# Synthesis of diethoxy(phenyl)silane and its polycondensation in acetic acid\*

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Low-temperature reaction between phenylmagnesium chloride and triethoxysilane at lowered affords diethoxy(phenyl)silane, whose polycondensation in acetic acid gives oligomeric (phenyl)hydrosiloxanes.

Key words: silanes, hydrosilanes, hydrosiloxane oligomers, polycondensation.

One of the urgent modern tendencies in the synthesis of organosilicon polymers is the use of organoalkoxysilanes as the starting compounds instead of their chlorosilane analogs. Accessibility of new types of organoalkoxysilanes plays the determining role in the further development of structural diversity of polymers based on these organoalkoxysilanes. The latter are usually obtained by the alkoxylation of the corresponding chlorosilanes, such as tetrachloro- and trichloromethyl- or trichlorophenylsilanes.<sup>1</sup> Hydride-containing alkoxysilanes form a special group. and the methods for their synthesis, on the whole, are insufficiently developed. (Alkoxy)(alkyl)hydrosilanes are fairly accessible, since they can be synthesized by the esterification of the corresponding commercial chlorosilanes. Similar prospects for the production of phenyl-containing alkoxyhydrosilanes are less reliable, because the respective chlorosilanes are formed as minor admixtures in the synthesis of trichlorophenylsilane.<sup>2</sup> Another way seems more efficient: the synthesis of these compounds using the Grignard reaction from large-tonnage triethoxysilane. At the same time, its application in the Grignard reactions is impeded by disproportionation processes to form silane, which makes these reactions dangerously explosive.<sup>3</sup> Unfortunately, similar reactions are insufficiently studied; in addition, literature data on the use of (alkoxy)(phenyl)hydrosilanes for synthesis of oligomers and polymers are lacking.

Meanwhile, oligomers and polymers with (phenyl)hydrosilane units seem to be rather promising for a whole series of reasons. Among the most substantial ones are the problem of compatibility of organosilicon polymers with organic polymers in various composites and compositions. In this case, the use of phenyl-containing siloxanes has explicitly more advantages over methylsiloxane analogs. The introduction of (phenyl)hydrosilyl units into the composition of siloxane hydride-containing composites is promising from the viewpoint of controlling the reactivity of hydrosilyl fragments. These circumstances are especially important for the synthesis of siloxane composites with a high refractive index.<sup>4</sup>

Several methods for synthesis of (dialkoxy)(organyl)hydrosilanes are known to date<sup>5,6</sup>; however, none of them has preparative significance. The purpose of this work is the synthesis of hydride-containing alkoxyphenylsilanes and functional oligomers based on them. It seemed urgent to develop a convenient method for the synthesis of hydride-functional alkoxyphenylsilanes by the Grignard reaction from industrial triethoxysilane (Scheme 1).

#### Scheme 1

PhCI 
$$\xrightarrow{Mg}$$
 PhMgCl  $\xrightarrow{HSi(OEt)_3}$   
 $\longrightarrow$  PhSiH(OEt)<sub>2</sub> + Ph<sub>2</sub>SiH(OEt)

The study showed that the determining parameter, in this case, is the reaction temperature, which depends, in turn, on the rate of addition of the Grignard reagent to the reaction mixture: a solution of phenylmagnesium chloride in THF should be added to pure triethoxysilane in such a way that the temperature should not exceed -30 °C. When the temperature is decreased to -60 °C, the target reaction proceeds smoothly and is not accompanied by side rearrangement that afford dangerous silane. As the temperature increases to ambient, tetraethoxysilane, which could be formed by triethoxysilane disproportionation, was observed in the reaction mixture in the presence of ethoxymagnesium chloride (Scheme 2).

#### Scheme 2

\* Dedicated to the Academician of the Russian Academy of Sciences I. P. Beletskaya on the occasion of her anniversary.

4  $HSi(OEt)_3 \longrightarrow SiH_4 + 3 Si(OEt)_4$ 

Published in Russian in Izvestiya Akademii Nauk. Seriya Khimicheskaya, No. 3, pp. 0705-0709, March, 2013.

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Undesirable reactions were inhibited after the process ceased by immediate dilution with hexane and filtration off of the solid residue. The filtrate containing the target product was stable, and no evolution of gaseous products from side reactions was observed. Thus, a mixture containing 35-40% PhSiH(OEt)<sub>2</sub> and 45-50% Ph<sub>2</sub>SiH(OEt) was obtained. Individual compounds were isolated by rectification *in vacuo*.

