# Synthesis and some properties of silanes and siloxanes with 5,5,6,6,7,7,7-heptafluoro-4,4-bis(trifluoromethyl)heptyl substituents

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Methods for syntheses of new polyfluorinated compounds, *viz.*, silanes containing substituents  $CF_3CF_2CF_2C(CF_3)_2(CH_2)_3$  (R<sup>F</sup>) at the silicon atom and 1,3,5-tris(R<sup>F</sup>)-1,3,5-trimethylcyclotrisiloxane that can be used for the synthesis of fluorocontaining oligo- and polysiloxanes of different structure, were developed. The polymerization of cyclotrisiloxane in the presence of 1,3-divinyltetramethyldisiloxane gave linear oligomers, whose chain contain  $-(R^F)Si(Me)O-$  units.

**Key words:** hydrosilylation, polyfluorinated silanes, fluorocontaining cyclosiloxanes, fluorocontaining polysiloxanes.

The most part of studies in the field of organofluosilicon polymers are related to the investigation of oligoand polysiloxanes containing  $\gamma$ -trifluoropropyl substituents in side chains. They formed a basis for the production of thermally, oil-, and gasoline-resistant resins, lubricants, chemically stable coatings, and electrically insulating materials.<sup>1</sup> The fluorine content in these compounds does not exceed 36.5%. At the same time, it is of great theoretical and practical interest to create new organofluosilicon oligomers and polymers of different structure with a higher fluorine content. The works on the synthesis and study of these compounds with bulky polyfluorinated linear alkyl substituents CF<sub>3</sub>(CF<sub>2</sub>)<sub>n</sub>CH<sub>2</sub>CH<sub>2</sub> at the silicon atom have been carried out recently in Japan and USA.<sup>2,3</sup>

In this work, we describe the methods for syntheses of silanes containing a 5,5,6,6,7,7,7-heptafluoro-4,4bis(trifluoromethyl)heptyl substituent (R<sup>F</sup>) at the silicon atom and 1,3,5-tris(R<sup>F</sup>)-1,3,5-trimethylcyclotrisiloxane and related oligomers, the fluorine content in which exceeds 50%. In these compounds, the polyfluorinated substituent at the silicon atom contains a branched perfluorohexyl group. Therefore, based on the known data,<sup>5</sup> we can assume that the surface tension of the related siloxane derivative would be lower than that for analogs with linear perfluoroalkyl substituents. The calculated data<sup>6</sup> show that a polymer with an elementary unit  $-(R^F)Si(Me)O-can$ possess several valuable properties: low dielectric constant (2.19), refractive index (1.33), and surface tension  $(17.9 \text{ mN m}^{-1})$ , which are much lower than those for the known polysiloxanes with  $\gamma$ -trifluoropropyl substituents at silicon.1,7

The synthesis of the most part of highly fluorinated alkylsilanes and siloxanes is based on olefins with linear perfluoroalkyl substituents  $CF_3(CF_2)_nCH=CH_2$ (n = 3-6) obtained in moderate yields from perfluoroalkyl bromides(iodides) and ethylene.<sup>4</sup> To prepare alkylsilanes and siloxanes, we used alkene 1, which was synthesized by the reaction of accessible and cheap hexafluoropropylene dimers  $CF_3CF=CFCF(CF_3)CF_3$  and  $CF_3C(CF_3)=CFCF_3CF_3$  with alkyl bromide in the presence of CsF.<sup>10-12</sup>

Alkene 1 was silvlated with chlorosilanes 2a-c in the presence of chloroplatinous acid to form, according to <sup>1</sup>H NMR, silanes 3a-c <sup>11</sup> in ~100% yield (Scheme 1).





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The reaction of trichlorosilane **3c** with excess triethyl orthoformate afforded triethoxysilane **4** (Scheme 2).

Scheme 2



*i*. 40 °C, 2 h

Monofunctional silanes are modifiers of the surface of different materials, in particular, derivatives of organic bases are most efficient.<sup>5</sup> For this purpose, we synthesized substituted morpholine **5** from dimethylchlorosilane **3a** Scheme 3).

#### Scheme 3



Contact angles of wettability of surfaces of glass plates treated with compounds **3a** or **5** are  $88-90^{\circ}$  (water) and  $76-77^{\circ}$  (oil VM-4).

