



# USE OF TETRAKIS(2-ETHOXYETHOXY)SILANE FOR THE PREPARATION OF ETHYLALKOXYSILANES OF A SINGLE STRUCTURE BY THE ORGANOMAGNESIUM METHODS

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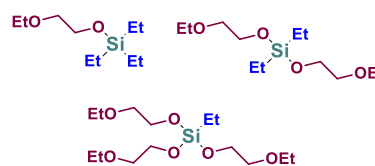
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## Abstract

A new method for obtaining individual ethylalkoxysilanes of various types of substitution without using chlorosilanes is proposed based on the reactions of tetrakis(2-ethoxyethoxy)silane with the Grignard reagents. The structures of the compounds obtained are confirmed by NMR spectroscopy and GLC.

**Key words:** alkoxy silanes, ethyltrialkoxysilane, diethyldialkoxysilane, triethylalkoxysilane, organomagnesium synthesis, tetrakis(2-ethoxyethyl)orthosilicate.



## Introduction

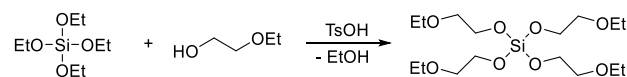
Ethylsiloxane polymers are unique and interesting representatives of organoelement high-molecular compounds [1–3]. There are both ethylsiloxane homopolymers and ethylsiloxane fluids and resins derived from a mixture of different ethylsilanes. The starting material for them are, as a rule, chlorosilanes obtained by the direct synthesis and difficult to separate due to close boiling points. Furthermore, the most valuable chlorosilanes are synthesized with not very high yields [4, 5].

In this communication, we suggest a new method for obtaining ethylalkoxysilanes utilizing organomagnesium synthesis: by the interaction of the Grignard reagent of ethyl bromide with high-boiling tetrakis(2-ethoxyethoxy)silane (compound **1**). A difference between the boiling points of the substitution products of compound **1** is greater than in the case of the derivatives of ethoxy- or methoxysilanes. This method allowed for isolating individual ethylalkoxysilanes—the products of variable degree of substitution of tetrakis(2-ethoxyethoxy)silane, which, in turn, can be obtained by the direct synthesis [6, 7].

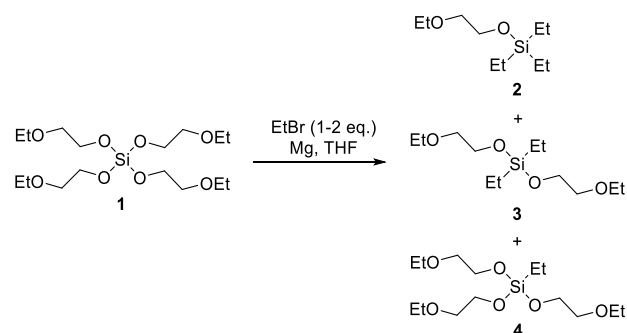
## Results and discussion

At the first step, tetrakis(2-ethoxyethoxy)silane **1** was obtained by the transesterification of tetraethoxysilane (TEOS) with ethyl cellosolve in the presence of *p*-toluenesulfonic acid followed by the distillation of ethanol (Scheme 1). The product purity was established by GLC and <sup>1</sup>H NMR spectroscopy (98%) (see Figs. S1, S2 in the Electronic supplementary information (ESI)). The yield of **1** was 70%.

At the next step, the reaction between compound **1** (1 equiv) and the Grignard reagent derived from ethyl bromide (1–2 equiv) and magnesium (1.2–2.4 equiv) in dry THF was carried out (Scheme 2).