The synthesized phenyl-substituted hydrosilanes are promising for the synthesis of earlier inaccessible polymers. First, a molecule of  $PhSiH(OEt)_2$  can be considered as bifunctional monomer in the condensation of alkoxy groups. Based on this monomer, one can obtain oligomers with the latent functional Si—H groups of both linear and cyclic structure and branched oligomer in a mixture with other alkoxysilanes. Second, a  $Ph_2SiH(OEt)$  molecule is a compound monofunctional with respect to the alkoxy group and can be used as blocking agent containing the screened hydrosilyl group.

We have previously shown<sup>7,8</sup> that the condensation of bifunctional alkoxysilanes in anhydrous acetic acid, which acts as both solvent and reagent, is a promising method for the selective synthesis of linear or cyclic siloxane oligomers and polymers. Therefore, it is promising to study the condensation of the obtained compounds by the indicated method. In this case, the main problem is a fairly high lability of the hydrosilyl group, which can result, under the proposed conditions, in undesirable secondary reactions of this bond cleavage and, hence, in the appearance of defect branching units.

The course of condensation was monitored by a change in the intensity of signals from protons of the ethoxysilyl groups in the <sup>1</sup>H NMR spectrum of samples of the reaction mixture. After cessation of the process, *i.e.*, after the complete conversion of the Si–OEt groups, the reaction product was analyzed by GPC, <sup>1</sup>H NMR spectroscopy, and IR spectroscopy.

According to the IR spectroscopic data, the oligomeric products of alkoxysilane condensation in an active medium always contains residual hydroxysilyl groups. To evaluate their amount and to obtain the stable product, the synthesized oligomers were blocked with trimethylchlorosilane (Scheme 3) under the conditions that, as shown previously,<sup>8</sup> do not distort the structure of the reaction products.

## Scheme 3



In fact, after the complete conversion of hydroxysilyl groups, which was confirmed using IR spectroscopy by the absence of absorption in the region of 3100-3600 cm<sup>-1</sup>



**Fig. 1.** GPC curves for oligo(phenyl)hydrosiloxane obtained in entry I (see Table 1) before (I) and after (2) blocking the terminal groups by trimethylchlorosilane.

characteristic of OH groups, the GPC curves of the polycondensation product before and after blocking almost coincided (Fig. 1). The quantitative determination of hydroxysilyl groups in the synthesized compounds is possible from the ratio of intensities of signals from protons of the methyl and phenyl groups in the <sup>1</sup>H NMR spectra of the blocked samples.

An analysis of the product of condensation of diethoxy-(phenyl)silane in acetic acid with reflux (see Table 1, entry *I*) by the procedures described above showed that the synthesized oligosiloxane is a mixture of oligomers with the monomodal distribution (from 40 000 to 500 amu) (see Fig. 1) with the maximum intensity at 1000 amu. The content of hydroxy groups in the synthesized product was ~0.5 wt.%.

A significant decrease in the content of hydrosilyl groups was observed upon condensation. According to the <sup>1</sup>H NMR spectroscopic data, the conversion of hydrosilyl groups due to side reactions was ~30%. An additional introduction of anhydrous ethanol into the reaction mixture on reflux of diethoxy(phenyl)silane in acetic acid (see Table 1, entry 2) resulted in an increase in the conversion of hydrosilyl groups to 50%. The obtained oligo(phenyl)-hydrosiloxane was characterized by a broader molecular weight distribution (from 75 000 to 500 amu) (Fig. 2) and contained the same 0.5 wt.% of OH groups. It was shown previously<sup>7</sup> that the introduction of alcohol into the reaction mixture on reflux is an efficient method for enhancing



**Fig. 2.** GPC curves for oligo(phenyl)hydrosiloxane obtained in entry *2* (see Table 1).

Entry	Conditions of condensation		Characteristics of product		
	Composition of reaction mixture (molar ratio)	<i>T<sup>a</sup></i> /°C	$\overline{C^b\left(\% ight)}$	N <sup>c</sup> (%)	$n_{\rm D}^{20d}$
1	PhSiH(OEt) <sub>2</sub> —AcOH $(1:10)$	B.p.	30	0.50	1.5732
2	PhSiH(OEt) <sub>2</sub> -AcOH-EtOH (1:3:0.5)	B.p.	50	0.51	1.5670
3	$PhSiH(OEt)_2 - AcOH - H_2O$ (1:10:5)	~20	0	0.14	1.5682

Table 1. Characterization of the products of diethoxy(phenyl)silane condensation in an active medium

<sup>*a*</sup> Condensation temperature.

