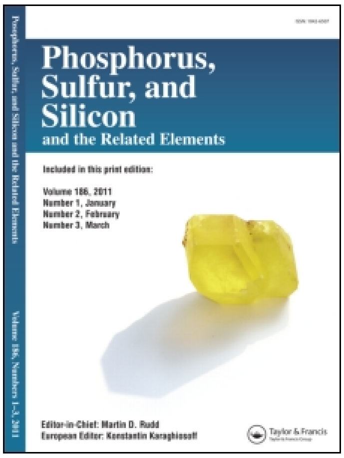

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THE SYNTHESIS OF FLUORINE CONTAINING POLYSILOXANES. PART 1. THE SYNTHESIS OF FLUORINE CONTAINING CYCLOSILOXANES

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A new facile preparative method for the synthesis of semifluorinated organocyclosiloxanes is reported. Ring closure of the dichlorosilanes with $NaHCO_3$ and pyridine gave a mixture of semifluorinated organocyclosiloxanes with cyclotrisiloxane as the main product in yields 95–98% with yield of cyclotrisiloxanes up to 80%.

Keywords: Cyclization; semifluorinated cyclosiloxanes; semifluorinated dichlorosilanes; semifluorinated organosilicon compounds

Polysiloxanes are commercially the most important type of organic/inorganic polymeric materials. They are materials that combine unique properties of wide scientific and technological interest. In the search for high temperature elastomers, efforts have been directed toward the preparation and evaluation of fluorine containing polysiloxanes as they are possible to deposition of hard transparent coatings with adjustable refractive index, biocompatible thin films, and gas-vapor barrier layers.[1] Silicone- and fluorine-containing polymers are usually quite susceptible to rapid surface rearrangement. In particular, the materials with most interest, those with low-energy surfaces as fluorinated polymers, often have the greatest thermodynamic driving force for reconstruction when in contact with polar liquid as such as water.

Molecules in which hydrocarbon and fluorocarbon segments are linked to each other consist of two incompatible segments. They

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represent a still little investigated class of amphiphilic compounds. Low temperatures and large fluorinated segments favor self-organization into defined supramolecular structure in the bulk as well as in nonaqueous solution (for example, micelles or monomolecular surface layers), but also induce crystallization and entail poor solubility. However, this can be overcome by introducing irregularities such as branchings, heteroatoms, cycles, etc., into the perfluorinated or the hydrocarbon segments.

Until now, anionic polymerization of cyclosiloxanes combined with appropriate linking chemistry is the most powerful tool for synthesizing polysiloxanes with controlled macromolecular architecture.[2] Living anionic ring-opening polymerization of cyclotrisiloxanes has been used to prepare narrow molecular weight distribution polysiloxanes. Regio specific anionic ring-opening polymerization of monosubstituted cyclotrisiloxanes has been used to prepare highly regular polysiloxanes. Polydisperse high molecular weight linear polysiloxanes are often prepared by acid-catalyzed ring-opening polymerization of cyclotetrasiloxanes.

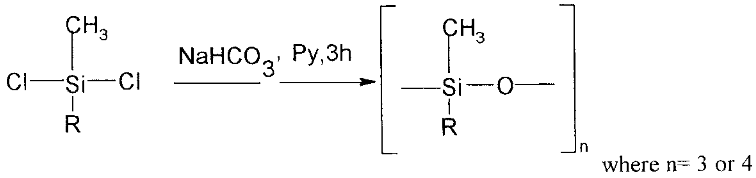
The aim of this article was to find a facile preparative method for the synthesis of cyclosiloxanes with fluorinated fragments of variable structures (linear, branched, or with cyclic fragments). This article describes our recent efforts to prepare and characterize semifluorinated cyclosiloxanes.

