1250 *Russian Chemical Bulletin, International Edition, Vol. 54, No. 5, pp. 1250—1253, May, 2005*

New organosiloxanes based on 1-vinyl-2-perfluoroalkoxy-2,3,3-trifluorocyclobutanes

A. E. Shamaev,** *A. A. Glazkov, A. V. Ignatenko, and A. M. Sakharov

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,
47 Leninsky prosp., 119991 Moscow, Russian Federation.
Fax: +7 (095) 135 5328. E-mail: as@zelinsky.ru

A new method for the synthesis of polyfluorinated compounds, *viz.*, chlorosilanes with 2-perfluoroalkoxy-2,3,3-trifluorocyclobutane substituents containing different numbers of tetrafluoro(ethylene oxide) $(CF_2CF_2O)_n$ units (n = 3—6), was developed. The structures of siloxanes formed by the hydrolysis of these chlorosilanes were studied: the hydrolysis of monochlorosilanes affords disiloxanes and that of dichlorosilanes produces cyclotrisiloxanes, cyclotetrasiloxanes, and cyclic (the number of siloxane units >4) and linear polysiloxanes.

Key words: cyclobutanes with polyfluoropolyether substituents, hydrosilylation, polyfluorinated silanes, fluorocontaining cyclosiloxanes, fluorocontaining polysiloxanes.

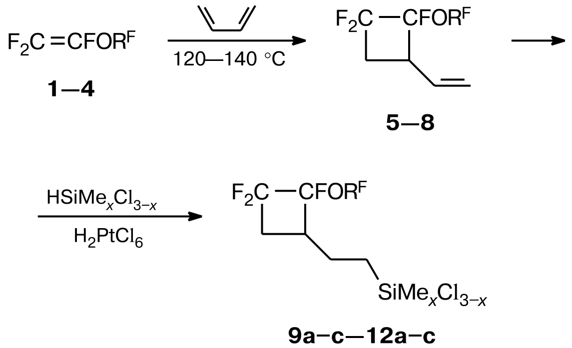
The study of aliphatic polyfluorinated organosilicon compounds is of great practical and scientific interest. The main methods for the preparation of fluorocontaining organosilicon compounds containing fluorine atoms in organic substituents are generalized in the monograph.[1] The most significant of them are organometallic synthesis and methods based on reactions of silicon hydrides with functional compounds, as well as the cyclodimerization of alkenylsilanes with perfluoroolefins.

In this work, we proposed a method for the synthesis of chlorosilanes with 2-perfluoroalkoxy-2,3,3-trifluorocyclobutane substituents and related fluorinated organosiloxanes with different numbers of tetrafluoro(ethylene oxide) units. Some properties of siloxanes formed by the hydrolysis of the corresponding chlorosilanes were studied.

The method proposed for the synthesis of fluorocontaining organosilicon compounds assumes two steps: the first step is the synthesis of a cyclobutane adduct with a vinyl group in the side chain, and the second step is the use of the widely applied hydrosilylation of an unsaturated compound. This method enables one to vary the structure and size of the fluorinated radical and use different silylating agents and, correspondingly, obtain related polyfluorinated siloxanes of different structure.

The condensation of perfluorovinyl ethers **1—4** with butadiene afforded 1-vinyl-2-perfluoroalkoxy-2,3,3-trifluorocyclobutanes **5—8**,[2] whose hydrosilylation gave chlorosilanes **9a—c—12a—c** (Scheme 1).

Scheme 1



$R^F = (CF_2CF_2O)_nCF_3$ (n = 3, 4, 5, 6)
9—12: x = 2 (**a**), 1 (**b**), 0 (**c**)
n = 3 (**1**, **5**, **9**), 4 (**2**, **6**, **10**), 5 (**3**, **7**, **11**), 6 (**4**, **8**, **12**)

Silanes **9—12** were characterized by ^1H, ^{29}Si, and ^{19}F NMR spectroscopy. The boiling points and yields of silanes **9—12** are presented in Table 1.

It is known[3,4] that the hydrolysis of dichlorosilanes affords a mixture of siloxanes containing cyclosiloxanes and linear polysiloxanes.

The ^{29}Si NMR spectra of the hydrolysis products of silanes **9b—12b** contain signals with δ −10.2, −20.5, and −22.9 (the middle of the signal base). Hydrolysis product

---

* Dedicated to Academician N. K. Kochetkov on the occasion of his 90th birthday.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 5, pp. 1215—1217, May, 2005.