<sup>b</sup> Percentage of losses of silyl hydride moieties calculated from the <sup>1</sup>H NMR spectrum of the product.

<sup>c</sup> Number of terminal OH groups calculated from the <sup>1</sup>H NMR spectrum of the condensation product blocked

by trimethylchlorosilane.

<sup>d</sup> Refractive index of the obtained condensation product.

selectivity of condensation towards cyclic product formation. Unfortunately, in our case, the introduction of alcohol only increased the undesirable loss of silyl hydride moieties.

Since hydrosilyl groups of  $PhSiH(OEt)_2$  are unstable on reflux in acetic acid, they cannot be considered as a latent functional group. At the same time, the controlled character of their conversion can be used for the synthesis of branched polycyclic structures. A simple comparison of the molecular weight of the obtained products, conversion of hydrosilyl groups, and residual hydroxy groups suggests that a branched polycyclic structure of the obtained polymer was formed (Scheme 4).

# Scheme 4

EtO-Si-OEt 
$$\xrightarrow{AcOH}$$
 HO  $\xrightarrow{Ph}$   $\xrightarrow{I}$   $\xrightarrow$ 

It has earlier been shown<sup>8</sup> that for the processes carried out under the conditions of active medium, *i.e.*, in an excess of anhydrous acetic acid, the reaction follows the mechanism of hydrolysis condensation. Its main distinctive feature is that the all water necessary for the reaction is formed in the course of esterification of acetic acid with alcohol that is evolved by the acetoxylation of alkoxysilane (Scheme 5).

## Scheme 5

AcOH + EtOH 
$$\implies$$
 AcOEt + H<sub>2</sub>O  
H  $\downarrow$   
EtO-Si-Ac + H<sub>2</sub>O  $\implies$  EtO-Si-OH + AcOH  
Ph Ph Ph

If we assume that this is the esterification stage which requires to carry condensation at elevated temperatures, the addition of water should allow the process to be carried out in acetic acid at ambient temperature. An analysis by <sup>1</sup>H NMR spectroscopy of the condensation product with the ratio of the initial reactants PhSiH(OEt)2-AcOH-H2O 1:10:5 showed that the ratio of intensities of signals from protons of the hydrosilyl and phenyl groups of the product corresponded to the initial one, which indicates the stability of the hydride group at the silicon atom under these conditions. The products obtained under these conditions possessed, according to the GPC data, the bimodal molecular weight distribution (Fig. 3). The low-molecular-weight fraction was  $\sim 60\%$  of the weight of the whole product and was characterized by a narrow dispersion distribution with  $M_{\text{peak}} = 600$  amu and a minimum (0.14%) amount of hydroxy groups. The GLC method established that this fraction was a mixture of cis- and trans-isomers of hydride-containing phenylcyclotri- and tetrasiloxanes (see Table 1, entry 3). Summating the obtained results, one can conclude the predominantly cyclic structure of the synthesized product and the



**Fig. 3.** GPC curves for oligo(phenyl)hydrosiloxane obtained at ambient temperature (see Table 1, entry *3*).

absence of side reactions involving hydrosilyl groups (Scheme 6).

## Scheme 6



Thus, in the course of the performed study, we proposed an efficient method for the synthesis of hydridecontaining ethoxyphenylsilanes and found the conditions for the preparation from them branched polycyclic polymers formed due to the complete conversion of ethoxy groups and partial conversion of hydrosilyl groups during condensation in an active medium. It was found that the hydrolytic condensation in acetic acid at ambient temperature can produce products of predominantly cyclic structure. In this case, the complete conversion of ethoxysilyl groups is achieved but, unlike the previous case, the hydrosilyl groups are not involved in the reaction.

# Experimental

Tetrahydrofuran, hexane, acetic acid, and ethanol were purified according to earlier described procedures.<sup>9</sup> Triethoxysilane with the content of the major component  $\geq$ 98.5% was used without additional purification.

<sup>1</sup>H NMR spectra were recorded on a Bruker WP-250 SY spectrometer (250.13 MHz) using Me<sub>4</sub>Si as an internal standard and CDCl<sub>3</sub> as a solvent. A Chromatec-Crystal 5000 chromatograph (Russia) was used for GLC (catharometer served as a detector, helium as a carrier gas, columns 2 m S 3 mm, stationary phase SE-30 (5%) on Chromaton-H-AW).

