Synthesis of new cyclolinear permethyloligosilane-siloxanes

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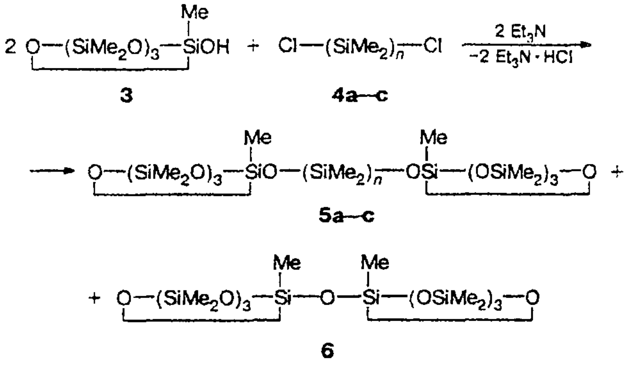
α,ω-Bis(heptamethylcyclotetrasiloxanyloxy)oligodimethylsilanes were synthesized for the first time by heterofunctional condensation of hydroxyheptamethylcyclotetrasiloxane with α,ω-dichloropermethyloligosilanes, $Cl(Me_2Si)_nCl$ (n = 2, 4, or 6). The compounds obtained were characterized by spectroscopic methods.

Key words: heterofunctional condensation, hydroxyheptamethylcyclotetrasiloxane, α,ω-dichloropermethyloligosilanes; IR, UV, ^{29}Si NMR, and mass spectra.

Previously, compounds with the completely methyl environment of the silicon atoms (the so-called "dumbbell-like" structures[1]) have been prepared, namely, α,ω-bis[permethylcyclotri(tetra)siloxy]oligodimethylsiloxanes[2,3] (**1**) and α,ω-bis[permethylcyclopenta(hexa)silanyl]oligodimethylsilanes[4–8] (**2**), which contain only the siloxane or silylene units, respectively.

In this work, mixed silane-siloxane compounds with analogous structures, namely, α,ω-bis(heptamethylcyclotetrasiloxanyloxy)oligodimethylsilanes (**5**), were first synthesized by heterofunctional condensation of hydroxyheptamethylcyclotetrasiloxane (**3**) with α,ω-dichloropermethyloligosilanes $Cl(SiMe_2)_nCl$ (n = 2, 4, or 6) (**4**) (Scheme 1).

Scheme 1



n = 2 (**a**), 4 (**b**), 6 (**c**)

The reaction was carried out in ethyl ether at temperatures from 0 to −5 °C in the presence of triethylamine as an acceptor of HCl. The yields of compounds **5a—c** were 46—64%. The products of the reaction of cyclosiloxane **3** with oligosilanes **4** were analyzed by GLC and GLC-mass spectroscopy. It was demonstrated that in all the cases under study, a small amount of bis(heptamethylcyclotetrasiloxanyl) oxide (**6**) (up to 5%) was formed along with oligosilane-siloxanes **5**. In the mass spectrum, compound **6** is characterized by the ion peak $[M-Me]^+$ at m/z 563. In their physical state, oligosilane-siloxanes **5a—c** (Table 1) are intermediate between compounds **1** and **2**, which have purely siloxane and silane structures, respectively. Oligosilane-siloxanes **5a,b** are pale-yellow viscous liquids (more viscous than oligosiloxanes **1**), compound **5c** is a crystalline compound with a low melting temperature, whereas oligosilanes **2** are crystalline compounds with high melting temperatures.

The structures of compounds **5a—c** were confirmed by spectral methods (see the Experimental section).

Experimental

The GLC analysis was carried out on an LKhM-8MD chromatograph (a 0.3×100 cm stainless steel column; 5% SE-30 on Chromaton N-AW-DMCS; a thermal conductivity detector; the temperature was increased from 30 to 300 °C with a rate of 12 K min^{-1}; helium as the carrier gas). The GLC-mass spectrometric analysis was performed on a Kratos-MS-890

Table 1. Yields and characteristics of compounds **5a—c**

Compound	Yield (%)	B.p. /°C (*p*/Torr)	n_D^{20}	Found/Calculated (%) C	H	Si	Molecular formula
5a	64.7	121—122 (0.01)	1.4174	30.79 30.38	7.44 7.65	38.97 39.48	$C_{18}H_{54}O_{10}Si_{10}$
5b	59.6	158—160 (0.008)	1.4413	32.06 31.92	8.12 8.04	40.21 40.72	$C_{22}H_{66}O_{10}Si_{12}$
5c	46.8	197—198 (0.007)*	—	33.61 33.08	8.42 8.33	41.17 41.65	$C_{26}H_{78}O_{10}Si_{14}$

* M.p. 37—38 °C.

