The Synthesis of Volatile Triorganylsiloxy- and Triorganylgermoxyoligosiloxanes from Natural or Synthetic Compounds

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Abstract

Linear, cyclic and carcass triorganylsiloxy- and triorganylgermoxyoligosiloxanes have been obtained with practically quantitative yield from the powders of natural and specially synthesized silicate materials in organic solvents (pyridine, dioxane). The factors that influence the direction of the process and the yield of final products are considered.

New organosilicon materials are winning wide application in all the fields of human practice. However, technological processes of their preparation are very complicated, they require much energy and special equipment, are dangerous from the ecological viewpoint. Because of this, the development of new safe methods to prepare organosilicon monomers and polymers on the basis of available and cheap natural or synthetic raw materials retains much scientific and practical interest.

The compounds that have won most wide application for the creation of various types of organosilicon materials are oligoorganyl- and polyorganylsiloxanes. They comprise silicon-oxygen chemical bonds, the so-called siloxane bonds that render a series of useful properties necessary for modern technologies including space technology, microelectronics, *etc*.

A common way to prepare oligo- and polyorganylsiloxanes is hydrolysis or co-hydrolysis of organosilicon monomers containing silicon-chlorine, silicon-alkoxy, silicon-acyloxy-groups:

$$R_n SiX_{4-n} + H_2O \rightarrow R_n Si(OH)_{4-n}$$
$$\rightarrow [R_n SiO\!\!-\!\!]_m$$
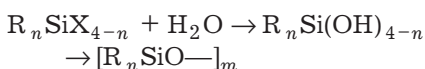
X = halide, OR, OCOR.

However, other (side) reactions also occur during this process. They decrease the yield and hinder the isolation of products.

These shortcomings can be easily eliminated if available inorganic silicon-containing compounds (either natural widespread ones or specially synthesized) are used to obtain organosilicon compounds.

Many natural minerals or synthetic glasses contain ready silicon-oxygen groups [1]. Their structure is chain-type, cyclic or polyhedral composed of alternating silicon and oxygen atoms, for example:
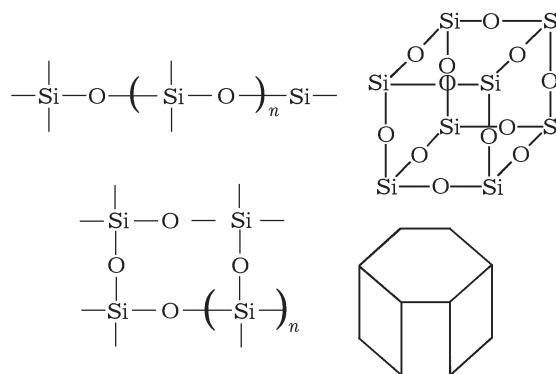
New methods of the synthesis of volatile triorganylsiloxy- or triorganylgermoxyoligosil-

oxanes have been developed at the Irkutsk Institute of Chemistry, SB RAS. These methods are based on the reaction of finely ground minerals or specially synthesized silicate materials with triorganylhalosilanes, triorhanylacyloxysilanes or triorganylhalogermanes in organic solvents [2−4].
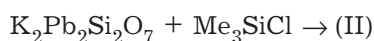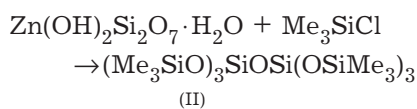
For example, the reaction of lithium orthosilicate powder with triorganylchlorosilanes in pyridine leads to tetrakis(triorganylsiloxy)silanes (I) at a quantitative yield:

$$Li_4SiO_4 + 4R_3SiCl \rightarrow (R_3SiO)_4Si + 4LiCl$$
$$\text{(I)}$$
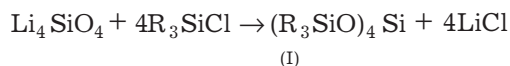
R = Me, Ar, Vin.