A GPC analysis was carried on a chromatographic system consisting of a Staier seriya 2 high-pressure pump (Akvilon, Russia), a RIDK 102 refractometric detector (Czechia), and a Jetstream 2 Plus thermostat of columns (Knauer, Germany). The thermostatting temperature was 40 °C ( $\pm$ 0.1 °C); THF as an eluent, flow rate 1.0 mL min<sup>-1</sup>; column 300S7.8 mm packed with the sorbent Phenogel (Phenomenex, USA), particle size 5  $\mu$ m, pore size 10<sup>3</sup> Å (passport rage of separation was up to 75 000 D). The data were recorded and calculated using the UniChrom 4.7 program (Belarus). The molecular weight was estimated from the ratio to linear polystyrene standards.

IR spectra were recorded on an Equinox 55/S IR spectrometer (Bruker). Liquid cells with KBr glasses were used for measurements (solvent  $CCl_4$ ).

An IRF-454B2M refractometer was used to measure the refractive index.

Diethoxy(phenyl)silane and ethoxy(diphenyl)silane. A solution of phenylmagnesium chloride (0.5 mol), which was ob-

tained from 0.5 mole of (56.5 g) of chlorobenzene and 0.55 mole (13.5 g) of magnesium in THF (400 mL) and then transferred with a needle to a dropping funnel under argon, was added with permanent stirring in an continuous argon flow for 4 h to 164 g (1 mol) of triethoxysilane at -60 °C. A white precipitate was formed during the addition. Then the temperature was brought to ambient, after which anhydrous hexane (300 mL) was immediately added to the obtained reaction mixture. The precipitate was filtered off and washed with hexane (3S100 mL). Hexane and a triethoxysilane excess were distilled off in vacuo (247 Torr). Target PhSiH(OEt)<sub>2</sub> was isolated by fractionation in vacuo, the yield was 38 g (40%), colorless liquid, b.p. 97–98 °C (12 Torr). <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ: 7.35–7.67 (m, 5 H,  $(C_{6}H_{5})(H)Si)$ ; 4.93 (s, 1 H (H)Si); 3.84–3.93 (m, 4 H,  $(CH_3CH_2O)Si$ ; 1.27 (t, 6 H,  $(CH_3CH_2O)Si$ )). The second product Ph<sub>2</sub>SiH(OEt) was isolated continuing distillation at 0.75 Torr, the yield was 25 g (45%), colorless liquid, b.p. 67 °C (0.75 Torr). <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$ : 7.37–7.68 (m, 10 H, (C<sub>6</sub>H<sub>5</sub>)(H)Si); 5.45 (s, 1 H (H)Si); 3.84–3.92 (m, 2 H, (CH<sub>3</sub>CH<sub>2</sub>O)Si); 1.28 (t, 3 H,  $(C\underline{H}_{3}CH_{2}O)Si)).$ 

**Condensation of PhSiH(OEt)**<sub>2</sub> in acetic acid in a molar ratio of 1: 10. A mixture of PhSiH(OEt)<sub>2</sub> (2.0 g, 0.01 mol) and anhydrous AcOH (6.1 g, 0.10 mol) was refluxed with vigorous stirring until the signals from protons of the ethoxy groups completely disappeared from the <sup>1</sup>H NMR spectra of samples of the reaction mixture. Then volatiles were removed at 20–25 °C (0.75 Torr). The yield of the product was 1.26 g (99%). <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$ : 4.75–5.25 (m, 1 H, <u>H</u>(C<sub>6</sub>H<sub>5</sub>)Si); 7.10–7.80 (m, 5 H, H(C<sub>6</sub>H<sub>5</sub>)Si). IR (CCl<sub>4</sub>), v/cm<sup>-1</sup>: 3300 (OH) w. The amount of terminal hydroxy groups in the obtained poly(phenyl)hydrosilane calculated by the <sup>1</sup>H NMR spectroscopic data of the samples blocked with trimethylchlorosilane was 0.50%.  $n_D^{20} = 1.5732$ . GPC: 40000–500 amu,  $M_{peak} = 1000$  amu. Found (%): Si, 22.90; C, 57.06; H, 4.50. C<sub>6</sub>H<sub>5.67</sub>O<sub>1.17</sub>Si. Calculated (%): C, 57.88; H, 4.56; Si, 22.50.

