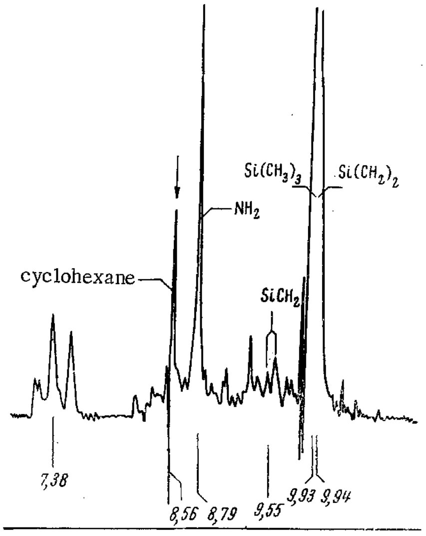


Fig. 2. NMR spectrum of γ-aminopropylpentamethyldisiloxane.

Sym-Bis(γ-aminopropyl)methylphenyldisiloxane. This was obtained by a procedure analogous to the synthesis of γ-amino-propylpentamethyldisiloxane. A mixture of 12.9 g of sym-methylphenyldisiloxane and 5.7 g of allylamine in the presence of 0.5 ml of a 0.1 M solution of $H_2PtCl_6 \cdot 6H_2O$ in absolute $i\text{-}C_3H_7OH$ gave 10 g (53.75%) of sym-bis(γ-aminopropyl)methylphenyldisiloxane, bp 178°C (2 mm); n_D^{20} 1.5449; d_4^{20} 1.10300. Found: Si 15.24 15.00; C 63.88; 64.17; H 8.00; 8.31; N 7.30; 7.42%; MR 114.17; mol. wt. 360; 371; $C_{20}H_{32}Si_2N_2O$. Calculated: Si 15.05; C 64.51 H 8.60; N 7.52%; MR 114.02; mol. wt. 372.

CONCLUSIONS

1. The reactions of pentamethyldisiloxane and sym-methylphenyldisiloxane with allylamine have been studied.

2. The reactions of linear siloxanes with allylamine lead to the formation of addition products containing an amino group in the γ-position in an organic radical attached to the silicon atom.

3. The structures of the compounds obtained have been confirmed by independent synthesis and by analysis of their IR absorption spectra and NMR spectra.

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