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Synthesis of triethoxysilanol

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Triethoxysilanol was isolated for the first time by hydrolysis of chloro(triethoxy)silane in an organic solvent in the presence of a heterogeneous base and identified as an individual compound. The synthesis of this compound made it possible to study its physicochemical properties and substantially extended its potentialities for the synthesis of hyperbranched polyethoxysiloxanes and functional oligomers.

Key words: chloro(triethoxy)silane, triethoxysilanol, hyperbranched polyethoxysiloxane.

The synthesis of triethoxysilanol was mentioned[1] for the first time in the late XIX century. However, the reported results were not substantiated and triethoxysilanol was regarded in scientific literature only as a reactive intermediate in the hydrolysis of tetraethoxysilane almost for the next hundred years.[2—5] Progress in analytical techniques and especially in ^{29}Si NMR spectroscopy made it possible to detect the presence of triethoxysilanol in reaction mixtures. The reported[6] chemical shift for the Si atom in triethoxysilanol (δ –76.95) gives some objective grounds for numerous assumptions. The value obtained agrees with the previous[7,8] assignments and is now universally accepted. As a major intermediate that is stable for at least several hours in THF, triethoxysilanol is used as the reagent AB_3 in the synthesis of hyperbranched polyethoxysiloxanes.[9—11] It should be emphasized that triethoxysilanol was isolated as an individual compound in none of the above studies.

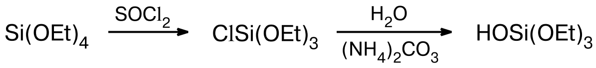
The instability of triethoxysilanol is associated with the presence of functional groups of two types (—OH and —OEt) in its molecule, which can undergo subsequent transformations and interact with each other. It is well known that the reactivities of such functional groups are determined by the presence of ionic impurities; without them, silanols very sluggishly interact with both the hydroxy and ethoxy groups of other molecules.[12] Even reactive silanols can be distilled in the absence of ionic impurities.[13]

Owing to its chemical structure,[12] triethoxysilanol should be relatively stable in a neutral medium containing no ionic impurities. The goal of the present work was to select an appropriate starting reagent and conditions for its conversion into silanol.

We started from chloro(triethoxy)silane prepared in 85% yield by chlorination of tetraethoxysilane[14] with thionyl chloride[15] in the presence of catalytic amounts of DMF.

It is known[16] that the condensation of hydrolysis products from chlorosilanes is mainly due to heterofunctional condensation of chlorosilyl groups with hydroxyl ones. To suppress this process, an excess of water was used for hydrolysis. The hydrolysis of chloro(triethoxy)silane ($c \le 5\%$) was carried out in THF at 0 °C in the presence of $(NH_4)_2CO_3$ as a heterogeneous base. A dilute solution of chloro(triethoxy)silane was added to a mixture of THF, water, and the base to give the target triethoxysilanol, which was isolated by distillation *in vacuo* in 70% yield (Scheme 1).

Scheme 1



$$Si(OEt)_4 \xrightarrow{SOCl_2} ClSi(OEt)_3 \xrightarrow[(NH_4)_2CO_3]{H_2O} HOSi(OEt)_3$$

Triethoxysilanol is a transparent mobile liquid, b.p. 52 °C (1 Torr). Its structure was confirmed by ^{1}H and ^{19}Si NMR and mass spectra and elemental analysis data.

The synthesis and isolation of triethoxysilanol substantially extends the possibilities of obtaining silicon-containing compounds, including hyperbranched polyethoxysiloxanes. The fact itself of the stability of triethoxysilanol is also important, which makes it promising to develop simpler routes to this compound.

Experimental

GLC analysis was performed on a 3700 chromatograph (Russia) with a katharometer as a detector (helium as a carrier gas,

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column dimensions 2 m × 3 mm, SE-30 stationary phase (5%) on Chromaton-H-AW). ^{1}H NMR spectra were recorded on a Bruker WP-200 SY instrument (200.13 MHz) in $CDCl_3$ with Me_4Si as the internal standard. IR spectra were recorded on a Bruker Equinox 55/S instrument. Mass spectra (EI, 70 eV) were recorded on a Finnigan MAT INCOS instrument. Commercial chemicals $Si(OEt)_4$ and DMF were additionally purified by distillation.

Chloro(triethoxy)silane. Tetraethoxysilane (104.18 g, 0.5 mol) was added at 25 °C for 1 h to a stirred mixture of $SOCl_2$ (59.49 g, 0.5 mol) and DMF (0.5 mL). The reaction mixture was stirred for 4 h and distilled *in vacuo* to give chloro(triethoxy)silane (84.45 g, 85%), b.p. 75 °C (45 Torr) (*cf.* Ref. 13: b.p. 68.5—69 °C (32 Torr)).

Triethoxysilanol. A solution of chloro(triethoxy)silane (20.27 g, 0.102 mol) in THF (200 mL) was added at 0 °C to a stirred mixture of $(NH_4)_2CO_3$ (58.19 g, 0.51 mol) and water (9.19 g, 0.51 mol) in THF (500 mL). The precipitate was filtered off and the filtrate was dried over Na_2SO_4. Distillation *in vacuo* gave a product (12.87 g, 70%) with b.p. 51.5—52 °C (1 Torr), d_4^{25} 1.0184, n_D^{20} 1.3962. Found (%): C, 39.76; H, 8.72; Si, 15.60. $C_6H_{16}O_4Si$. Calculated: C, 39.98; H, 8.96; Si, 15.57. ^{1}H NMR ($CDCl_3$), δ: 1.189, 1.218, 1.245 (t, OCH_2CH_3, 3 H, $J = 2.9$ Hz); 3.80, 3.83, 3.85, 3.88 (q, OCH_2CH_3, 2 H, $J = 2.0$ Hz). ^{29}Si NMR (toluene), δ: −78.82 (s, 1 Si). MS, m/z: 179 $[M]^+$, 165 $[M - Me]^+$, 151 $[M - Et]^+$, 135 $[M - EtO]^+$, 121 $[M^+ - 2 Et]^+$, 107 $[M - Me - 2 Et]^+$, 91 $[M - Me - Et - EtO]^+$, 77 $[M - 2 Et - EtO]^+$.

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