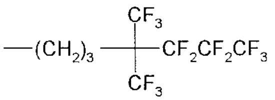
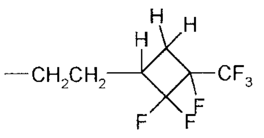
RESULTS AND DISCUSSION

Synthetic Procedure

In principle organocyclosiloxanes can be prepared by any reaction in which silicon-oxygen bonds are formed.[3] Among reactions of silicon functional derivatives with substances that can provide oxygen to form Si—O—Si bonds, the most important for the synthesis of organocyclosiloxanes is the hydrolysis of difunctional derivatives of silicon (organodichlorosilanes, organoalkoxysilanes, etc). In most cases organocyclosiloxanes are formed together with linear silaxanols, in variable proportions, depending upon the conditions of the hydrolysis. A disadvantage of this reaction is that in this process the most important for polymerization cyclotrisiloxanes are formed only in very low yields (up to 1%) because of their high strength structure.[4] Another way to obtain fluorinated cyclosiloxanes is hydrosilylation of n-methyl-cyclo-n-siloxanes.[5] A disadvantage of this method is the possibility of incomplete transformation and a tendency to polymerization of cyclotrisiloxanes. Recently new synthetic methods was proposed for the synthesis of cyclotrisiloxanes starting form dichlorosilanes by using dimethylsulfoxide[6] or gallium triiodide[7] with yields of cyclotrisiloxane up to 50% (all cyclosiloxane in yields up to 80%).

An initial requirement for us was to develop a simple, clean, and efficient synthesis of a variety of fluorinated cyclosiloxanes derived from dichlorosilanes by using cheap reagents. It is known from the patent literature that metal salts can be used as oxygen sources in the synthesis of cyclosiloxanes. For example, in a Russian patent,[8] $NaHCO_3$ or $KHCO_3$ was used for synthesis of various cyclosiloxanes from dichlorosilanes. We report in this article an experimentally simple new approach to synthesis of fluorinated organocyclosiloxanes starting from dichlorosilanes using $NaHCO_3$as the oxygen source and pyridine as the HCl acceptor. The reaction was carried out in solution at room temperature with equimolar quantities of pyridine, dichlorosilane, and sodium bicarbonate and gave a mixture of organocyclosiloxanes in 95–99% yields.

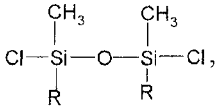


	R	n=3	n=4
I	$—(CH_2)_3OCH_2(CF_2CF_2)_2H$	a	b
II	$—(CH_2)_3OCH_2C_4F_9$	a	b
III	$—(CH_2)_3OCH_2(CF_2CF_2)_3H$	a	b
IV	 $—(CH_2)_3C(CF_3)_2CF_2CF_2CF_3$	a	b
V		a	

Propyl ethers of linear fluorinated alcohols, branched fluorinated alkane, and organic semifluorinated cycle were used as fluorinated fragments. Ethyl acetate or tetrahydrofurane were used as solvent. The requirement is that this solvent should be good both for starting dichlorosilane and for resulting cyclosiloxanes.

The yield and contents of cyclotri- and tetrasiloxanes in the synthesis are described in Table I. Yields of cyclotrisiloxanes ranged from 40 to 80%. To the best of our knowledge, this is the highest yield in one-pot synthesis of cyclotrisiloxanes from dichlorosilanes.

The stepwise feature of this reaction can be postulated. The ^{29}Si NMR spectra of reaction mixture contain signals of starting dichlorosilanes (7–10 ppm), dichlorosiloxanes (2–5 ppm), for example



$$Cl\text{—}\overset{CH_3}{\underset{R}{Si}}\text{—}O\text{—}\overset{CH_3}{\underset{R}{Si}}\text{—}Cl,$$

and silanols (-10 to -16 ppm) together with signals of cyclosiloxanes.

IR, multinuclear NMR, and elemental analysis were used to confirm the formation of the cyclosiloxanes I–V.

IR Data

Infrared analysis is very sensitive to the siloxane cycle structure. The strained structure of cyclotrisiloxane leads to the appearance a strong band at 1015–1020 cm^{-1} corresponding a Si—O—Si valence vibration. This band is very evident and well developed (Figure 1). On the other hand, the band at 1077–1085 cm^{-1} is present in the spectra of cyclotetrasiloxanes (Figure 1). This confirms low strain in cyclotetrasiloxanes. The IR results are given in Table II.

