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New cyclolinear permethyloligosilane-siloxanes

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Abstract

α,ω-Bis(heptamethylcyclotetrasiloxanyloxy)oligodimethylsilanes have been synthesized by heterofunctional condensation of hydroxyheptamethylcyclotetrasiloxane with α,ω-dichloropermethyloligosilanes, $Cl(Me_2Si)_nCl$ ($n = 1$–4, or 6). The substances are characterized by mass spectrometry, ^{29}Si-NMR, IR and UV spectroscopy. © 1999 Elsevier Science S.A. All rights reserved.

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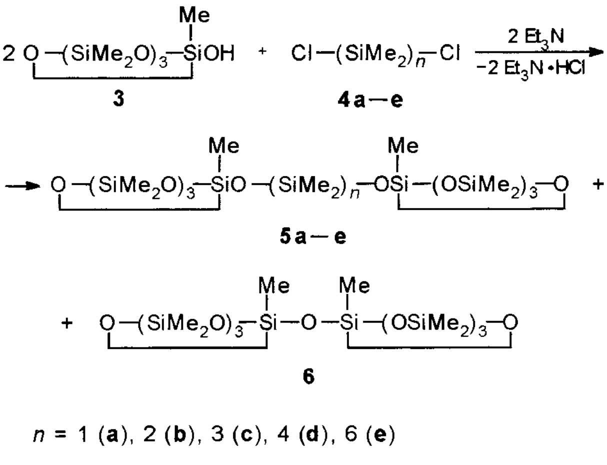
1. Introduction

During the last 10 years, linear permethylpolysilane-siloxanes of formula $-[O(SiMe_2)_k-(OSiMe_2)_m]_n-$ ($k =$ 2–4, 6; $m = 0$–3) have been prepared by heterofunctional copolycondensation of α,ω-dihalopermethyloligosilanes with siloxanediols [1–3], hydrolytic polycondensation of α,ω-dichloropermethyloligosilanes [1,2,4], and cationic ring-opening polymerization of a fully methylated silicon analogues of dioxane, THF and oxepane, i.e. octamethyl-1,4-dioxa-2,3,5,6-tetrasilacyclohexane [1,4–7], octamethyloxatetrasilacyclopentane [1,4] and dodecamethyloxahexasilacycloheptane [2], respectively. All these polymers have a regular well-defined structure intermediate between polydimethylsilane and polydimethylsiloxane. But till now, permethylated cyclolinear polysilane-siloxane of regular structure are unknown. Here we describe the preparation of the first representatives of this new class of compounds, namely α,ω - bis(heptamethylcyclotetrasiloxanyloxy) - oligodimethylsilanes.

2. Results and discussion

Previously, α,ω-bis[permethylcyclotri(tetra)siloxy]-oligodimethylsiloxanes (**1**) [9] and α,ω-bis[permethylcyclopenta(hexa)silanyl]oligodimethylsillanes (**2**) [10–14], having the so-called 'dumbbell-like' structures [8], have been prepared. Such compounds contain only the siloxane or silylene units, respectively.

In this work, mixed silane-siloxane compounds, having similar structure, namely, α,ω-bis(heptamethylcyclotetrasiloxanyloxy)oligodimethylsilanes (**5**) were synthesized by heterofunctional condensation of hydroxyheptamethylcyclotetrasiloxane (**3**) with α,ω-dichlorooligosilanes $Cl(SiMe_2)_nCl$ ($n = 1$–4, 6) (**4**):



n = 1 (**a**), 2 (**b**), 3 (**c**), 4 (**d**), 6 (**e**)

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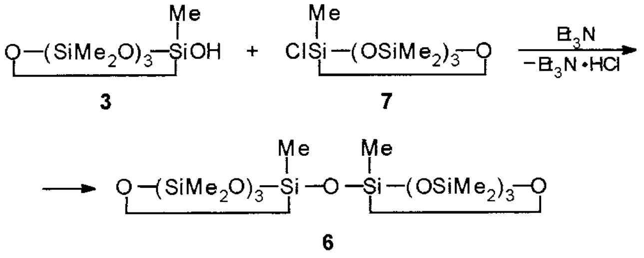
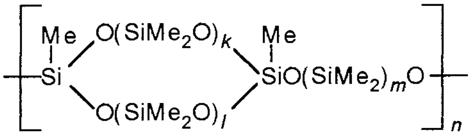
The reaction was carried out in anhydrous diethyl ether at temperatures from −5 to −10°C in the presence of triethylamine as an acceptor of HCl. The yields of **5a**–**e** were 40–66%. The analysis of the reaction products by GC/MS was shown that in all cases under study, bis(heptamethylcyclotetrasiloxanyl)oxide (**6**) was formed along with **5** in a small yield (up to 5%). Bisoxide **6** was also synthesized by condensation of **3** with chloroheptamethylcyclotetrasiloxane (**7**):



5b–**e** are intermediates between compounds **1** and **2**, which have exclusively siloxane or silane structures, respectively. **5b**–**d** are pale-yellow viscous liquids (more viscous then **1**), **5e** is crystalline compound having low melting point, whereas **2** is a high melting crystalline compound. Compounds **5** are stable in air and soluble in common organic solvents, such as benzene, toluene, *n*-alkanes and ethers. The structures of **5** were confirmed by spectral methods (the data of GC/MS and ^{29}Si-NMR, IR, UV spectroscopy are given in Section 3).