The reaction takes place when the reaction mixture is mixed for an hour at room temperature, the products (I) are isolated by vacuum distillation and do not contain any impurities as gas-liquid chromatography shows.

Per(trimethylsiloxy)disiloxane (II) has been obtained with a yield of about 100 % by treating kalomine mineral powder ($Zn_4(OH)_2Si_2O_7 \cdot H_2O$) or the powder of synthetic silicate $K_2Pb_2Si_2O_7$ with trimethylchlorosilane in the mixture of organic solvents (dimethylformamide DMFA − dioxane):

$$Zn(OH)_2Si_2O_7 \cdot H_2O + Me_3SiCl$$
$$\rightarrow (Me_3SiO)_3SiOSi(OSiMe_3)_3$$
$$\text{(II)}$$
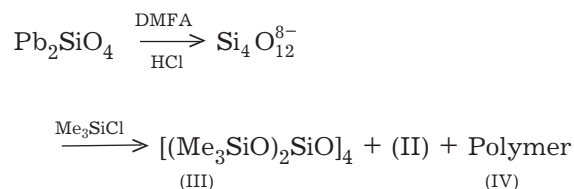
$$K_2Pb_2Si_2O_7 + Me_3SiCl \rightarrow \text{(II)}$$

The product (II) is a solid compound. It was purified by sublimation in vacuum.

A cyclic product octakis(trimethylsiloxy)cyclotetrasiloxane (III) was obtained with a 98 % yield by the reaction of trimethylchlorosilane with lead silicate according to the scheme

$$Pb_2SiO_4 + Me_3SiCl \rightarrow [(Me_3SiO)_2SiO]_4$$
$$\text{(III)}$$
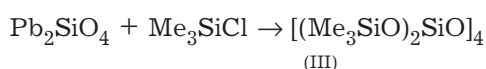
If this reaction is conducted in the mixture of DMFA with chloric acid, reaction rate increases. However, the cyclic anion $Si_4O_{12}^{8-}$ formed at the first stage gets partially decomposed, and a side product (II) is formed in the reaction mixture, along with the polymer (IV). These side products cause a decrease in the yield of (III) and complicate its isolation:
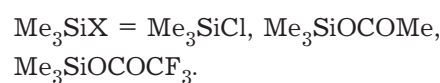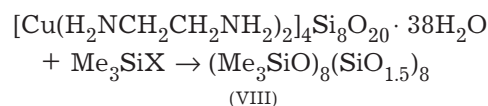
$$Pb_2SiO_4 \xrightarrow[HCl]{DMFA} Si_4O_{12}^{8-}$$

$$\xrightarrow{Me_3SiCl} [(Me_3SiO)_2SiO]_4 + \text{(II)} + \text{Polymer}$$
$$\text{(III)} \hspace{5cm} \text{(IV)}$$

In order to obtain hexakis(trimethylsiloxy)cyclotrisiloxane $[(Me_3SiO)_2SiO]_3$ (V), silicate $Ca_3Si_3O_9$ was trimethylsilylated. However, the rate of this reaction is small, it takes more than 10 days. A linear product is also formed in this reaction, along with (V).

Dodecakis(trimethylsiloxy)cyclohexasiloxane (VI) has been obtained with a yield of 96 % from the pyrosilicate $Na_2Ca_4Si_6O_{18}$ according to the scheme

$$Na_2Ca_4Si_6O_{18} + Me_3SiCl \rightarrow [(Me_3SiO)_2SiO]_6$$
$$\text{(VI)}$$

Macrocyclic pertrimethylsiloxydodecacyclosiloxane $[(Me_3SiO)_2SiO]_{12}$ (VII) has been synthesized from the silicates $Pb_{12}Si_{12}O_{36}$ and $Na_{16}Ca_4Si_{12}O_{36}$. Their reaction with trimethylchlorosilane in DMFA takes place at a low rate. This is explained by the formation of thin film of (VII) on the surface of silicate which prevents it from further decomposition to form $Si_{12}O_{36}^{24-}$ anions followed by their trimethylsilylation. Because of this, hexane was added to speed the reaction up since it dissolves the formed (VII).