NMR Data

The ^{29}Si NMR data are very important for the characterization of cyclosiloxanes. Trimethyltrifluoroalkylcyclotrisiloxanes may exist as a mixture of two isomers- cis and trans. In agreement with this, its ^{29}Si NMR spectrum should contain two lines corresponding to these two isomers. In our case experimental spectra contain two signals (Table III) only for cyclotrisiloxanes Ia and IIa (intensity ratio 1:2 in upfield order). Downfield signal corresponds to the cis isomer.[9]

TABLE I Properties of Semifluorinated Cyclosiloxanes I–V

Cyclosiloxane	Solvent[a]	Yields[b]	Bp°C/mm Hg	n_D^{20}	d_4^{20}	Elemental analysis
Ia	THF	42	180/1	1.3840	1.4294	Calcd. for $C_{27}H_{36}O_6F_{24}Si_3$: C,32.54; H,3.64; F,45.76; Si,8.43. Found: C,32.40; H,3.60; F,45.90; Si, 8.40
Ib	THF	58	220/1	1.3812	1.4280	Calcd. for $C_{36}H_{48}O_8F3_2Si_4$: C,32.54; H,3.64; F,45.76; Si,8.43. Found: C,32.45; H,3.58; F,45.94; Si, 8.33
IIa	THF	75	252/1	1.3674	1.5083	Calcd. for $C_{33}H_{36}O_6F_{36}Si_3$: C,34.63; H,3.17; F,46.48; Si,7.34. Found: C, 34.51; H,3.10; F,46.70; Si, 7.11
IIb	THF	25	280/1	1.3680	1.5062	Calcd. for $C_{44}H_{48}O_8F_{48}Si_4$: C,34.63; H,3.17; F,46.48; Si,7.34. Found: C, 34.42; H,3.08; F,46.81; Si, 7.10
IIIa	THF	65	92/1	1.3670	1.4315	Calcd. for $C_{27}H_{33}O_6F_{25}Si_3$: C,31.93; H,3.47; F,46.77; Si,8.27. Found: C,31.82; H,3.30; F,46.95; Si, 8.10
IIIb	THF	35	115/1	1.3651	1.4310	Calcd. for $C_{36}H_{44}O_8F_{36}Si_4$: C,31.93; H,3.47; F,46.77; Si,8.27. Found: C,31.72; H,3.36; F,47.00; Si, 8.13
IVa	THF	60	110/1	1.3570	1.6370	Calcd. for $C_{30}H_{27}O_3F_{39}Si_3$: C,28.58; H,2.16; F,58.78; Si,6.66. Found: C,28.42; H,2.06; F,58.81; Si, 6.31
IVb	THF	40	140/1	1.3562	1.6365	Calcd. for $C_{40}H_{36}O_4F_{52}Si_4$: C,28.58; H,2.16; F,58.78; Si,6.66. Found: C,28.40; H,2.05; F,58.85; Si, 6.70
V	THF	80	98/1	1.3874	1.3840	Calcd. for $C_{24}H_{30}O_3F_{18}Si_3$: C,36.37; H,3.82; F,43.15; Si,10.10. Found: C,36.20; H,3.70; F,43.35; Si, 10.0

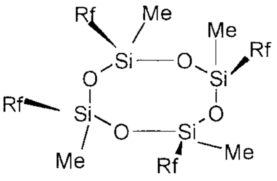
[a] Solvent used for synthesis.

[b] Part of cyclotrisiloxane/cyclotetrasiloxane.