Scheme 2

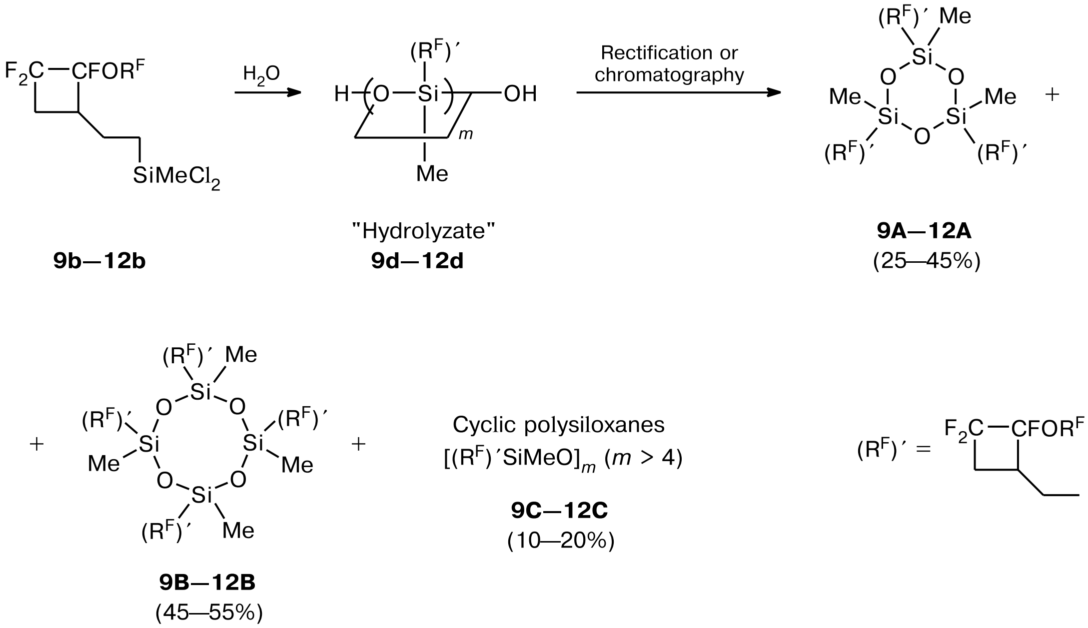


Table 1. Yields and boiling points of silanes **9a–c—12a–c**

Compound	Yield (%)	B.p./°C (*p*/Torr)
9a	90	91—93 (9)
9b	87	83—86 (1)
9c	89	142—143 (15)
10a	85	99—102 (9)
10b	86	147—150 (1)
10c	90	150—153 (25)
11a	87	109—111 (9)
11b	90	114—115 (0.1)
11c	85	160—162 (15)
12a	86	120—121 (9)
12b	89	119—121 (0.04)
12c	90	170—172 (15)

10d was separated by rectification and column chromatography into fractions. The ^{29}Si NMR spectrum of each fraction exhibited only one of the above-indicated signals, which allowed us to assume that the "hydrolyzate" is a mixture of siloxanes of structures **10A**, **10B**, and **10C** (Scheme 2).

The chemical shift values of the ^{29}Si signals of siloxane structures **A**, **B**, and **C** agree with the data for cyclic siloxanes with methyl[5,6] and polyfluoroalkyl substituents.[7] The ratio of cyclosiloxanes with structures **A**, **B**, and **C** for compounds **9d**, **11d**, and **12d** was determined from the integral intensities of signals of the silicon atoms in the spectra of these products.

Cyclic polysiloxanes are known[8] to have different thermodynamic stabilities. According to this, when cyclotrisiloxane **10A** is heated in a nickel-plated autoclave at 175 °C for 38 h, it is partially transformed into cyclotetrasiloxane **10B** according to the ^{29}Si NMR spectra. This is indicated by the appearance of a signal at δ –20.51 corresponding to cyclotetrasiloxane in the ^{29}Si NMR spectrum. Under the same conditions, cyclotetrasiloxane **10B** undergoes no changes.