As known, the hydrolysis of dichlorosilanes with alkyl substituents at the silicon atom affords a mixture of linear and cyclic siloxanes existing in a mobile equilibrium.<sup>13</sup> The ratio between linear and cyclic siloxanes in the hydrolyzate depends substantially on the temperature and substituent structure and is shifted completely, in the case of bulky alkyl radicals, toward cyclic siloxanes.<sup>7</sup> Individual cyclosiloxanes isolated from the hydrolyzate have different activities in polymerization. Of cyclosiloxanes with fluorocontaining alkyl substituents, cyclotrisiloxane is most active in polymerization,<sup>7</sup> while cyclotetrasiloxane  $[CF_3(CF_2)_4CH_2CH_2Si(Me)O]_4$  with linear polyfluoroalkyl substituents do not polymerize even at elevated temperatures.<sup>16,17</sup>

Methyldichlorosilane **3b** was hydrolyzed in ether in the presence of excess water. A comparison of the signals of siloxanes in the <sup>29</sup>Si NMR spectra of the hydrolyzate with the published signals of siloxanes<sup>14,15</sup> and determination of the ratio of their integral intensities showed that the hydrolyzate contained 32% cyclotrisiloxane  $[(R^F)Si(Me)O]_3$  (two signals: -10.5 ppm and -10.7 ppm), 35% cyclotetrasiloxane  $[(R^F)Si(Me)O]_4$  (three signals: -21.1, -21.3, and -21.7 ppm), and 33% cyclic (with the degree of oligomerization n > 4) and linear siloxanes (signals: -13.7 ppm (HO(R<sup>F</sup>)Si(Me)O-) and -23.2 ppm (-(R<sup>F</sup>)Si(Me)O-)).

We isolated cyclotrisiloxane 6 by continuous rectification from a mixture of siloxanes formed on heating the hydrolyzate to 300-350 °C in the presence of 3-5 wt.% KOH (Scheme 4).





Cyclotrisiloxane **6** is a mixture of *trans*- and *cis*-isomers. The boiling points, weight of the isolated fractions of cyclotrisiloxane, and ratio of isomers in the fractions determined by GLC are presented in Table 1. It can be assumed that cyclotrisiloxane **6** is enriched in the *trans*-isomer as in the case of cyclotrisiloxane  $[CF_3(CF_2)_3CH_2CH_2Si(Me)O]_3$  with linear nonafluorohexyl substituents.



Polymerization of 1,3,5-tris(3,3,4,4,5,5,6,6,6-nonafluorohexyl)-1,3,5-trimethylcyclotrisiloxane in the bulk under the action of acids and alkalis has been studied previously.<sup>16,17</sup> In both cases, more thermodynamically stable products were formed: cyclotetrasiloxane (74.3%)

 Table 1. Boiling points, weights, and ratios of *cis*- and *trans*isomers of cyclotrisiloxane 6 in fractions

Fraction	B.p./°C*	<i>m</i> /g** (% of load)	cis/trans***
Forerun fraction	101-132	30 (13.6)	1:2.2
1	132-137	16 (7.2)	1:2.9
2	137-143	10 (4.5)	1:3.7
3	144-148	26 (11.8)	1:4.4
4	148-152	18 (8.2)	1:4.9
5	152-155	42 (19.1)	1:5.5

\*  $p = (2-8) \cdot 10^{-2}$  Torr.

\*\* Weight of the fraction.

\*\*\* Ratio of isomers according to the GLC data.

and higher cycles (n > 4). This is related to the fact that depolymerization with the formation of higher cycles is observed along with polymerization (siloxane chain growth). We carried out the cationic polymerization of cyclotrisiloxane **6** in the presence of 1,3-divinyltetramethyldisiloxane **7** (molar ratio 7 : 1) and CF<sub>3</sub>SO<sub>3</sub>H as catalyst. Oligomer **8** containing reactive vinyl groups at the chain ends was obtained (Scheme 5).

## Scheme 5



i. Catalyst CF<sub>3</sub>SO<sub>3</sub>H, 100 °C, 20 h.

A comparison of the integral intensities of the <sup>1</sup>H signals in the spectrum of the isolated oligomer showed that the number of siloxane units in the middle of the chain was 10–12, which agrees well with the GPC data ( $\overline{M}_n = 4790$ ,  $\overline{M}_w = 4960$ ). Thus, we developed a method for the synthesis of polyfluorinated polysiloxane oligomers by the polymerization of 1,3,5-tris[5,5,6,6,7,7,7-heptafluoro-4,4-bis(trifluoromethyl)heptyl]-1,3,5-trimethylcyclotrisiloxane in the presence of 1,3-divinyltetramethyldisiloxane; oligomers with terminal vinyl groups were obtained.

