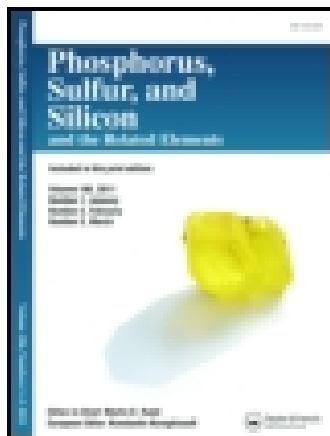


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## A FACILE AND EFFICIENT SYNTHESIS OF ORGANOCYCLOSILOXANES

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*A new facile preparative method for the synthesis of organocyclosiloxanes is reported. Ring closure of the dichlorosilanes with NaHCO<sub>3</sub> and pyridine gave mixture of organocyclosiloxanes with cyclotrisiloxane as a main product.*

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

Organocyclosiloxanes have attracted considerable attention because of their utility as monomers in synthesis of polysiloxanes.<sup>1</sup> Polysiloxanes are commercially the most important type of inorganic/organic polymeric materials. 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 often are prepared by acid-catalyzed ring-opening polymerization of cyclotetrasiloxanes.

In principle, organocyclosiloxanes can be prepared by any reaction in which silicon-oxygen bonds are formed.<sup>2</sup> Among reactions of silicon functional derivatives with substances which 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

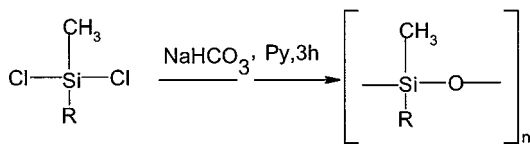
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organocyclosiloxanes are formed together with linear siloxanols, in variable proportions, depending the conditions of the hydrolysis. A disadvantage of this reaction is that in this process the cyclotrisiloxanes (most important monomers for polymerization) are formed only in very low yields (up to 1%) because of their high-strength structure.<sup>3</sup> Recently a new synthetic methods was proposed for the synthesis of cyclotrisiloxanes starting from dichlorosilanes by using dimethylsulfoxide<sup>4</sup> or gallium triiodide<sup>5</sup> with yields of cyclotrisiloxanes up to 50% (all cyclosiloxanes in yields up to 80%).

An initial requirement for this research was to develop a simple, clean, and efficient synthesis of a variety of organocyclosiloxanes 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,  $\text{Me}_2\text{SiCl}_2$  and  $\text{Na}_2\text{CO}_3$  in column at 300–400°C from a mixture of cyclosiloxanes in 98% yield.<sup>6</sup> In almost the same conditions, diethyldichlorosilane with  $\text{NaHCO}_3$  produces a trimeric cyclosiloxane  $(\text{Et}_2\text{SiO})_3$  in low yield.<sup>7</sup> In a Russian patent,<sup>8</sup>  $\text{NaHCO}_3$  or  $\text{KHCO}_3$  was used in similar conditions for synthesis various cyclosiloxanes starting from dichlorosilanes. High temperature conditions may lead to the degradation of starting materials and products having sensitive substituents.

## RESULTS AND DISCUSSION

We report in this article an experimentally simple new approach to the synthesis of organocyclosiloxanes starting from dichlorosilanes using  $\text{NaHCO}_3$  as source of oxygen and pyridine as acceptor of  $\text{HCl}$ . 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 with 95–99% yields. Diethyl ether, acetone, hexane, benzene, toluene, ethyl acetate, among others, may be used as solvents. One requirement, but not a stringent one, is that this solvent should be good both for starting dichlorosilane and for resulting cyclosiloxanes. However, it also is possible to carry out this reaction without any solvent.



where  $n = 3, 4, 5, 6$

The yields and contents of different rings in the synthesis of organocyclosiloxanes are described in Table I. The spectral and analytical data on of organocyclosiloxanes synthesized for the first time are given in Table II. Yields of cyclotrisiloxanes ranged from 33 to 67%. To the best our knowledge, this is the highest yield in one-pot synthesis of cyclotrisiloxanes from dichlorosilanes.

In conclusion, the procedure reported here represents a new synthetic approach to the 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

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. Dichloro- $\alpha$ -naphthylmethylsilane was synthesized by the reaction of a Grignard reagent prepared from  $\alpha$ -bromonaphthalene with methyltrichlorosilane.<sup>9</sup> Dichloromethyl-6,6',7,7',8,8',9,9'-octafluoro-4-oxa-nonylsilane was synthesized from methyl-dichlorosilane and allyl ether of 2,2',3,3',4,4',5,5'-octafluoropentanol by published hydrosilylation reactions.<sup>10</sup>

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

### Dimethylcyclosiloxanes

To 8.4 g (0.1 mmol) of water free NaHCO<sub>3</sub> and 7.9 g (0.1 mmol) dry pyridine in 80 ml ethyl acetate 12.9 g (0.1 mmol) dimethyldichlorosilane in 50 ml ethyl acetate was added dropwise throughout 1 h. After stirring for 3 h at room temperature, the solution was filtered and the residue was washed with 30 ml ethyl acetate. The solvent was evaporated. The distillation of residue 7.9 g (99% yield) gave 4.38 g (60%) of hexamethylcyclotrisiloxane, 1.46 g (20%) of octamethylcyclotetrasiloxane, 1.10 g (15%) of decamethylcyclopentasiloxane, and 0.36 g (5%) of a mixture of cyclohexacyclooctasiloxanes.