Compounds **5** are interesting model compounds of cyclolinear permethylpolysilane-siloxanes:



3. Experimental

3.1. General comments

All reactions were carried out under an atmosphere of dry nitrogen. Diethyl ether was dried with sodium/benzophenone and distilled under nitrogen prior to use. Triethylamine was distilled over sodium hydroxide pellets before use. Compounds **3**, **4b**–**e** and **7** were prepared as described in refs. [3,9]. ^{29}Si-NMR spectra (79.46 MHz) were recorded on a Bruker WP-400 SY spectrometer at 20°C. Samples were dissolved in CCl_4:$CDCl_3$ (9:1, v/v) and Me_4Si was used as internal standard. IR and UV spectra were obtained on a Specord M-80 and Specord M-40 spectrophotometers, respectively. GC/MS measurements were performed on a Kratos-MS-890 instrument (a 15 m × 0.32 mm capillary column; SE-30 liquid phase; helium as the carrier gas; the temperature was programmed to rise from 30 to 270°C at a rate of 12° min^{-1}; ionization energy was 70 eV). All reactions were monitored by GLC. The GLC analysis was carried out on a 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° min^{-1}; helium as the carrier gas). Elemental analysis were performed by the Laboratory of Microanalysis of the Institute of Organoelement Compounds.

3.2. General procedure for the preparation of α,ω-bis(heptamethylcyclotetrasiloxanyloxy)oligodimethylsilanes (5)

In a general reaction pattern, a solution of **4** in ether was added dropwise to a solution of **3** and Et_3N in ether at −5 to −10°C. The reaction mixture was stirred at −5 to −10°C for 2 h and then at room temperature for 20 h. The $Et_3N·HCl$ residue was filtered off. The ether solution was washed three times with equal volumes of water and dried over anhydrous Na_2SO_4. After removal of the solvent the fractionated distillation of the liquid residue under reduced pressure afforded of desired **5**.

3.2.1. Bis(heptamethylcyclotetrasiloxanyloxy)-dimethylsilane (5a)

In the same way as described above, the reaction of 0.85 g (6.7 mmol) **4a** with 4.0 g (13.4 mmol) **3** and 1.36 g (13.4 mmol) Et_3N yields 2.91 g (66.5%) of **5a**.

B.p.: 133–134°C (3 Torr). Anal. Calc. for $C_{16}H_{48}O_{10}Si_9$: C, 29.42; H, 7.41; Si, 38.69%. Found: C, 29.15; H, 7.26; Si, 38.37%. ^{29}Si-NMR: δ −19.05 (OSiO*Si*OSiO), −19.24 [O*Si*OSiMe(O–)$_2$], −21.15 [Me(–O)$_2$SiO*Si*OSi(O–)$_2$Me], −65.03 [MeSi(O–)$_3$] ppm. GC/MS: *m/e* (rel. int., %) 637 (M^+ − Me, 21), 549 ($Si_8O_{10}Me_{11}$, 10), 533 ($Si_8O_{10}Me_4CH_2$, 10), 475 ($Si_7O_9Me_9$, 22), 461 ($Si_7O_{10}Me_7$, 45), 401 ($Si_6O_8Me_7$, 10), 355 ($Si_5O_5Me_9$, 24), 341 ($Si_5O_6Me_7$, 14), 327 ($Si_5O_7Me_5$, 11), 281 ($Si_4O_4Me_7$, 52), 221 ($Si_3O_2Me_7$, 36), 207 ($Si_3O_3Me_5$, 18), 147 (Si_2OMe_5, 60), 73 ($SiMe_3$, 100). IR (CsI): ν 2960, 2896 (C–H); 1262, 859, 808, 762 (Si–Me); 1080, 1039 (Si–O–Si) cm^{-1}.

3.2.2. 1,2-Bis(heptamethylcyclotetrasiloxanyloxy)-tetramethyldisilane (5b)

In the same way as described above, the reaction of 0.63 g (3.35 mmol) **4b** with 2.0 g (6.7 mmol) **3** and 0.68 (6.7 mmol) Et_3N produced 1.54 g (64.7%) of **5b**.

