SYNTHESIS OF NEW KINDS OF SILICON-CONTAINING MONOMERS


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In the last decade there have been numerous investigations devoted to new problems in the synthesis of organosilicon compounds: 1) methods of introducing various functional groups into the hydrocarbon groups of alkylchlorosilanes (introduction of double bonds, halogens, and groups such as cyano, butadienyl, and carboxyl); 2) the discovery of polymerizable silahydrocarbons and their derivatives; 3) methods of preparing compounds in which metals and other elements (Al, Ti, B, etc.) are introduced into the siloxane chain. These methods and the substances prepared by them are discussed in our review articles [1], in a review by George, Prober, and Elliot [2], and in papers by Andrianov [3]. In the present paper we shall discuss mainly material from investigations that have not yet been published, and we shall classify this as follows: 1) catalytic addition of silanes containing silicon-attached hydrogen to unsaturated and aromatic compounds; 2) high-temperature condensation of silanes containing silicon-attached hydrogen with alkyl, aryl, and alkenyl halides; 3) synthesis of polymerizable silahydrocarbons and their derivatives.

Catalytic Addition of Silanes Containing Silicon-Attached Hydrogen to Unsaturated and Aromatic Compounds

Work of American investigators [4] showed that the highest yields in the addition of silanes to substances containing a multiple bond in presence of peroxides are given by compounds of the type HSiX₄ (X = halogen). We found that in presence of catalysts (platinized charcoal, ruthenium on alumina, which was used by us for the first time, and others) silanes of the types RSiHC₁₂ and R₂SiHC₁ give higher yields than trichlorosilane. It was later shown that the highest yields of addition products are given by substances having an "active" double bond (butadiene, allyl and 2-methylallyl chlorides), whereas lower yields are obtained with compounds in which the double bond is "screened" by halogens (tetrafluoroethylene, chlorotrifluoroethylene). It was shown also that, whereas in the latter cases addition requires more severe conditions (high pressure, 160-180°, and platinized charcoal catalyst), in the simpler cases of these reactions it is possible, as Ponomarenko and Cherkaev [12] showed, to use extremely mild conditions: 20-60°, low or even atmospheric, pressure, and homogeneous conditions of reaction in presence of Speier's catalyst (solution of H₂PtCl₆ in isopropyl alcohol):

\[
\begin{align*}
\text{CH}_2\text{Cl}_2\text{SH} + \text{CH}_2 = \text{CH}_2 & \rightarrow \text{CH}_2\text{C}_2\text{H}_5\text{SiCl}_2 \quad (\sim 100\%) \\
\text{CH}_3\text{Cl}_2\text{SH} + \text{CH} & \rightarrow \text{CH}_2\text{C}_2\text{H}_5\text{SiCH} = \text{CH}_2 \quad (\sim 100\%) \\
(C_2\text{H}_5)_2\text{SiH} + \text{CH}_2 = \text{CH} & \rightarrow \text{CH} = \text{CH}_2 \rightarrow (C_2\text{H}_5)_3\text{SiCH} = \text{CHCH}_3 \quad (50\%) \\
(C_2\text{H}_5)_2\text{SiH} + \text{CH} & \rightarrow \text{CH} = \text{CH}_2 \rightarrow (C_2\text{H}_5)_3\text{SiCH} = \text{CHCH} = \text{CH}_2 \quad (50\%)
\end{align*}
\]

In spite of the use of such mild conditions in the first two reactions, almost quantitative yields are obtained, which, considered in relation to the accessibility of dichloroalkylsilanes, is of practical interest. In the case of butadiene and 1-butene-3-yne the yields are lower as a result of side reactions (polymerization) of these hydrocarbons.
It was finally shown that in the catalytic addition of silanes containing silicon-attached hydrogen not only the yields, but also the direction of addition are determined by the structure of the unsaturated compound to which addition is occurring. In the case of allyl and 2-methylallyl chlorides the silicon-attached hydrogen adds to the less hydrogenated atom of the hydrocarbon, and the residue to the more hydrogenated atom. In the case of vinyl chloride addition is in the opposite direction. As Nesmeianov and Freidlina showed \[5\], addition of silanes containing silicon-attached hydrogen to unsaturated compounds can occur not only in presence, but also in absence of catalysts (under pressure). In this case addition is accompanied by telomerization.