### Phenylmethylcyclosiloxanes

To 8.4 g (0.1 mmol) of water free NaHCO<sub>3</sub>, and 7.9 g (0.1 mmol) dry pyridine in 80 ml acetone, 19.1 g (0.1 mmol) methylphenyldichlorosilane in 30 ml acetone was added dropwise throughout 1 h. After stirring

TABLE I Cyclosiloxanes Prepared

R	Solvent in synthesis	Yield (%)	n (part %)	m.p. (°C) or b.p. (°C)/torr	Molecular formula <sup>a</sup> or Lit. <sup>11</sup> m.p. (°C) or b.p. (°C)/torr	n <sub>D</sub> <sup>20</sup>	Lit. <sup>11</sup> n <sub>D</sub> <sup>20</sup>
Me	Ethyl acetate	99	3(60) 4(20) 5(15)	64 75/20 100/20	64.5 74/20 101/20	— 1.3970 1.3980	— 1.3968 1.3982
Ph	Acetone	98.5	3(33) 4(65.5)	— 171/1.5 235/1.5	— 168/1 232/1	— 1.5410 1.5415	— 1.5402 1.5420
Naph	Ethyl acetate	98	3(34) 4(65)	240/1 265/1	C <sub>33</sub> H <sub>30</sub> O <sub>3</sub> Si <sub>3</sub> C <sub>44</sub> H <sub>40</sub> O <sub>4</sub> Si <sub>4</sub>	1.6253 1.6224	— —
Ph <sup>b</sup>	Toluene	97	3(67.2) 4(30.3)	188–189 199–200	188–189 200–201	— —	— —
(CH <sub>2</sub> ) <sub>3</sub> OCH <sub>2</sub> (CF <sub>2</sub> ) <sub>4</sub> H	Ethyl acetate	98	3(64) 4(33)	180/1 220/1	C <sub>27</sub> H <sub>36</sub> O <sub>6</sub> Si <sub>3</sub> F <sub>24</sub> C <sub>36</sub> H <sub>48</sub> O <sub>8</sub> Si <sub>4</sub> F <sub>32</sub>	1.3840 1.3812	— —

<sup>a</sup>Satisfactory microanalysis obtained: C ± 0.25, H ± 0.15, Si ± 0.3, F ± 0.2.<sup>b</sup>Both substituents at Si are Ph.

R is the radical on the reaction scheme.