According to the data of GLC, IR spectroscopy, and ^{29}Si NMR spectroscopy, the hydrolysis of silanes **9a—12a** affords disiloxanes of general formula $(R^F)'SiMe_2$—O—$SiMe_2(R^F)'$.

Oligomeric siloxane products formed by hydrolysis, which is accompanied by the condensation of alkyltrichlorosilanes, have a complex, irregular structure.[8] The structure of these products is usually presented by empirical formulas $[(R^F)'Si(OH)_2O_{0.5}]_n$, $[(R^F)'Si(OH)_{1.5}O]_n$, $[(R^F)'SiO_{1.5}]_n$.[9—11] We studied the hydrolysis of trichlorosilanes **10c—12C** and determined the molecular weights of the hydrolyzates ($\overline{M}_n$, $\overline{M}_w$) by gel permeation chromatography (GPC).

Thus, in this work, we developed the method for syntheses of polyfluorinated chlorosilanes containing tetrafluoro(ethylene oxide) units and studied some properties of their hydrolysis products.

Experimental

The starting chlorosilanes (Acros Organics, purity ≥96 wt.%) were used as received. The catalyst was prepared as follows:

$H_2PtCl_2 \cdot 6H_2O$ (1 g) was placed in THF (100 mL), which was pre-distilled over CaH_2, and the resulting solution was stored in a closed flask at room temperature in the dark for 7 days.

^1H, ^{19}F, and ^{29}Si NMR spectra were recorded on a Bruker AC-200P spectrometer with a working frequency of 200 MHz without a solvent using Me_4Si (^1H, ^{29}Si) and $CFCl_3$ (^{19}F) as external standards. GLC analysis was carried out on an LKhM-8MD chromatograph (column 1000×3.5 mm, carrier Chromatone 0.160—0.200 mm impregnated with 5% Silicone SE-30 (Chemapol)). The molecular weight of the oligomer was determined by GPC on a Bruker LC21 instrument (column IBM GPC/SEC (10u 300×7.7), eluent velocity 0.8 mL min^{-1}, eluent trifluorotrichloroethane, refractometer as detector). IR spectra were recorded on a Specord IR-75 spectrophotometer (liquid samples in thin layer between KBr plates). A Finnigan MAT INCOS 50 quadrupole mass spectrometer (EI, 70 eV) was used for analyses of molecular structures.

Cyclobutanes **5—8** were synthesized according to a known procedure.[2]

Hydrosilylation of cyclobutanes 5—8 with chlorosilanes (general procedure). Cyclobutane **5—8** (0.05 mol) was placed in a two-necked flask equipped with a condenser filled with a carbon-dioxide ice and a dropping funnel, and argon was passed through the flask. One droplet of a 10^{-2} *M* solution of $H_2[PtCl_6]$ in THF was added to cyclobutane **5—8** heated to 70 °C, and then chlorosilane (0.055 mol) was slowly added dropwise with vigorous stirring. The reaction mixture was stirred at this temperature for 2 h, and compounds **9a—c—12a—c** formed were isolated by fractionation. The boiling points and yields of silanes are presented in Table 1.

Dimethylchlorosilanes 9a—12a were synthesized from dimethylchlorosilane. The chemical shifts in the ^{19}F NMR spectra of compounds **9a—12a** coincide within measurement accuracy with the chemical shifts of the corresponding groups in the spectra of compounds **5—8** given in Ref. 2. Compound **10a**. Found (%): C, 26.59; H, 1.48. $C_{11}H_{12}ClF_{13}Si$. Calculated (%): C, 26.22; H, 1.68. ^1H NMR, δ: 0.06 (d, 6 H, MeSi, *J* = 2.2 Hz); 0.49 (m, 2 H, $CH_2C\underline{H}_2Si$, *J* = 8.0 Hz); 2.27 (m, 2 H, CH_2 (in cycle)); 1.70, 1.52, 1.33 (all m, 3 H, $C\underline{H}_2CH_2Si$ and CH (in cycle)). ^{29}Si NMR, δ: 29.0 (c). Mass spectrum, *m/z* (I_{rel} (%)): 93 $[SiMe_2Cl]^+$ (100); 116 $[CF_2CF_2O]^+$ (35); 713 $[M - (CF_2)_{cycl}(CH_2)_{cycl}]^+$ (4). The chemical shifts in the ^1H and ^{29}Si NMR spectra of compounds **9a**, **11a**, and **12a** coincided within measurement accuracy with the chemical shifts of the corresponding groups in compound **10a**.