### **Experimental**

Hexafluoropropylene dimers were purchased from the Perm Branch of the GIPKh (FOL-62 Sort A; isomeric fraction of hexapropylene dimers >99.8 wt.%, b.p. 46–51 °C). Allyl bromide, 1,3-divinyltetraethyldisiloxane, and starting chlorosilanes (Acros Organics, purity  $\geq$  96 wt.%) were used without additional purification. Diglyme was refluxed above CaH<sub>2</sub> until gas stopped evolving and then distilled. The catalyst was prepared according to the following procedure: crystalline H<sub>2</sub>PtCl<sub>2</sub>•6 H<sub>2</sub>O (1 g) was placed in THF preliminarily distilled above CaH<sub>2</sub>, and the resulting solution was stored in a closed flask at room temperature in the dark for 7 days.

<sup>1</sup>H, <sup>19</sup>F, and <sup>29</sup>Si NMR spectra were obtained on a Bruker AC-200P spectrometer with a working frequency of 200 MHz without a solvent using Me<sub>4</sub>Si (<sup>1</sup>H, <sup>29</sup>Si) and CFCl<sub>3</sub> (<sup>19</sup>F) as external standards. GLC analysis was carried out on an LKhM-8MD chromatograph (column  $1000 \times 3.5$  mm, carrier Chromatone 0.160–0.200 mm with 5% Silicone SE-30 (Chemapol)). The molecular weight of the oligomer was deter-

mined by GPC on a Bruker LC21 instrument (column IBM GPC/SEC ( $10 \,\mu m$ ,  $300 \times 7.7 \,mm$ ), eluent flow rate 0.8 mL min<sup>-1</sup>, trichlorotrifluoroethane as eluent, refractometer as a detector).

5,5,6,6,7,7,7-Heptafluoro-4,4-bis(trifluoromethyl)hept-1ene (1) was synthesized by somewhat modified procedure described previously.<sup>10</sup> Anhydrous CsF (91.2 g, 0.6 mol), freshly distilled diglyme (200 g, 1.2 mol), and a mixture of hexafluoropropylene dimers (180.1 g, 0.6 mol) were placed in a threenecked flask equipped with a stirrer with a mercury-free seal under anhydrous argon. The reaction mixture warmed slightly. Then allyl bromide (72.6 g, 0.6 mol) was added with vigorous stirring for 2 h at 40 °C. After the reaction mixture was stored at this temperature for 40 h, it was fractionated to three fractions with boiling intervals of 67-110, 110-140, and 140-160 °C. The first two fractions were combined and rectified on a column of  $1000 \times 15$  mm (spiral prismatic packing  $3 \times 3 \times 0.2$ ) with a reflux ratio of 1:30, and the fraction with b.p. 107-113 °C was collected (226 g). According to GLC, the purity of the resulting alkene 1 was equal to 96–97%. The <sup>1</sup>H and <sup>19</sup>F NMR spectra corresponded to those presented in Ref. 12.

Hydrosilylation of alkene 1 with chlorosilanes 2a-c (general procedure). Compound 1 (180.05 g, 0.5 mol) was placed in a two-necked flask equipped with a condenser with dry ice and a dropping funnel, and argon was passed through the flask. One droplet of a  $10^{-2} M$  solution of H<sub>2</sub>PtCl<sub>6</sub> in THF was added to alkene 1 heated to 70 °C, and chlorosilane 2a-c (0.55 mol) was slowly added dropwise with vigorous stirring. The reaction mixture was stirred at this temperature for 2 h, and the resulting compounds 3a-c were isolated by fractionate distillation.

**5,5,6,6,7,7,7-Heptafluoro-4,4-bis(trifluoromethyl)heptylmethyldichlorosilane (3b)** was synthesized from **1** and methyldichlorosilane **2b** in 89% yield (211.4 g), b.p.  $50-51 \degree C$  (1 Torr). Found (%): C, 25.56; H, 2.01.  $C_{10}H_9Cl_2F_{13}Si$ . Calculated (%); C, 25.28; H, 1.91. <sup>1</sup>H NMR,  $\delta$ : 1.58 (t, 2 H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si, J = 8.0 Hz); 1.18 (m, 2 H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si); 0.37 (t, 2 H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si, J = 7.8 Hz); 0.03 (s, 3 H, CH<sub>3</sub>Si). <sup>19</sup>F NMR,  $\delta$ : -64.49 (quintet, 3 F, (CE<sub>3</sub>)<sub>2</sub>CCF<sub>2</sub>, J = 11.1 Hz); -81.26 (t, 3 F, CE<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>, J = 13.6-14.4 Hz); -107.95 (septet, 2 F, CF<sub>3</sub>CE<sub>2</sub>CF<sub>2</sub>, J = 11.1 Hz); -123.72 (m, 2 F, CF<sub>3</sub>CF<sub>2</sub>CE<sub>2</sub>). <sup>29</sup>Si NMR,  $\delta$ : 31.1 (br.s).