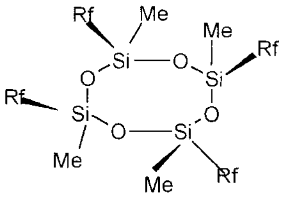
TABLE II IIR Data of Cyclosiloxanes I–V

Cyclosiloxane	IR data
Ia	2940,2885, 1260,1166, 1126,1020, 808
Ib	2940,2885, 1260,1166, 1126,1080, 808
IIa	2941,2883, 1263,1198,1141,1017,832
IIb	2941,2883, 1263,1198,1141,1083,832
IIIa	2943,2884,1358,1308,1230,1206,1136,1021,883,808
IIIb	2943,2884,1358,1308,1230,1206,1136,1081,883,808
IVa	2940,2890,1343,1306,1280-1260,1143,1020,898,805
IVb	2940,2890,1343,1306,1280-1260,1143,1080,898,805
V	2964,2935,2890,1343,1306,1263,1235,1192,1112,1017,803

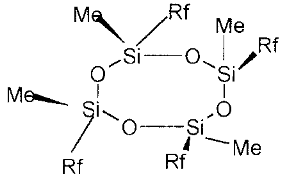
Tetramethyl-tetrakisfluoroalkylcyclotetrasiloxanes are a mixture of four isomers (A-“eeee”, B-“aeee”, C-“aaee”, and D-“aeae”).



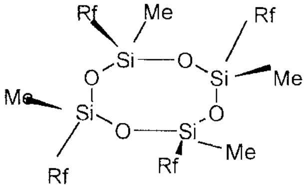
A



B



C



D

The additive scheme of Pestunovich et al.[10] can be used to simulate the number of lines in spectrum. This number is six and it attributed to isomers B, D, C, D, A, and B in the upfield order. In agreement with this (Figure 2) the ^{29}Si NMR spectrum of cyclotetrasiloxane IVb contains six lines. For all other cyclotetrasiloxanes the instrument used does not provide resolution of all lines in the spectra (Table III). The ^{13}C NMR spectra of cyclotetrasiloxanes also contain separate signals of these isomers (Table III).

As can be seen from ^{1}H and ^{13}C NMR spectra 1,1,2-trifluoro-2-trifluoromethyl-4-ethylcyclobuthyl fragment in cyclotrisiloxane V exists as a mixture of cis and trans isomers in ratio 1:2. This could induce irregularities in the structure of polymers synthesized from this monomer.

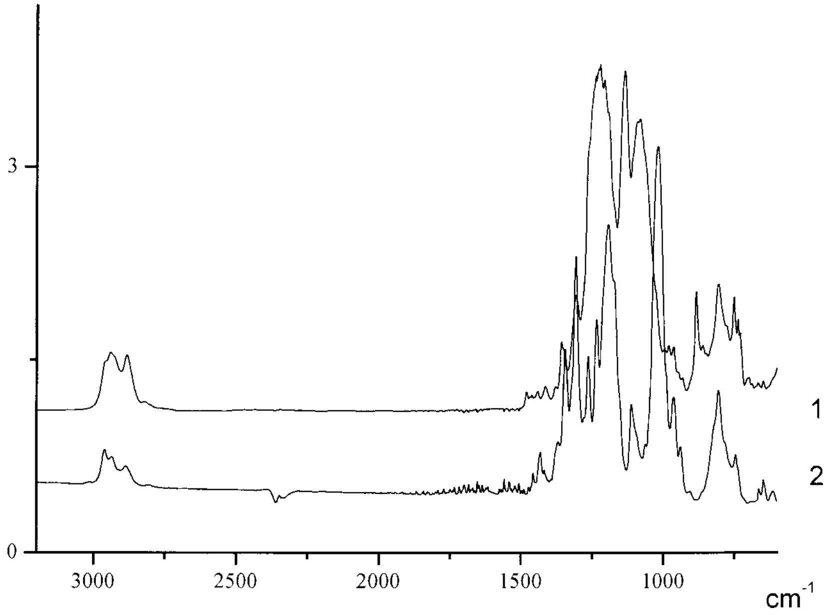


FIGURE 1 IR spectra of cyclotetrasiloxane IVb (1) and cyclotrisiloxane V (2).