Methyldichlorosilanes 9b—12b were synthesized from methyldichlorosilane. The chemical shifts in the ^{19}F NMR spectra of compounds **9b—12b** coincide within measurement accuracy with the chemical shifts of the corresponding groups in the spectra of compounds **5—8** presented in Ref. 2. Compound **10b**. Found (%): C, 24.23; H, 1.38. $C_{11}H_{12}ClF_{13}Si$. Calculated (%): C, 24.05; H, 1.26. ^1H NMR, δ: 0.73 (d, 3 H, MeSi, *J* = 2.1 Hz); 1.11 (t, 2 H, $CH_2C\underline{H}_2Si$, *J* = 3.8 Hz); 2.32 (m, 2 H, CH_2 (in cycle)); 1.75, 1.95 (both m, 3 H, $C\underline{H}_2CH_2Si$, CH (in cycle)). ^{29}Si NMR, δ: 30.0 (s). Mass spectrum, *m/z* (I_{rel} (%)): 115 $[SiMeCl_2]^+$ (30), 116 $[CF_2CF_2O]^+$ (30), 185 $[M - (CF_2)_{cycl}(CH_2)_{cycl}—O(CF_2CF_2O)_4CF_3]^+$ (4), 251 $[M - O(CF_2CF_2O)_4CF_3]^+$ (3), 735 $[M - (CF_2)_{cycl}(CH_2)_{cycl}]^+$ (4). The chemical shifts in the ^1H and ^{29}Si NMR spectra of compounds **9b**, **11b**, and **12b** coincide within measurement accuracy with the chemical shifts of the corresponding groups in compound **10b**.

Trichlorosilanes 9c—12c were synthesized from trichlorosilane. The chemical shifts in the ^{19}F NMR spectra of compounds **9c—12c** coincide within measurement accuracy with the chemical shifts of the corresponding groups in compounds **5—8** presented in Ref. 2. Compound **10c**. Found (%): C, 24.23; H, 1.38. $C_{11}H_{12}ClF_{13}Si$. Calculated (%): C, 24.05; H, 1.26. ^1H NMR, δ: 1.43 (quint, 2 H, $CH_2C\underline{H}_2Si$, *J* = 5.3 Hz); 2.63 (m, 2 H, CH_2 (in cycle)); 2.05, 1.85 (both m, 3 H, $C\underline{H}_2CH_2Si$ and CH (in cycle)). ^{29}Si NMR, δ: 10.0 (s). Mass spectrum, *m/z* (I_{rel} (%)): 135 $[SiCl_3]^+$ (28), 116 $[CF_2CF_2O]^+$ (30), 205 $[M - (CF_2)_{cycl}(CH_2)_{cycl}—O(CF_2CF_2O)_4CF_3]^+$ (4); 271 $[M - O(CF_2CF_2O)_4CF_3]^+$ (3); 753 $[M - (CF_2)_{cycl}(CH_2)_{cycl}]^+$ (4).

Hydrolysis of chlorosilanes 9a—c—12a—c (general procedure). A mixture of chlorosilane **9a—c—12a—c** (0.1 mol) and H_2O (0.4 mol) were stirred for 2 h at 20 °C. The aqueous layer was separated, and the organofluoric layer was dried on a high-vacuum setup and analyzed.

Hydrolyzates of monochlorosilanes 9a—12a. ^1H NMR, δ: 0.11 (br.s, 6 H, Me_3Si); 0.58 (t, 2 H, $CH_2C\underline{H}_2Si$, *J* = 7.8 Hz); 2.57 (t, 2 H, CH_2 (in cycle), *J* = 9.2 Hz); 1.58 (m), 1.80 (br.s), 2.05 (br.s) (3 H, $C\underline{H}_2CH_2Si$ and CH (in cycle)). ^{29}Si NMR, δ: −7.1. Hydrolyzate **10a**. Found (%): C, 27.30; H, 1.54. $C_{34}H_{26}F_{44}O_{11}Si_2$. Calculated (%): C, 27.18; H, 1.74.