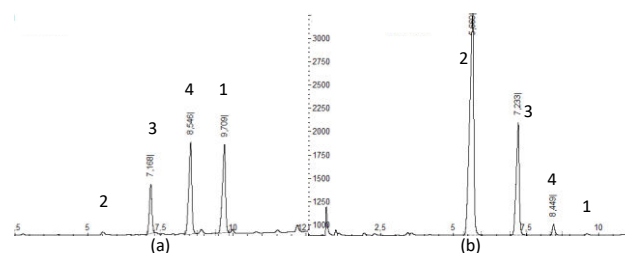


**Scheme 1.** Synthesis of tetrakis(2-ethoxyethoxy)silane.



**Scheme 2.** Synthesis of ethyl(2-ethoxyethoxy)silanes.

Figure 1 shows the GLC curve of the product mixture depending on the ratio of ethyl bromide and compound **1** after separation from the precipitate and removal of the excess solvent. Unlike the products of the interaction of TEOS with ethyl bromide, this mixture can readily be separated.



**Figure 1.** GLC curves of the reaction products at the EtBr/**1** ratios of 1:1 (a) and 2:1 (b).

The products of mono-, di-, trisubstitution of compound **1** were separated by distillation under reduced pressure. Di(2-ethoxyethoxy)diethylsilane **3** had a boiling point of 140 °C at 100 mbar. Its structure was confirmed by <sup>1</sup>H, <sup>29</sup>Si, and <sup>13</sup>C NMR spectroscopy (Figs. S3–S6 in the ESI). According to the results of the GLC analysis, (2-ethoxyethoxy)triethylsilane **2** was obtained with 98.5% purity; its boiling point was *ca.* 105 °C at 100 mbar. The <sup>1</sup>H and <sup>29</sup>Si NMR spectra (Figs. S7–S9 in the ESI) indicated the presence of a by-product, which we assume to be hexamethyldisiloxane.

Tri(2-ethoxyethoxy)ethylsilane **4** was obtained with a lower purity of 95% due to the presence of impurities featuring close boiling points and difficult to separate at small substance amounts. The product was distilled at *ca.* 190 °C at 0.5 mbar. Its structure was confirmed by <sup>1</sup>H NMR spectroscopy and GLC (Figs. S10, S11 in the ESI).

## Experimental section

### General remarks

The reagents were purchased from commercial sources and used without further drying and purification. Dry THF was prepared by refluxing over calcium hydride for 3–5 h followed by the distillation under an argon atmosphere.

The <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR spectra were recorded on a Bruker Avance AV-300 spectrometer (300 MHz for <sup>1</sup>H, 77.5 MHz for <sup>13</sup>C, 59.6 MHz for <sup>29</sup>Si).

### Syntheses

**Reaction at the 1/EtBr/Mg ratio of 1:2:2.4.** A portion (30 mL) of a solution of tetrakis(2-ethoxyethoxy)silane **1** (200 g, 0.52 mol) and ethyl bromide (114 g, 1.05 mol) in THF (8000 mL) was added dropwise to Mg (30 g, 1.25 mol) under an argon atmosphere. After the reaction initiation, the addition of the reagents was continued. The reaction mixture was refluxed for 3 h. The solvent was removed under vacuum. Then hexane was added, and the resulting precipitate was filtered off. The filtrate was evaporated under reduced pressure. The residue obtained was distilled at reduced pressure to give compound **3** with 98.5% purity. Yield: 35%. Bp: 140–145 °C/100 mbar.

**Reaction at the 1/EtBr/Mg ratio of 1:1:1.2.** The reaction was performed analogously to the above-described procedure and afforded compound **2** with 98.5% purity in 54% yield (bp: 105 °C/100 mbar) and compound **4** with 95% purity in 15% yield (bp: 190 °C/0.5 mbar).

## Conclusions

To summarize the results presented, we proposed a new method for synthesis of ethylalkoxysilanes featuring different degrees of substitution of the alkoxysilyl groups at the silicon atom and their isolation in the individual form. Thus, the reactions of tetrakis(2-ethoxyethyl)orthosilicate with ethyl bromide under conditions of organomagnesium synthesis afforded ethylalkoxysilanes that have a large difference in boiling points, in contrast to ethylethoxysilanes derived from the most common reagent—tetraethoxysilane. We hope that the

suggested approach will facilitate the isolation of organoalkoxysilanes, including those hard-to-reach, in laboratory practice.

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## Electronic supplementary information

Electronic supplementary information (ESI) available online: the <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR spectra; the GPC curves. For ESI, see DOI: 10.32931/io2403a.

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