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Abstract

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SYNTHESIS OF ORGANOSILICON POLYHYDRIC ETHER ALCOHOLS

A number of works have been devoted to the synthesis of organosilicon polyhydric alcohols ($^{1-4}$); however, almost all of them concern derivatives based on tetra-substituted alkyl(aryl)silanes. The synthesis of ether alcohols is described only in three papers ($^{5-7}$), the authors of which report the preparation of dihydric ether alcohols by the hydrolysis reaction of heterocyclic organosilicon compounds obtained by the interaction of halomethylhalosilanes or halomethylalkoxysilanes with organic dihydric alcohols or phenols.

In our work, the synthesis was carried out of tri- and tetrahydric ether alcohols containing in their composition a β-oxyethoxymethyl group. Taking advantage of the ready hydrolyzability of the 1,1-dimethylsila-2,5-dioxacyclohexane synthesized by us earlier (^{7}), we carried out the reaction of its cohydrolysis with methyl-, ethyl-, phenyltriethoxysilanes and tetraethoxysilane according to the following general scheme:

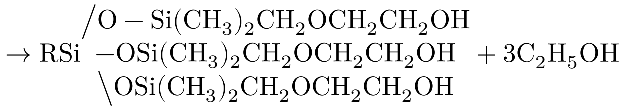
$$RSi(OC_2H_5)_3 + 3\,(CH_3)_2Si\langle\substack{O - CH_3 \\ CH_2 - O}\rangle CH_2 \xrightarrow{H_2O} RSi[OSi(CH_3)_2CH_2OCH_2CH_2OH]_3 + 3C_2H_5OH.$$

In the case of cohydrolysis with tetraethoxysilane, the corresponding tetrahydric ether alcohol $Si[OSi(CH_3)_2CH_2OCH_2CH_2OH]_4$ was obtained.

In cohydrolysis reactions, 1,1-dimethylsila-2,5-dioxacyclohexane reacts as a monofunctional derivative, and ethoxysilanes as tri- and tetrafunctional ones. Taking into account the different rates of hydrolysis of the starting compounds, the cohydrolysis reaction was carried out in such a way that first 1,1-dimethylsila-2,5-dioxacyclohexane was hydrolyzed with the calculated amount of water acidified with HCl, and then the ethoxysilane was immediately introduced.

It may be assumed that the reaction proceeds through the stage of formation of a silanol, which, however, cannot be isolated. The silanol formed enters into a condensation reaction with the ethoxysilane, eliminating ethyl alcohol and forming a Si–O–Si bond:

$$(CH_3)_2Si\langle\substack{O - CH_3 \\ CH_2 - O}\rangle CH_2 + H_2O \rightarrow \left[(CH_3)_2Si\substack{\langle OH \\ \langle CH_2 - OCH_2CH_2OH}\right] \xrightarrow{RSi(OC_2H_5)_3}$$



$$\rightarrow \mathrm{RSi}\begin{array}{l} /\mathrm{O-Si(CH_3)_2CH_2OCH_2CH_2OH} \\ -\mathrm{OSi(CH_3)_2CH_2OCH_2CH_2OH} \\ \backslash\mathrm{OSi(CH_3)_2CH_2OCH_2CH_2OH} \end{array} + 3\mathrm{C_2H_5OH}$$

The condensation reaction was carried out at a temperature of 40-50° with simultaneous evacuation of the mixture, collecting the ethyl alcohol evolved in a trap. The cohydrolysis reaction proceeds smoothly, with quantitative evolution of ethyl alcohol and with the formation of tri- and tetrahydric ether alcohols of the indicated structure. The ether alcohols obtained are colorless, transparent, viscous liquids, readily soluble in polar solvents and incompletely soluble in aromatic hydrocarbons. Their freezing temperatures lie in the range from −70 to −75°.

To prove the structure of the alcohols obtained, one of them—the tetrahydric alcohol—was subjected to hydrolysis in the presence of an excess of water acidified with HCl. Boiling the mixture for one hour led to no changes, which permits the conclusion that the alcohol under investigation contains no Si—O—C bonds, which might have remained in the event of separate hydrolysis of tetraethoxysilane and 1,1-dimethylsila-2,5-dioxacyclohexane.

Evidence that the synthesized alcohols contain no hydroxyl groups bonded to the silicon atom is provided by the agreement between the values for the percentage content of hydroxyl groups determined by two different methods—the Chugaev-Tserevitinov method, which makes it possible to determine labile hydrogen in any hydroxyl groups, and the acetylation method according to Verley, which makes it possible to determine hydroxyl groups located only in the organic radical.