5,5,6,6,7,7,7-Heptafluoro-4,4-bis(trifluoromethyl)heptyldimethylchlorosilane (3a) was synthesized from 1 and dimethylchlorosilane 2a in 86% yield (195.54 g), b.p. 76–79 °C (9 Torr). Chemical shifts in the <sup>19</sup>F NMR spectrum coincided within measurement accuracy with the chemical shifts of the corresponding groups in compound 3b. Found (%): C, 28.89; H, 3.38. C<sub>11</sub>H<sub>12</sub>ClF<sub>13</sub>Si. Calculated (%); C, 29.05; H, 2.66. <sup>1</sup>H NMR,  $\delta$ : 2.42 (t, 2 H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si, *J* = 8.0 Hz); 2.01 (m, 2 H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si); 1.02 (t, 2 H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si, *J* = 7.8 Hz); 0.61 (s, 3 H, CH<sub>3</sub>Si). <sup>29</sup>Si NMR,  $\delta$ : 29.09 (br.s).

5,5,6,6,7,7,7-Heptafluoro-4,4-bis(trifluoromethyl)heptyltrichlorosilane (3c) was synthesized from 1 and trichlorosilane 2c in 90% yield (220.1 g), b.p. 81 °C (14 Torr). Chemical shifts in the <sup>19</sup>F NMR spectrum coincided within measurement accuracy with the chemical shifts of the corresponding groups in compounds 3a and 3b. <sup>1</sup>H NMR,  $\delta$ : 2.11 (t, 2 H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si, J = 8.0 Hz); 1.83 (m, 2 H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si); 1.24 (t, 2 H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si, J = 7.8 Hz). <sup>29</sup>Si NMR,  $\delta$ : 10.4 (c).

**4-{[5,5,6,6,7,7,7-Heptafluoro-4,4-bis(trifluoromethyl)heptyl]dimethylsilyl}morpholine (5).** Anhydrous morpholine (11.7 g, 0.14 mol) freshly distilled above CaH<sub>2</sub> was slowly added to **3a** 

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(30.3 g, 0.066 mol), resulting in the precipitation of white morpholinium hydrochloride. The mixture was diluted with Freon-113 (50 mL), and the contents of the flask was vigorously shaken and filtered. The solvent was removed from the filtrate on a rotary evaporator, and compound **5** that formed was isolated by fractionation. The yield of **5** was 30.0 g (90%), b.p. 94–96 °C (9 Torr). <sup>1</sup>H NMR,  $\delta$ : 2.20 (br.s, 2 H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si); 1.69 (br.s, 2 H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si); 0.55 (br.s, 2 H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si); 0.01 (br.s, 6 H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si)(CH<sub>3</sub>)<sub>2</sub>); 2.43 (br.s, 4 H, N(CH<sub>2</sub>CH<sub>2</sub>OH<sub>2</sub>)<sub>2</sub>O); 2.79 (br.s, 4 H, N(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>O). <sup>19</sup>F NMR,  $\delta$ : -64.43 (m, 3 F, (CE<sub>3</sub>)<sub>2</sub>CCF<sub>2</sub>); -81.29 (m, 3 F, CE<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>); -107.87 (m, 2 F, CF<sub>3</sub>CE<sub>2</sub>CF<sub>2</sub>); -123.66 (m, 2 F, CF<sub>3</sub>CF<sub>2</sub>CE<sub>2</sub>). <sup>29</sup>Si NMR,  $\delta$ : 4.6 (s).