TABLE II Spectral Data of New Cyclosiloxanes Prepared

R	n	IR (film) $\nu$ cm <sup>-1</sup>	<sup>1</sup> H NMR (CDCl <sub>3</sub> , TMS) $\delta$ , J (Hz)	<sup>13</sup> C NMR (CDCl <sub>3</sub> , TMS) $\delta$ , J (Hz)	<sup>29</sup> Si NMR (CDCl <sub>3</sub> , TMS) <sup>b</sup>
Naph	3 <sup>c</sup>	3061, 3038, 1504, 1260, 1020, 780	1.61 (s, CH <sub>3</sub> , cis), 1.48/1.47 (2:1, CH <sub>3</sub> , trans), 7.86–7.91 (m, 3 + 7 + 6), 8.19–8.30 (m, 5 + 2), 8.47–8.56 (m, 8), 8.95–9.01 (m, 4)	4.09 (CH <sub>3</sub> , cis), 4.02 (CH <sub>3</sub> , trans): cis:131.50 (1), 131.85 (2), 125.73 (3), 134.04 (4), 128.87 (5), 126.34 (6), 127.57 (7), 124.62 (8), 135.36 (4a), 133.19 (8a) trans: 131.38 (1), 131.81 (2), 125.68 (3), 134.04 (4), 128.87 (5), 126.29 (6), 127.47 (5), 126.29 (6), 127.47 (7), 124.59 (8), 135.36 (4a), 133.15 (8a)	4.14 (cis) 4.75, 4.24 (trans)
	4 <sup>b</sup>	3061, 3038, 1504, 1260, 1072, 780	1.43 (CH <sub>3</sub> , aaaa), 1.32, 1.23, 1.20 (CH <sub>3</sub> , aaaa), 1.28 (CH <sub>3</sub> , aaaa), 0.98 (CH <sub>3</sub> , aaaa), 7.86–7.91 (m, 3 + 7 + 6), 8.19–8.30 (m, 5 + 2), 8.47–8.56 (m, 8), 8.95–9.01 (m, 4)	0.87, 1.0, 1.11, 1.18, 1.55, 1.75, 1.84 (CH <sub>3</sub> ), 130.51, 130.62, 130.71 (1), 132.95, 133.08, 133.16 (2), 125.23, 125.35, 125.43 (3), 134.49, 134.56, 134.81 (4), 128.58, 128.67, 128.76 (5), 125.58, 125.70/125.91 (6), 127.45, 127.66 (7), 124.79, 124.88, 124.99 (8), 136.16, 136.28, 136.37, 136.47 (4a), 133.68, 133.91 (8a)	-21.33 (aaaa) -18.98 (aaaa) -19.36 (aaaa) -19.54 (aaaa) -19.18 (aaaa) -16.96 (aaaa)
(CH <sub>2</sub> ) <sub>3</sub> OCH <sub>2</sub> (CF <sub>2</sub> ) <sub>4</sub> H	3 <sup>c</sup>	2940, 2885, 1260, 1166, 1126, 1020, 808	0.44 (s, CH <sub>3</sub> , cis), 0.45 (s, CH <sub>3</sub> , trans), 0.10–0.19 (m, Si-CH <sub>2</sub> , 2H), 1.69–1.78 (m, -CH <sub>2</sub> , 2H), 3.57 (p, CH <sub>2</sub> O, 2H, J = 6.4), 3.90 (t, CH <sub>2</sub> CF <sub>2</sub> , 2H, J = 13.9), 6.04 (tt, CF <sub>2</sub> H, <sup>1</sup> H, J1 = 51.85, J2 = 5.8)	15.15 (CH <sub>3</sub> ), 1.63 (Si-CH <sub>2</sub> ), 22.48 (CH <sub>2</sub> ), 74.40 (CH <sub>2</sub> O), 67.35 (t, CH <sub>2</sub> CF <sub>2</sub> , J = 25.8), 109–112 (CF <sub>2</sub> ), 107.79 (t, CF <sub>2</sub> H, J = 30.4), 115.60 (t, CH <sub>2</sub> CF <sub>2</sub> , J = 30.4)	-4.39 -4.59
	4	2940, 2885, 1260, 1166, 1126, 1080, 808	0.55–0.68 (m, CH <sub>3</sub> 3H), 0.11–0.20 (m, Si-CH <sub>2</sub> , 2H), 1.69–1.78 (m, -CH <sub>2</sub> , 2H), 3.55 (p, CH <sub>2</sub> O, 2H, J = 6.5), 3.90 (t, CH <sub>2</sub> CF <sub>2</sub> , 2H, J = 13.9), 6.05 (tt, CF <sub>2</sub> H, <sup>1</sup> H, J1 = 51.85, J2 = 5.8)	15.35 (CH <sub>3</sub> ), 1.73 (Si-CH <sub>2</sub> ), 22.67 (CH <sub>2</sub> ), 75.58 (CH <sub>2</sub> O), 67.36 (t, CH <sub>2</sub> CF <sub>2</sub> , J = 25.8), 109–112 (CF <sub>2</sub> ), 107.88 (t, CF <sub>2</sub> H, J = 30.4), 115.69 (t, CH <sub>2</sub> CF <sub>2</sub> , J = 30.4)	-18.98 -21.08 -21.50

<sup>a</sup> cis/trans ratio 33/67 from <sup>1</sup>H NMR data.<sup>b</sup> aaaa/aaaae/aaaae ratio 0.27:0.43:0.19:0.11 from <sup>1</sup>H NMR data.<sup>c</sup> cis/trans ratio 47/53 from <sup>1</sup>H NMR data.

for 3 h at room temperature, the solution was filtered and the residue was washed with 30 ml acetone. The solvent was evaporated. The distillation of residue 13.4 g (98.5% yield) in vacuo gave 4.26 g (33%) of trimethyltriphenylcyclotrisiloxane and 8.45 g (65.5%) of tetramethyltetraphenylcyclotetrasiloxane.

## Diphenylcyclosiloxanes

To 30.5 g (0.363 mmol) of water free  $\text{NaHCO}_3$ , and 28.5 g (0.363 mmol) dry pyridine in 250 ml toluene 91.8 g (0.363 mmol) diphenyldichlorosilane in 90 ml toluene was added dropwise throughout 1 h. After stirring for 3 h at room temperature, the solution was filtered and the residue was washed with 200 ml benzene for complete dissolution of silicon-organic derivatives. The combined benzene and toluene solution was washed with water ( $2 \times 450$  ml). The organic layer was separated and, after adding of 200 ml of ethanol, was evaporated. Crystalline residue was recrystallized from ethyl acetate to give 48 g (67.2%) of hexaphenylcyclotrisiloxane and 21.8 g (30.3%) of octaphenyltetracyclosiloxane.

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