Experimental Part

1. Synthesis of tris-(β-hydroxyethoxymethyldimethylsiloxy)-methylsilane

$\mathrm{CH_3Si[OSi(CH_3)_2CH_2OCH_2CH_2OH]_3}$.

To 20 g (0.15 mole) of 1,1-dimethylsila-2,5-dioxacyclohexane, placed in a three-necked flask equipped with a stirrer and thermometer, 2.7 ml (0.15 mole) of water acidified with HCl was added. The viscosity of the mixture increased noticeably. After several minutes, methyltriethoxysilane (8.9 g—0.05 mole) was added to the mixture, and after 20 min of heating at 40-50° the reaction mixture was evacuated at the same temperature and a residual pressure of 1 mm. The liberated ethyl alcohol was collected in a receiver cooled with a mixture of dry ice and acetone. 6.8 g of alcohol was isolated, n_D^{20} 1.3665 (yield 99% of theory).

The residue after distillation of the alcohol was a colorless, transparent, viscous liquid; n_D^{20} 1.4455, d_4^{20} 1.063. MR_{found} 123.10; MR_{calc} 124.02; weight 20.8 g. Yield 84.7% of theory.

Found, %: C 39.16, 39.09; H 8.59, 8.46; Si 22.67, 22.87; OH 10.66, 10.49
$C_{16}H_{42}O_9Si_4$. Calculated, %: C 39.14; H 8.62; Si 22.89; OH 10.39

2. Synthesis of tris-(β-hydroxyethoxymethyldimethylsiloxy)-ethylsilane

$C_2H_5Si[OSi(CH_3)_2CH_2OCH_2CH_2OH]_3$.

The synthesis was carried out by an analogous procedure. For the reaction, 52.8 g (0.4 mole) of 1,1-dimethylsila-2,5-dioxacyclohexane, 25.6 g (0.13 mole) of ethyltriethoxysilane, and 7.2 g (0.4 mole) of water were taken. After evacuation, 56.9 g of trihydric alcohol was obtained, yield 84.6% of theory. n_D^{20} 1.4450; d_4^{20} 1.055. MR_{found} 129.80; MR_{calc} 128.79.

Found, %: C 39.57, 39.51; H 8.83, 8.61; Si 22.32, 22.76;
OH 10.31, 10.35
$C_{17}H_{44}O_9Si_4$. Calculated, %: C 40.44; H 8.78; Si 22.25;
OH 10.12

3. Synthesis of tris-(β-hydroxyethoxymethyldimethylsiloxy)-phenylsilane

$C_6H_5Si[OSi(CH_3)_2CH_2OCH_2CH_2OH]_3$.

The synthesis was carried out by an analogous procedure. From 19.0 g (0.15 mole) of 1,1-dimethylsila-2,5-dioxacyclohexane, 12.0 g (0.05 mole) of phenyltriethoxysilane, and 2.7 ml (0.15 mole) of water acidified with HCl, 6.5 ml of ethyl alcohol (n_D^{20} 1.3701) was obtained (yield 94% of theory) and 24.9 g of tris-(β-hydroxyethoxymethyldimethylsiloxy)-phenylsilane, yield 90.2% of theory. n_D^{20} 1.4775; d_4^{20} 1.108; MR_{found} 142.50; MR_{calc} 144.15.

Found, %: C 46.00, 46.25; H 7.86, 7.93; Si 19.96, 19.68; OH 9.20, 9.05
$C_{21}H_{44}O_9Si_4$. Calculated, %: C 45.62; H 8.02; Si 20.30; OH 9.22

4. Synthesis of tetrakis-(β-hydroxyethoxymethyldimethylsiloxy)-silane

$Si[OSi(CH_3)_2CH_2OCH_2CH_2OH]_4$.

By an analogous procedure, from 26.5 g (0.2 mole) of 1,1-dimethylsila-2,5-dioxacyclohexane, 10.4 g (0.05 mole) of tetraethoxysilane, and 3.6 ml (0.2 mole) of water, 30.0 g of tetrahydric alcohol was obtained; yield 96.5% of theory.
n_D^{20} 1.4500; d_4^{20} 1.089; MR_{found} 154.85; MR_{calc} 155.31.

Found, %: C 38.01, 38.02; H 8.24, 8.23; Si 22.44, 22.30;
OH 10.15, 10.65

$C_{20}H_{52}O_{12}Si_5$. Calculated, %: C 38.43; H 8.38; Si 22.46;
OH 10.87

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