B.p.: 121–122°C (0.01 Torr). Anal. Calc. for $C_{18}H_{54}O_{10}Si_{10}$: C, 30.39; H, 7.65; Si, 39.48%. Found: C, 30.79; H, 7.44; Si, 38.97%. ^{29}Si-NMR: δ 1.43 (OSiSiO), −18.94 (O*Si*O*Si*OSiO), −19.23 [OSiOSiMe(O–)$_2$],

−63.74 [MeSi(O–)$_3$] ppm. GC/MS: *m*/*e* (rel. int., %) 695 (M$^+$ − Me, 0.3), 549 ($Si_8O_{10}Me_{11}$, 1), 473 ($Si_7O_7Me_{11}$, 2), 461 ($Si_7O_{10}Me_7$, 4), 413 ($Si_6O_5Me_{11}$, 5), 355 (M$^+$/2, 100), 325 ($Si_5O_5Me_7$, 8), 281 ($Si_4O_4Me_7$, 12), 267 ($Si_4O_5Me_5$, 31), 207 ($Si_3O_3Me_5$, 7), 147 (Si_2OMe_5, 19), 73 ($SiMe_3$, 77). UV: λ_{max} ~ 199 nm. IR (KBr): *v* 2964, 2904 (C–H); 1262, 854, 844, 806 (Si–Me); 1082, 1055 (Si–O–Si) cm^{-1}.

*3.2.3. 1,3-Bis(heptamethylcyclotetrasiloxanyloxy)-hexamethyltrisilane (**5c**)*

In the same way as described above, the reaction of 1.64 g (6.7 mmol) **4c** with 4.0 g (13.4 mmol) **3** and 1.36 g (13.4 mmol) Et_3N gave 3.08 g (59.7%) of **5c**.

B.p.: 132–133°C (0.007 Torr). Anal. Calc. for $C_{20}H_{60}O_{10}Si_{11}$: C, 31.21; H, 7.86; Si, 40.14%. Found: C, 31.47; H, 7.97; Si, 40.38%. ^{29}Si-NMR: δ 8.55 (O*Si*Si*Si*O), −19.05 (OSiO*Si*OSiO), −19.44 [O*Si*OSiMe(O–)$_2$], −52.71 (OSi*Si*SiO), −64.18 [MeSi(O–)$_3$] ppm. GC/MS: *m*/*e* (rel. int., %) 753 (M$^+$ − Me, 0.2), 549 ($Si_8O_{10}Me_{11}$, 0.4), 471 ($Si_7O_5Me_{13}$, 3), 413 ($Si_6O_5Me_{11}$, 18), 383 ($Si_6O_5Me_9$, 4), 355 ($Si_5O_5Me_9$, 100), 325 ($Si_5O_5Me_7$, 16), 281 ($Si_4O_4Me_7$, 13), 267 ($Si_4O_5Me_5$, 53), 207 ($Si_3O_3Me_5$, 31), 147 (Si_2OMe_5, 17), 73 ($SiMe_3$, 73). UV: λ_{max} 221 nm. IR (CsI): *v* 2962, 2902 (C–H); 1262, 856, 811, 777 (Si–Me); 1082, 1057 (Si–O–Si) cm^{-1}.

*3.2.4. 1,4-Bis(heptamethylcyclotetrasiloxanyloxy)-octamethyltetrasilane (**5d**)*

In the same way as described above, the reaction of 1.91 g (6.3 mmol) **4d** with 3.75 g (12.6 mmol) **3** and 1.27 g (12.6 mmol) Et_3N yields 3.1 g (59.6%) of **5d**.

B.p.: 158–160°C (0.008 Torr). Anal. Calc. for $C_{22}H_{66}O_{10}Si_{12}$: C, 31.92; H, 8.04; Si, 40.71%. Found: C, 32.06; H, 8.12; Si, 40.21%. ^{29}Si-NMR: δ 9.45 (O*Si*Si$_2$*Si*O), −19.04 (OSiO*Si*OSiO), −19.46 [O*Si*OSiMe(O–)$_2$], −47.63 (OSi*SiSi*SiO), −64.20 [MeSi(O–)$_3$] ppm. GC/MS: *m*/*e* (rel. int., %) 811 (M$^+$ − Me, 0.2), 471 ($Si_7O_5Me_{13}$, 15), 413 (M$^+$/2, 3), 383 ($Si_6O_5Me_9$, 5), 355 ($Si_5O_5Me_9$, 24), 341 ($Si_5O_6Me_7$, 12), 325 ($Si_5O_5Me_7$, 11), 281 ($Si_4O_4Me_7$, 12), 267 ($Si_4O_5Me_5$, 45), 249 ($Si_4O_2Me_7$, 11), 207 ($Si_3O_3Me_5$, 17), 147 (Si_2OMe_5, 25), 117 (Si_2OMe_3, 17), 73 ($SiMe_3$, 100). UV: λ_{max} 236.5 nm. IR (KBr): *v* 2958, 2900 (C–H), 1259, 849, 806 (Si–Me), 1071, 1056 (Si–O–Si) cm^{-1}.