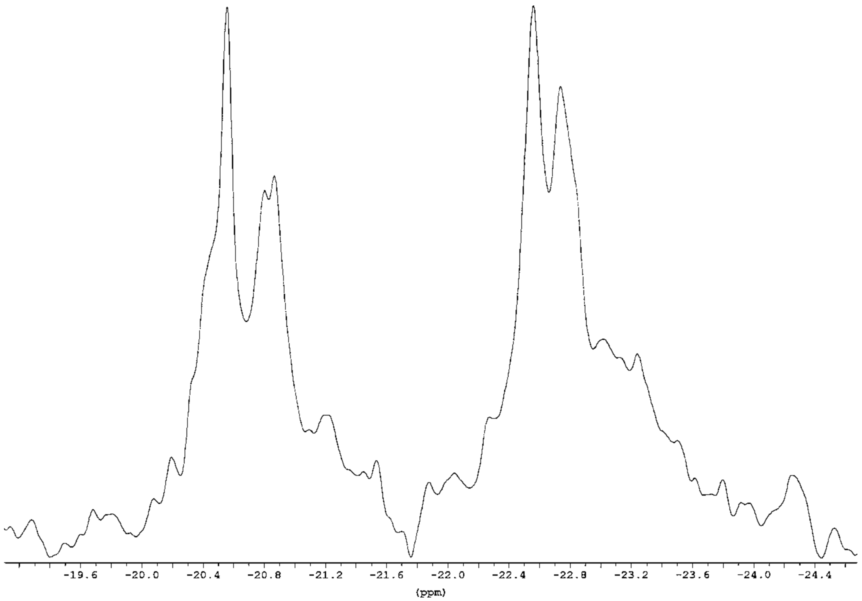


FIGURE 2 ^{29}Si NMR spectra of cyclotetrasiloxane IVb.

TABLE III NMR Data for Cyclosiloxanes I–V

Cyclosiloxane	^{1}H NMR (300.13 MHz, $CDCl_3$, TMS) δ, J (Hz)	^{13}C NMR (75.468 MHz, $CDCl_3$, TMS) δ, J (Hz)	^{29}Si NMR (59.627 MHz, $CDCl_3$,TMS)δ
Ia	0.44 (s, CH_3, cis), 0.45 (s, CH_3, trans), 0.10–0.19 (m, Si—CH_2, 2H), 1.69–1.78 (m, CH_2, 2H), 3.57 (p, CH_2O, 2H, J = 6.4), 3.90 (t, CH_2CF_2, 2H, J = 13.9), 6.04 (tt, CF_2H, 1H, $J_1 = 51.85$, $J_2 = 5.8$)	15.15 (CH_3), 1.63 (Si—CH_2), 22.48 (CH_2), 74.40 (CH_2O), 67.35 (t, $\underline{C}H_2CF_2$, J = 25.8), 109–112 (CF_2), 107.79 (t, CF_2H, J = 30.4), 115.60 (t, $CH_2\underline{C}F_2$, J = 30.4)	−9.39 −9.59
Ib	0.55–0.68 (s, CH_3, 3H), 0.11–0.20 (m, Si—CH_2, 2H), 1.63–1.78 (m, —CH_2—, 2H), 3.55 (p, H_2O, 2H, J = 6.5), 3.90 (t, CH_2CF_2, 2H J = 13.9), 6.05 (tt, CF_2H, 1H, J_1 = 51.85, $J_2 = 5.8$)	15.35 (CH_3), 1.73 (Si—CH_2), 22.67 (CH_2), 75.58 (CH_2O), 67.36 (t, $\underline{C}H_2CF_2$, J = 25.8), 109–112 (CF_2), 107.88 (t, CF_2H, J = 30.4), 115.69(t, $CH_2\underline{C}F_2$, J = 30.4)	−18.98 −21.08 −21.50
IIa	−0.05 (s, CH_3, 3H), −0.01 (s, CH_3, trans), 0.48 (s, Si—CH_2, 2H), 1.53 (s, CH_2, 2H), 3.39 (s, CH_2O, 2H), 3.72 (t, CH_2CF_2, 2H, J = 13.9), 5.86 (tt, CF_2H, 1H, $J_1 = 51.62$, $J_2 = 5.8$)	13.16 (CH_3), −1.31 (Si—CH_2), 23.15 (CH_2), 75.51 (CH_2O), 68.05 (t, $\underline{C}H_2CF_2$, J = 25.3), 106.7–117.0, 119.5–120.5 $(CF_2)_4$, 108.38 (t, CF_2H, J = 31.0), 105.02 (t, $CH_2\underline{C}F_2$, J= 31.0)	−9.08 −9.24
IIb	−0.08 (s, CH_3, 3H), 0.40 (s, Si—CH_2, 2H), 1.50 (s, CH_2, 2H), 3.36 (s, CH_2O, 2H), 3.70 (t, CH_2CF_2, 2H, J = 13.9), 5.82 (tt, CF_2H, 1H, $J_1 = 51.62$, $J_2 = 5.8$)	13.19, 13.43, 13.65, 13.72 (CH_3),), −1.28, −1.14, −0.99, −0.72 (Si—CH_2), 23.77 (CH_2), 75.97 (CH_2O), 68.26 (t, $\underline{C}H_2CF_2$, J = 24.3), 106.8–117.0, 119.5–120.5 $(CF_2)_4$, 108.60 (t, CF_2H, J=31.0), 105.23 (t, $CH_2\underline{C}F_2$, J= 31.0)	−19.69 −21.98 −22.55
IIIa	0.34 (s, CH_3, 3H), 0.60 (t, Si—CH_2, 2H, J = 6.9), 1.69 (s, CH_2, 2H), 3.57 (t, CH_2O, 2H, J = 6.9), 3.90 (t, CH_2CF_2, 2H, J = 13.9)	12.16 (CH_3), −1.31 (Si—CH_2), 23.15 (CH_2), 75.28 (CH_2O), 67.75 (t, $\underline{C}H_2CF_2$, J = 25.0), 105–115, $(CF_2)_3$, 117.68 (kt, CF_3, J_1 = 288.6, $J_2 = 34.5$)	−9.28