Octa(trimethylsiloxy)silsesquioxane (VIII) with a carcass cubic structure was obtained by trimethylsilylation of the cyclic complex $[CuH_2NCH_2CH_2NH_2)_2]_4$ $Si_8O_{20} \cdot 38H_2O$ by trimethylchloro-, trimethylacetoxy-, or trimethyl(trifluoromethylacetoxy)silane in the DMFA − dioxane mixture:

$$[Cu(H_2NCH_2CH_2NH_2)_2]_4Si_8O_{20} \cdot 38H_2O$$
$$+ Me_3SiX \rightarrow (Me_3SiO)_8(SiO_{1.5})_8$$
$$\text{(VIII)}$$

$$Me_3SiX = Me_3SiCl, Me_3SiOCOMe,$$
$$Me_3SiOCOCF_3.$$

Depending on the nature of silylating reagent, the yield of (VIII) was 73.9, 86 and 86 % for trimethyl(trifluoromethylacetoxy)-, trimethylchloro-, and trimethylacetoxysilane, respectively. We did not study the kinetics of this reaction.

However, the data available allow us to conclude that the reaction proceeds *via* three stages:

1) the hydrolysis of trimethylsilylating reagent by water present in silicate or solvent which results in the formation of acids;

2) acidic decomposition of the silicate to form oligosilicic acids corresponding to the anion composition of the silicate;

3) their trimethylsilylation by the interaction with trimethylchloro-, or trimethylorganylacyloxysilane resulting in the formation of the corresponding pertrimethylsiloxyoligosiloxanes.

The necessity of the presence of hydrochloric or other strong acids at the first stages of the process is confirmed by the fact that trimethylsilylating reagents of the basic character (hexamethyldisilazane or bis(trimethylsilyl)acetamide) do not react though in the mixture with trimethylchlorosilane these compounds allow to obtain, in DMFA medium, per-(trimethylsiloxy)oligosiloxanes with quantitative yields. The addition of strong inorganic or organic acids to the reaction mixture allows to increase the reaction rate of silicate trimethylsilylation. The limiting stage of the process is probably acidic decomposition of silicates (stage 2). The rate of trimethylsilylation of silicates with linear or cyclic anions of small size is practically independent of the structure of silicon-oxygen skeleton. The quantitative yield of the target products is the evidence that no rearrangement of the siloxane skeleton of the silicate is observed during the reaction. Optimal solvents for the reaction are weakly basic solvents dimethylformamide or pyridine. When trimethylsilylating the silicates of complicated anion structure, it is necessary to add dioxane or hexane into the reaction mixture. In this case, the rate of silicate decomposition increases due to more intense purification of the sample surface from the reaction products.

The method developed for the preparation of oligoorganylsiloxanes is versatile and can be used also to obtain the compounds containing silicon and germanium atoms − triorganylgermoxyoligosiloxanes. For example, the treatment of lithium or lead orthosilicate with triethylbromogermane resulted in tetrakis(triethylgermoxy)silane and cyclic octakis(triethylgermoxy)cyclotetrasiloxane, respectively, according to the scheme

$$Li_4 SiO_4 + Et_3 GeBr \rightarrow (Et_3 GeO)_4 Si$$

$$Pb_2 SiO_4 + Et_3 GeBr \rightarrow [(Et_3 GeO)_2 SiO]_4$$
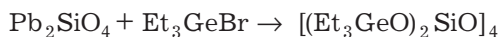
Thus synthesized triorganylsiloxy- and triorganylgermoxyoligosiloxanes form thin films on the surface of different materials when sublimated in vacuum, so they can be used as resists in microlithography and as protective films.

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