In the further development of the investigation of the catalytic addition of silanes containing silicon-attached hydrogen to fluoro olefins we recently showed, in collaboration with Odabashian, that, unlike tetrafluoro- and chlorotrifluoro-ethylene, fluorinated ethers (allyl tetrafluoroethyl and chlorotrifluoroethyl ethers) form addition products with silanes containing silicon-attached hydrogen in high yields. The resulting fluoro ethers, containing chlorosilyl groups, are shown in Table 1. Addition was carried out under constant conditions: 160-170°, 3 hours, 0.3 g of 1% Pt-C catalyst. It will be seen that in the case of unsaturated ethers the highest yields are given by silanes in which the number of chlorine atoms is 2 or 1; silanes containing three chlorine atoms follow, and the lowest yields of addition products are given by trialkylsilanes. For comparison purposes, in Table 1 we give also the yield of the product of the addition (under the same conditions) of dichloromethylsilane to CF₂CFCI₂.

**Table 1**

<table>
<thead>
<tr>
<th>Original silane</th>
<th>Addition product</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HSiCl₃</td>
<td>Cl₃SiCH₂CH₂CH₃OCF₂CFCI₂</td>
<td>38</td>
</tr>
<tr>
<td>CH₃Cl₂SiH</td>
<td>CH₃Cl₂SiCH₂CH₂CH₃OCF₂CFCI₂</td>
<td>78</td>
</tr>
<tr>
<td>C₂H₅Cl₂SiH</td>
<td>C₂H₅Cl₂SiCH₂CH₂CH₃OCF₂CFCI₂</td>
<td>78</td>
</tr>
<tr>
<td>n-C₅H₁₁Cl₂SiH</td>
<td>n-C₅H₁₁Cl₂SiCH₂CH₂CH₃OCF₂CFCI₂</td>
<td>61</td>
</tr>
<tr>
<td>CH₃(Cl₅H₁₂)SiH</td>
<td>CH₃(Cl₅H₁₂)SiCH₂CH₂CH₃OCF₂CFCI₂</td>
<td>50</td>
</tr>
<tr>
<td>CH₃(C₅H₁₂)₂SiH</td>
<td>CH₃(C₅H₁₂)₂SiCH₂CH₂CH₃OCF₂CFCI₂</td>
<td>14</td>
</tr>
<tr>
<td>CH₃Cl₂SiH</td>
<td>CH₃SiCl₂CFCICFCI₂</td>
<td>4,5</td>
</tr>
</tbody>
</table>

These ethers, containing fluorine and chlorosilyl groups, are fairly stable to heat; the fluoro ether grouping in these compounds is not affected in the course of Grignard reactions and in hydrolysis.

As Chernyshev showed \[6\], silanes containing silicon-attached hydrogen can condense also with aromatic hydrocarbons, though under more severe conditions (heating in an autoclave to 300°, Raney nickel or AlCl₃ catalyst). The following reactions have been carried out:

\[
\begin{align*}
  &\text{HSiCl}_3 + \text{C}_6\text{H}_5 \rightarrow \text{Cl}_3\text{SiC}_6\text{H}_5 \quad (32\%) \\
  &\text{CH}_3\text{Cl}_2\text{SiH} + \text{C}_6\text{H}_5 \rightarrow \text{CH}_3\text{Cl}_2\text{SiC}_6\text{H}_5 \quad (23\%) \\
  &\text{CH}_3\text{Cl}_2\text{SiH} + \text{C}_6\text{H}_5\text{CH}_3 \rightarrow \text{CH}_3\text{Cl}_2\text{SiC}_6\text{H}_5\text{CH}_3 \quad (30\%) \\
  &\text{CH}_3\text{Cl}_2\text{SiH} + \text{C}_6\text{H}_5\text{Cl} \rightarrow \text{CH}_3\text{Cl}_2\text{SiC}_6\text{H}_5\text{Cl} \quad \text{traces}
\end{align*}
\]

Here, the one-stage synthesis of methylphenyl- and methyltolyl-dichlorosilanes is the most interesting feature.

**High-Temperature Condensation of Silanes Containing Silicon-Attached Hydrogen With Alkyl, Aryl, and Alkenyl Halides**

Reactions of this kind were first studied by Agre; we extended them to new pairs of compounds and, in particular, we were the first to study the condensation of the readily accessible dichloromethyl- and dichloroethyl-silanes with various alkyl and aryl chlorides. The reactions were carried out in an empty glass tube heated to 550-600°. The reactions studied by Mironov \[7\] are given in Table 2, and those studied by Chernyshev and Li in Table 3.

It will be seen from Tables 2 and 3 that the high-temperature condensation reaction can be used for the synthesis of previously difficultly accessible compounds: some have not been prepared before, and some have been obtained only in very low yield.