IIIb	0.12 (s, CH_3, 3H), 0.60 (t, Si—CH_2, 2H, J = 6.9), 1.68 (s, CH_2, 2H), 3.57 (t, CH_2O, 2H, J = 6.9), 3.91 (t, CH_2CF_2, 2H, J = 13.9)	12.78, 12.84, 12.96 (CH_3), −1.46, −1.34, −1.29 (Si—CH_2), 23.19 (CH_2), 75.38 (CH_2O), 67.76 (t, $\underline{C}H_2CF_2$, J = 25.0), 105–115, $(CF_2)_3$, 117.68 (kt, CF_3, J_1 = 288.6, J_2 = 34.5)	−19.12, −19.71, −21.98, −22.57
IVa	0.01 (s, CH_3, 3H), 0.30 (bs, Si—CH_2, 2H), 1.50 (bs, CH_2, 2H), 1.95 (bs, CH_2, 2H)	17.40 (CH_3), −1.15 (Si—CH_2), 30.80 (CH_2), 57.60 (CH_2—$\underline{C}$), 60.74 (sept, $\underline{C}H_2C$, J = 24.15), 125.35 (k, C—CF_3, J = 288.5), 117.68 (kt, CF_2—$\underline{C}F_3$, J_1 = 287.5, J_2 = 34.5), 109.70 (tm, $\underline{C}F_2$—CF_3, J = 270.8), 115.23 (tt, C—$\underline{C}F_2$, J_1 = 270.8, J_2 = 34.0)	−9.11
IVb	0.01 (s, CH_3, 3H), 0.31 (bs, Si—CH_2, 2H), 1.53 (bs, CH_2, 2H), 1.95 (bs, CH_2, 2H)	17.14, 17.41, 17.63 (CH_3), −2.58, −2.20.−1.82 (Si—CH_2), 30.77, 30.97, 31.03 (CH_2), 57.58 (CH_2—$\underline{C}$), 60.75 (sept, $\underline{C}H_2C$, J = 24.15), 125.35 (k, C—CF_3, J = 288.5), 117.68 (kt, CF_2—$\underline{C}F_3$, J_1 = 287.5, J_2 = 34.5), 109.70 (tm, $\underline{C}F_2$—CF_3, J = 270.8), 115.23 (tt, C—$\underline{C}F_2$, J_1 = 270.8, J_2 = 34.0)	−20.58, −20.71, −20.99, −21.04, −22.77, −22.96
V	0.05 (s, CH_3, 3H), 0.49 (t, Si—CH_2, 2H, J = 7.7), 2.48 (dt, CH_2, 2H), 1.92(p, cis-CH-cycle, 2H), 2.13 (p, trans-CH-cycle, 2H), 1.48 (s, cis-CH_2-cycle), 1.68 (s, trans-CH_2-cycle)	20.99 (CH_3), −1.37 (Si—CH_2), 14.15-cis, 14.16-trans (CH_2), 34.75-cis, 34.53-trans (CH_2-cycle), 39.39-cis (k, CH, cycle J_1 = 66.23, J_2 = 32.0), 36.16 (t, CH-cycle, J = 82.3), 95.05 (dm, CF), 111.8–113.0, 115.5–116.9, 119.0–120.7, 122.8–123.7, 126.5–127.5 (5 of m, ratio 4:12:12:7:2, CF_2 and CF_3)	−9.81