Hydrolyzates of trichlorosilanes 10c—12c. Hydrolyzate **10c**, $\overline{M}_n$ = 2632, $\overline{M}_w$ =3007, n_D = 1.3375. Hydrolyzate **11c**, $\overline{M}_n$ = 2720, $\overline{M}_w$ = 3067, n_D = 1.3260. Hydrolyzate **12c**, $\overline{M}_n$ = 2980, $\overline{M}_w$ = 3100; n_D = 1.3205.

IR spectrum of hydrolyzate **10c**, ν/cm^{-1}: 2940, 2900, 2875 (ν(C—H)); 1430, 1370 (δ(C—H)); 1250—1050 (ν(C—F)); 1100—900 (ν(Si—O—Si)).

Separation of hydrolyzate 10d. A fraction with b.p. 120—140 °C ($(2-8) \cdot 10^{-2}$ Torr) was distilled off from hydrolyzate **10d**. According to the ^{29}Si, ^1H, and ^{19}F NMR spectra, the resulting product was cyclotrisiloxane **10A**. Found (%): C, 26.10; H, 1.27. $C_{48}H_{30}F_{66}O_{18}Si_3$. Calculated (%): C, 25.82; H, 1.35.

^{29}Si NMR, δ: −10.28. ^1H NMR, δ: 0.12 (br.s, 3 H, MeSi); 0.59 (br.s, 2 H, $CH_2C\underline{H}_2Si$); 2.54 (br.s, 2 H, CH_2 (in cycle)); 1.56, 1.80, 2.00 (all br.s, 3 H, $C\underline{H}_2CH_2Si$ and CH (in cycle)).

After **10A** was distilled off, the vat residue was separated by preparative column chromatography (phase silica gel 40/100 (Chemapol), eluent hexane—Freon 113 (9 : 1)). Cyclotetrasiloxane **10B** was separated. Found (%): C, 25.97; H, 1.24. $C_{64}H_{40}F_{88}O_{24}Si_4$. Calculated (%): C, 25.82; H, 1.35. ^{29}Si NMR, δ: −20.51.

The ^{29}Si NMR spectrum of **10d** isolated by column chromatography (15% yield) contains a broadened signal at δ −22.5 to −23.5. We believe that this fraction consists of oligomeric cyclosiloxanes with *m* > 4 (**10C**).

References

1. V. A. Ponomarenko and M. A. Ignatenko, *Khimiya ftorkremniiorganicheskikh soedinenii* [*Chemistry of Fluorocontaining Organosilicon Compounds*], Nauka, Moscow, 1979, 161 pp. (in Russian).

2. A. A. Glazkov, A. V. Ignatenko, S. P. Krukovskii, and V. A. Ponomarenko, *Izv. Akad. Nauk SSSR*, *Ser. Khim.*, 1988, 2372 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1988, **37**, 2137 (Engl. Transl.)].
3. K. A. Andrianov and N. N. Sokolov, *Dokl. Akad. Nauk SSSR*, 1952, **6**, 909 [*Dokl. Chem.*, 1952 (Engl. Transl.)].
4. Y. K. Kim, A. G. Smith, and O. R. Pierce, *J. Org. Chem.*, 1973, **38**, 1615.
5. D. J. Burton, R. K. Harris, K. Dogson, C. J. Pellow, and J. A. Semlyen, *Polym. Commun.*, 1983, **24**, 278.
6. B. Coleman, in *NMR of Newly Accessible Nuclei*, Academic Press, Paris, 1983, Vol. **2**, 197.
7. A. E. Shamaev, A. V. Ignatenko, and S. P. Krukovskii, *Izv. Akad. Nauk*, *Ser. Khim.*, 2004, 2133 [*Russ. Chem. Bull., Int. Ed.*, 2004, **53**, 2233].
8. K. A. Andrianov, *Kremniiorganicheskie soedineniya* [*Organosilicon Compounds*], Goskhimizdat, Moscow, 1955, 520 pp. (in Russian).
9. V. A. Ponomarenko, S. P. Krukovskii, and A. Yu. Alybina, *Ftorsoderzhashchie geterotsepnye polimery* [*Fluorocontaining Heterochain Polymers*], Nauka, Moscow, 1973, 304 pp. (in Russian).
10. J. F. Brown, *J. Am. Chem. Soc.*, 1965, **87**, 4317.
11. H. Kobayashi, *Makromol. Chem.*, 1993, **194**, 2569.

Received November 12, 2004;
in revised form January 26, 2005