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# Catalytic transformations of oligocarbosilanes induced by $AlCl_3$

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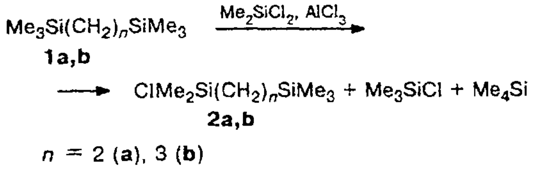
Catalytic activation of Si—C bonds in poly(vinyltrimethylsilane) was studied using a model reaction of catalytic transformations of oligocarbosilanes $Me_3Si(CH_2)_nSiMe_3$ ($n$ = 2, 3) in dichlorodimethylsilane in the presence of $AlCl_3$ as an example. The formation of $ClMe_2Si(CH_2)_nSiMe_3$ was established by chromato-mass spectrometry and GLC.

**Key words:** oligocarbosilanes, functionalization, catalysts, polymer-analogous transformation.

Previously,[1] we studied functionalization of high-molecular-weight poly(vinyltrimethylsilane) (PVTMS) by catalytic activation of Si—C bonds induced by catalysts based on Pt, Mo, and $AlCl_3$. It was established that new bonds and structural fragments are formed in the PVTMS chains as a result of cleavage of the ≡Si—Me bonds and the formation of the ≡Si—Cl bonds in the framing of the carbochain macromolecules. However, the PVTMS macromolecules also contain other types of chemical bonds that can be affected by catalytic systems of the $AlCl_3$ type. The high-molecular nature of the compounds undergoing functionalization impedes reliable establishment of the presence or absence of side processes of cleavage of the C—C bond in the main chain of PVTMS or of splitting of the trimethylsilyl groups in the framing of the carbochain macromolecules.

Using the model compounds, 1,2-bis(trimethylsilyl)ethane (**1a**) and 1,3-bis(trimethylsilyl)propane (**1b**) as examples, we studied the catalytic transformations of the Si—C bond of oligocarbosilanes **1a,b** in dichlorodimethylsilane as a chlorinating reagent using $AlCl_3$ as a catalyst (Scheme 1).

**Scheme 1**



$$\underset{\mathbf{1a,b}}{Me_3Si(CH_2)_nSiMe_3} \xrightarrow{Me_2SiCl_2,\ AlCl_3} \underset{\mathbf{2a,b}}{ClMe_2Si(CH_2)_nSiMe_3} + Me_3SiCl + Me_4Si$$

$n$ = 2 (**a**), 3 (**b**)

The reaction was performed at 63—65 °C with simultaneous distillation of low-boiling silanes. The products were identified by GLC and chromato-mass spectrometry. According to the data obtained, the reaction products are mainly monochloro derivatives **2a,b**. Their yields were 12% and 14% after 10 and 9 h, respectively. No optimization of reaction conditions aimed at increasing the yields of products **2a,b** was performed in this work.

The analysis of mass spectra of compounds **2a** and **2b** reduced to the monoisotopic composition of $^{12}C$ and $^{35}Cl$ isotopes confirmed their structure. Compound **2a** was characterized by peaks of $[M-Me]^+$ ions with $m/z$ 179 and $[ClMe_2Si]^+$ ions with $m/z$ 93. Peaks of $[M-Me]^+$ ions with $m/z$ 193 and $[ClMe_2Si]^+$ ions with $m/z$ 93 are characteristic of compound **2b**. No dichloro derivatives of oligocarbosilanes **1a,b** were detected. In addition, the chromato-mass spectrometric data showed that the products of the reaction of oligocarbosilanes **1a,b** do not contain compounds that could be formed in the side reactions of cleavage of the C—C bond or splitting of the $SiMe_3$ groups.

Thus, the transformations of oligocarbosilanes **1a,b** under the conditions indicated above occur virtually without side reactions. The results obtained in the studies of model systems also suggest the absence of side processes (cleavage of the C—C bonds and splitting of the trimethylsilyl groups) in the catalytic functionalization of PVTMS macromolecules in dichlorodimethylsilane as a chlorinating reagent in the presence of $AlCl_3$.

## Experimental

GLC analysis was performed on an LKhM-8MD chromatograph (stainless steel column 0.3×100 cm, with 5% of SE-30 on Chromaton N-AW-DMCS; katharometer as detector, temperature programming in the interval of 30 to 300 °C with rate of temperature rise 12 deg $min^{-1}$; helium as carrier gas). The chromato-mass spectrometric analysis was performed on a Kratos-MS-890 instrument (capillary column 25 m×0.32 mm with SE-30 as the liquid phase, helium as carrier gas, ionizing voltage 70 eV, temperature programming in the interval of 30 to 270 °C, at 12 deg $min^{-1}$).

Oligocarbosilane **1a** was synthesized by hydrosilylation of vinyltrimethylsilane (0.6 g, 6 mmol) with trimethylsilane (0.45 g, 6 mmol) in the presence of Speier's catalyst ($2 \cdot 10^{-2}$ mmol) in a sealed tube (60 °C, 8 h). Fractionation of

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the mixture gave product **1a** (0.4 g, 38.5%), b.p. 151 °C, $n_D^{20}$ 1.4209 (*cf.* Ref. 2: b.p. 150 °C).

Analogously, oligocarbosilane **1b** (1.35 g, 40%) was obtained from allyltrimethylsilane (2.1 g, 18 mmol) and trimethylsilane (1.48 g, 20 mmol) in the presence of Speier's catalyst ($2 \cdot 10^{-2}$ mmol, 80 °C, 10 h), b.p. 171—172 °C, $n_D^{20}$ 1.4220 (*cf.* Ref. 3: b.p. 171.7 °C).

The reactions of oligocarbosilanes **1a,b** with $Me_2SiCl_2$ were performed in a reactor equipped with a rectification column for distillation of highly volatile silanes. A mixture of carbosilane **1a** (1 g, 6 mmol), $Me_2SiCl_2$ (5.2 g, 40 mmol), and $AlCl_3$ (0.2 g, 1.5 mmol) was kept for 10 h at 65 °C with simultaneous distillation of volatile reaction products at a vapor temperature of 57 °C. The excess $AlCl_3$ was bound by anhydrous MeCN after filtration in a flow of inert gas. The yield of compound **2a** (12%) was determined by GLC. MS, $m/z$ ($I_{rel}$ (%)): 179 $[M-Me]^+$(67), 163 $[Si_2C_5H_{12}Cl]^+$ (2), 152 $[Si_2C_4H_{12}Cl]^+$ (9), 93 $[SiC_2H_6Cl]^+$ (18), 86 $[SiC_4H_{10}]^+$ (100), 73 $[SiC_3H_9]^+$ (91), 71 $[SiC_3H_7]^+$ (2), 58 $[SiC_2H_6]^+$ (17).

Analogously, compound **2b** was obtained in 14% yield (according to GLC) from carbosilane **1b** (1.8 g, 9.6 mmol), $Me_2SiCl_2$ (8.6 g, 67 mmol), and $AlCl_3$ (0.32 g, 2.4 mmol). MS, $m/z$ ($I_{rel}$ (%)): 208 $[M]^+$ (0.7), 193 $[M-Me]^+$ (17), 100 $[SiC_5H_{12}]^+$ (43), 93 $[SiC_2H_6Cl]^+$ (17), 85 $[SiC_4H_9]^+$ (11), 73 $[SiC_3H_9]^+$ (100), 59 $[SiC_2H_7]^+$ (17).

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