Condensation of PhSiH(OEt)<sub>2</sub> in acetic acid with an addition of ethanol in a molar ratio of 1 : 3 : 0.5. A mixture of PhSiH(OEt)<sub>2</sub> (9.1 g, 0.047 mol), AcOH (8.5 g, 0.141 mol), and anhydrous EtOH (1.1 g, 0.024 mol) was refluxed with vigorous stirring until the signals from protons of the ethoxy groups completely disappeared from the <sup>1</sup>H NMR spectra of samples of the reaction mixture. All volatiles were distilled off. The yield of the product was 5.9 g (99%). <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$ : 4.75–5.25 (m, 1 H, <u>H</u>(C<sub>6</sub>H<sub>5</sub>)Si); 7.10–7.80 (m, 5 H, H(C<sub>6</sub>H<sub>5</sub>)Si). IR (CCl<sub>4</sub>), v/cm<sup>-1</sup>: 3300 (OH) w. The amount of terminal hydroxy groups of obtained poly(phenyl)hydrosiloxane calculated from the data of <sup>1</sup>H NMR spectroscopy of the samples blocked with trimethylchlorosilane was 0.51%.  $n_D^{20} = 1.5670$ . GPC: 75000–500 amu,  $M_{peak} = 1800$  amu. Found (%): Si, 22.70; C, 56.8; H, 4.40. C<sub>6</sub>H<sub>5.55</sub>O<sub>1.26</sub>Si. Calculated (%): Si, 22.27; C, 57.3; H, 4.41.

Condensation of PhSiH(OEt)<sub>2</sub> in acetic acid with an addition of water in a molar ratio of 1 : 10 : 5. A mixture of PhSiH(OEt)<sub>2</sub> (1.36 g, 0.007 mol), AcOH (4.16 g, 0.069 mol), and water (0.62 g, 0.035 mol) was stirred at ~20 °C to the complete disappearance of signals from protons of the ethoxy groups in the <sup>1</sup>H NMR spectra of samples of the reaction mixture. Then the reaction mixture was dissolved in toluene, washed off with distilled water to neutral pH, dried over sodium sulfate, and evacuated on heating to 50 °C. The yield of the product was 0.86 g (97%). <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$ : 4.75–5.25 (m, 1 H, <u>H</u>(C<sub>6</sub>H<sub>5</sub>)Si); 7.10–7.80 (m, 5 H, H(C<sub>6</sub>H<sub>5</sub>)Si). IR (CCl<sub>4</sub>), v/cm<sup>-1</sup>: 3300 (OH) w. The amount of terminal hydroxy groups of obtained poly(phenyl)hydrosiloxane calculated by the <sup>1</sup>H NMR spectroscopic data for samples blocked with trimethylchlorosilane was 0.14%.  $n_D^{20} = 1.5682$ . GPC: 40%: 75000–2000 amu,  $M_{peak} = 18000$  amu; 60%: 2000–400 amu,  $M_{peak} = 600$  amu. GLC of the low-molecular-weight fraction: 20% [HPhSiO]<sub>3</sub>, 80% [HPhSiO]<sub>4</sub>. Found (%): Si, 22.80; C, 58.88; H, 4.92. C<sub>6</sub>H<sub>6.01</sub>O<sub>1.01</sub>Si. Calculated (%): Si, 22.92; C, 58.93; H, 4.92.

Blocking of terminal hydroxy groups of polyphenylsiloxane (general procedure). A 20% solution of poly(phenyl)hydrosiloxane (0.65 g, 0.005 mol) in anhydrous toluene was added dropwise to a solution of trimethylchlorosilane (1.33 g, 0.012 mol) and pyridine (1.97 g, 0.012 mol) in anhydrous toluene (10 mL), and the mixture was refluxed with stirring for 4 h. The obtained product was washed off with distilled water to neutral pH, dried over sodium sulfate, and evacuated with heating to 50 °C (0.75 Torr). The yield of the products was 1.2–1.3 g (90–98%). <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$ : 4.75–5.25 (m, 1 H, <u>H</u>(C<sub>6</sub>H<sub>5</sub>)Si); 7.10–7.80 (m, 5 H, H(C<sub>6</sub>H<sub>5</sub>)Si); 0.10–0.25 (m, 9 H, (CH<sub>3</sub>)<sub>3</sub>Si). IR (CCl<sub>4</sub>), v/cm<sup>-1</sup>: signals from OH groups in a region of 3300 cm<sup>-1</sup> are absent.

This work was financially supported by the Council on Grants at the President of the Russian Federation (Program for State Support of Leading Scientific Schools of the Russian Federation, Grant NSh 116.2012.3) and the Russian Foundation for Basic Research (Project No. 11-03-12095\_ofi\_m).

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Received October 4, 2012; in revised form February 26, 2013