**5,5,6,6,7,7,7-Heptafluoro-4,4-bis(trifluoromethyl)heptyltriethoxysilane (4).** Trifold excess triethyl orthoformate (44.4 g, 0.3 mol) was added to 5,5,6,6,7,7,7-heptafluoro-4,4-bis(trifluoromethyl)heptyltrichlorosilane **3c** (49.5 g, 0.1 mol). The mixture was heated at 40 °C for 2 h and then distilled. The yield was 98% (46.7 g), b.p. 80–81 °C (1 Torr). Found (%): C, 33.74; H, 4.03; F, 47.10.  $C_{15}H_{21}F_{13}O_{3}Si$ . Calculated (%); C, 34.36; H, 4.04; F, 47.05. <sup>1</sup>H NMR,  $\delta$ : 2.38 (t, 2 H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si, *J* = 7.8 Hz); 1.99 (br.s, 2 H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si); 1.00 (br.s, 2 H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si); 4.00 (quintet, 6 H, CH<sub>3</sub>CH<sub>2</sub>OSi, *J* = 7.1 Hz); 1.36 (t, 9 H, CH<sub>3</sub>CH<sub>2</sub>OSi, *J* = 7.1 Hz). <sup>19</sup>F NMR,  $\delta$ : -64.43 (t, 3 F, (CE<sub>3</sub>)<sub>2</sub>CCF<sub>2</sub>, *J* = 11.1 Hz); -81.26 (t, 3 F, CE<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>), *J* = 13.6–14.4 Hz); -107.84 (br.s, 2 F, CF<sub>3</sub>CE<sub>2</sub>CF<sub>2</sub>); -123.57 (br.s, 2 F, CF<sub>3</sub>CF<sub>2</sub>CE<sub>2</sub>). <sup>29</sup>Si NMR,  $\delta$ : -46.2 (s).

Hydrolysis of dichlorosilane 3b. Fourfold excess water was added to 3b (240 g, 0.51 mol) in diethyl ether, and the mixture was stirred at room temperature for 2 h. The ether layer was separated and dried above MgSO<sub>4</sub>, the solvent was evaporated *in vacuo*, and the residue was analyzed by <sup>29</sup>Si NMR. A mixture of siloxanes (220 g) was obtained. <sup>29</sup>Si NMR,  $\delta$ : -10.5, -10.7, -21.1, -21.3, -21.7, -13.7, -23.2.

**1,3,5-Tris(5,5,6,6,7,7,7-heptafluoro-4,4-bis(trifluoromethyl)heptyl)-1,3,5-trimethylcyclotrisiloxane (6).** The hydrolyzate of disiloxane **3b** (220 g) was loaded into a still of a rectification column, KOH (6.5 g, 3 wt.%) was added, and the mixture was heated to 300–350 °C. Rectification was carried out in a high vacuum  $(2 \cdot 10^{-2} - 8 \cdot 10^{-2} \text{ Torr})$  on a column of  $500 \times 5 \text{ mm}$  (spiral prismatic packing  $3 \times 3 \times 0.2 \text{ mm}$ ) with a reflux ratio of 1 : 50. The yield of trisiloxane **6** was 64% (142 g). Found (%): C, 28.42; H, 2.25. C<sub>30</sub>H<sub>27</sub>F<sub>39</sub>O<sub>3</sub>Si<sub>3</sub>. Calculated (%): C, 28.58; H, 2.16. <sup>1</sup>H NMR of fractions 1–5 (mixture of *cis*- and *trans*-isomers),  $\delta$ : 2.26 (t, 2 H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si, J = 7.1 Hz); 1.82 (br.s, 2 H, CH<sub>2</sub>CH<sub>2</sub>Si); 0.67 (t, 2 H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si, J = 7.3 Hz); 0.21 (s, 3 H, CH<sub>3</sub>Si). <sup>29</sup>Si NMR of fractions 1–5,  $\delta$ : –10.5, –10.7.

Polymerization of 1,3,5-tris[5,5,6,6,7,7,7-heptafluoro-4,4bis(trifluoromethyl)heptyl)]-1,3,5-trimethylcyclotrisiloxane 6 in the presence of 1,3-divinyltetramethyldisiloxane. Cyclotrisiloxane 6 (5 g, 0.0039 mol), disiloxane 7 (0.1063 g, 0.0006 mol), and catalyst CF<sub>3</sub>SO<sub>3</sub>H (0.0022 g) were placed in an ampule under dry argon. The ampule was sealed and placed in a thermostat at 100 °C. After 20 h, the ampule was opened, the contents was dissolved in trichlorotrifluoroethane, and CaCO<sub>3</sub> (0.5 g) was added to the solution. The solution was filtered, and the solvent was evaporated on a water-aspirator pump. Siloxane was washed with hexafluorobenzene, after which the benzene layer was removed, and siloxane was dried in a high-vacuum setup. Oligolymer **8** was obtained in 65% yield (3.3 g). All signals of the groups in the <sup>1</sup>H NMR spectrum of the oligomer are broadened.