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instrument (a 25 m × 0.32 mm capillary column; SE-30 liquid phase; helium as the carrier gas; ionizing voltage was 70 eV; the temperature was increased from 30 to 270 °C with a rate of 12 K min^{-1}). The ^{29}Si NMR spectra were recorded on Bruker WP-200 SY and Bruker WP-400 SY spectrometers; the chemical shifts are given relative to Me_4Si. The IR and UV spectra were obtained on Specord M-80 and Specord M-40 spectrophotometers, respectively.

Cyclosiloxane **3** and dichlorooligosilanes **4a—c** were prepared according to known procedures.[2,9,10]

All reactions were carried out under an atmosphere of dry argon.

1,2-Bis(heptamethylcyclotetrasiloxanyloxy)tetramethyldisilane (5a). A solution of dichlorodisilane **4a** (0.63 g, 3.35 mmol) in anhydrous ether (30 mL) was added dropwise to a solution of cyclosiloxane **3** (2 g, 6.7 mmol) and Et_3N (0.68 g, 6.7 mmol) in anhydrous ether (40 mL) at −5 °C. The reaction mixture was stirred at −5 °C for 2 h and then at ~20 °C for 20 h. The $Et_3N \cdot HCl$ residue was filtered off. The ethereal solution was washed three times with equal volumes of water and dried with Na_2SO_4. After removal of the solvent, the residue was fractionated. Compound **5a** was obtained in a yield of 1.54 g (Table 1). UV, λ_{max}/nm: ~199. IR (KBr), ν/cm^{-1}: 2964, 2904 (C—H), 1262, 854, 844, 806 (Si—Me); 1082, 1055 (SiOSi). ^{29}Si NMR (CCl_4), δ: 1.43 (OSiSiO); −18.94 ($\mathrm{OSiO\underline{Si}OSiO}$); −19.23 ($\mathrm{O\underline{Si}OSiMe(O{-})_2}$); −63.74 ($\mathrm{MeSi(O{-})_3}$). Mass spectrum, *m/z* (I_{rel} (%)): 695 $[M-Me]^+$ (1.9); $[M/2]^+$ (77.6).

Mass spectrum of compound **6**, *m/z* (I_{rel} (%)): 563 $[M-Me]^+$ (20.8).

1,4-Bis(heptamethylcyclotetrasiloxanyloxy)octamethyltetrasilane (5b). Compound **5b** was prepared from cyclosiloxane **3** (3.75 g, 12.6 mmol), Et_3N (1.27 g, 12.6 mmol), and dichlorooligosilane **4b** (1.91 g, 6.3 mmol) according to a procedure analogous to that described above. The yield was 3.1 g. UV, λ_{max}/nm: 236.5. IR (KBr), ν/cm^{-1}: 2958, 2900 (C—H); 1259, 849, 806 (Si—Me); 1071, 1056 (SiOSi). ^{29}Si NMR (CCl_4), δ: 9.45 ($\mathrm{O\underline{Si}Si_2\underline{Si}O}$); −19.04 ($\mathrm{OSiO\underline{Si}OSiO}$); −19.46 ($\mathrm{O\underline{Si}OSiMe(O{-})_2}$); −47.63 ($\mathrm{OSi\underline{Si}\underline{Si}SiO}$); −64.20 ($\mathrm{MeSi(O{-})_3}$). Mass spectrum, *m/z* (I_{rel} (%)): 811 $[M-Me]^+$ (0.4); 413 $[M/2]^+$ (15.9).

1,6-Bis(heptamethylcyclotetrasiloxanyloxy)dodecamethylhexasilane (5c). Compound **5c** was prepared from cyclosiloxane **3** (2.30 g, 7.7 mmol), Et_3N (0.78 g, 7.7 mmol), and dichlorooligosilane **4c** (1.62 g, 3.85 mmol) according to a procedure analogous to that used for preparing compound **5a**. The yield was 2.0 g (Table 1). After recrystallization from a 1 : 7 THF—EtOH mixture, compound **5c** was obtained in a yield of 1.7 g. UV, λ_{max}/nm: 260. IR (KBr), ν/cm^{-1}: 2962, 2894 (C—H); 1260, 852, 808, 767 (Si—Me); 1079, 1055 (SiOSi). ^{29}Si NMR (a 9 : 1 CCl_4—$CDCl_3$ mixture), δ: 9.14 ($\mathrm{O\underline{Si}Si_4\underline{Si}O}$); −19.16 ($\mathrm{OSiO\underline{Si}OSiO}$); −19.60 ($\mathrm{O\underline{Si}OSiMe(O{-})_2}$); −40.22 ($\mathrm{OSi_2\underline{Si}\underline{Si}Si_2O}$); −45.44 ($\mathrm{OSi\underline{Si}Si_2\underline{Si}SiO}$); −64.35 ($\mathrm{MeSi(O{-})_3}$). Mass spectrum, *m/z* (I_{rel} (%)): 927 $[M-Me]^+$ (0.4); 471 $[M/2]^+$ (67.8).

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