CONCLUDING REMARKS

The procedure reported here represents a new synthetic approach to the semifluorinated organocyclosiloxanes. The easy availability of the starting materials, the simplicity of this short and clean procedure and the good yields of products render this process particularly attractive.

EXPERIMENTAL

General Experimental Procedures

All starting materials were obtained from Reachim (USSR or Russia) and distilled or recrystallized prior to use. The solvents used for reactions are dried by standard methods. Dichloromethyl-6,6′,7,7′,8,8′,9,9′-octafluoro-4-oxa-nonylsilane, dichloromethyl-6,6′,7,7′,8,8′,9,9′,9″-nonafluoro-4-oxa-nonylsilane, and dichloromethyl-6,6′,7,7′,8,8′,9,9′,10,10′.11.11′-dodecafluoro-4-oxa-undecylsilane were synthesized from methyldichlorosilane and allyl ethers of 2,2′,3,3′,4,4′,5,5′-octafluoropentanol, 2,2′,3,3′,4,4′,5,5′,5″-nonafluoropentanol, or 2,2′,3,3′,4,4′,5,5′,6,6′,7,7′-dodecafluorogeptanol by published hydrosilylation reaction.[5] Other fluorinated methylalkyldichlorosilanes (methyl-1,1,2-trifluoro-2-trifluoromethyl-4-ethylcyclobuthyldichlorosilane and methyl-4,4′-ditrifluoromethyl-5,5′,6,6′.7,7′,7″-gepthafluorogepthyldichlorosilane) were synthesized as described in Russian patent.[11]

Melting points were measured on a Boetius apparatus (DDR). IR spectra were recorded on a Bruker IFS-88 spectrometer. ^{1}H, ^{13}C, and ^{29}Si NMR spectra were taken on a Bruker DPX-300 instrument.

General Synthetic Procedures

To 8.4 g (0.1 mmol) of water free NaHCO$_3$ (dried in vacuum at 110°C for 24 h used just after that), and 7.9 g (0.1 mmol) of dry pyridine in 80 ml tetrahydrofurane (THF), 0.1 mmol of dichlorosilane in 30 ml THF was added dropwise during 1 h. After stirring for 3 h at rt, the solution was filtered, the residue was washed with 30 ml THF. The combined solution was washed with water (2 × 150 ml). The organic layer was separated and the solvent was evaporated. The distillation of residue (95–98.5% yields) in vacuo gave cyclotrisiloxane and cyclotetrasiloxane.

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