*3.2.5. 1,6-Bis(heptamethylcyclotetrasiloxanyloxy)-dodecamethylhexasilane (**5e**)*

In the same way as described above, the reaction of 1.62 g (3.85 mmol) **4e** with 2.30 g (7.7 mmol) **3** and 0.78 g (7.7 mmol) Et_3N gave 2.0 g (46.8%) of **5e** (solidifies at ambient temperature). Recrystallization from THF:EtOH (1:7, v/v) afforded 1.7 g (39.8%) of white crystals of **5e**.

B.p.: 197–198°C (0.007 Torr), m.p.: 37–38°C. Anal. Calc. for $C_{26}H_{78}O_{10}Si_{14}$: C, 33.08; H, 8.33; Si, 41.65%. Found: C, 33.61; H, 8.42; Si, 41.17%. ^{29}Si-NMR: δ 9.14 (O*Si*Si$_4$*Si*O), −19.16 (OSiO*Si*OSiO), −19.60 [O*Si*OSiMe(O–)$_2$], −40.22 (OSi$_2$*SiSi*Si$_2$O), −45.44 (OSi*Si*Si$_2$*Si*SiO), −64.35 [MeSi(O–)$_3$] ppm. GC/MS: *m*/*e* (rel. int., %) 927 (M$^+$ − Me, 0.3), 587 ($Si_9O_5Me_{17}$, 0.4), 471 (M$^+$/2, 41), 413 ($Si_6O_5Me_{11}$, 4), 383 ($Si_6O_5Me_9$, 5), 355 ($Si_5O_5Me_9$, 22), 325 ($Si_5O_5Me_7$, 9), 281 ($Si_4O_4Me_7$, 20), 267 ($Si_4O_5Me_5$, 29), 249 ($Si_4O_2Me_7$, 19), 207 ($Si_3O_3Me_5$, 14), 147 (Si_2OMe_5, 27), 117 (Si_2OMe_3, 14), 73 ($SiMe_3$, 100). UV: λ_{max} 260 nm. IR (KBr): *v* 2962, 2894 (C–H); 1260, 852, 808, 767 (Si–Me), 1079, 1055 (Si–O–Si) cm^{-1}.

*3.2.6. Bis(heptamethylcyclotetrasiloxanyl)oxide (**6**)*

6 was prepared from 5.85 g (18.4 mmol) **7**, 5.70 g (18.4 mmol) **3** and 1.87 g (18.4 mmol) Et_3N according to the general procedure outlined for the preparation of **5**.

Yield: 7.78 g (73.0%). B.p.: 112°C (2 Torr). Anal. Calc. for $C_{14}H_{42}O_9Si_8$: C, 29.03; H, 7.31; Si, 38.79%. Found: C, 29.35; H, 7.43; Si, 38.47%. ^{29}Si-NMR: δ −19.04 [O*Si*OSiMe(O–)$_2$], −65.42 [MeSi(O–)$_3$] ppm. GC/MS: *m*/*e* (rel. int., %) 563 (M$^+$ − Me, 89), 475 ($Si_7O_9Me_9$, 100), 459 ($Si_7O_9Me_7CH_2$, 48), 401 ($Si_6O_8Me_7$, 44), 387 ($Si_6O_9Me_5$, 7), 341 ($Si_5O_6Me_7$, 19), 327 ($Si_5O_7Me_5$, 9), 281 ($Si_4O_4Me_7$, 7), 221 ($Si_3O_2Me_7$, 4), 207 ($Si_3O_3Me_5$, 7), 147 (Si_2OMe_5, 34), 73 ($SiMe_3$, 51). IR (CsI): *v* 2964, 2900 (C–H); 1261, 854, 809, 770 (Si–Me), 1084, 1048 (Si–O–Si) cm^{-1}.

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References

[1] J. Chojnowski, J. Kurjata, S. Rubinsztajn, M. Ścibiorek, in: A.R. Bassindale, P.P. Gaspar (Eds.), Frontiers of Organosilicon Chemistry, The Royal Society of Chemistry, Cambridge, 1991, p. 70.

[2] J. Chojnowski, W. Fortuniak, N. Gladkova, M. Pluta, M. Ścibiorek, B. Zavin, J. Inorg. Organomet. Polym. 5 (1995) 7.

[3] A.I. Chernyavskii, B.G. Zavin, Izv. Akad. Nauk, Ser. Khim. (1997) 1513 [Russ. Chem. Bull. 46 (1997) 1449 (English translation)].

[4] J. Chojnowski, J. Kurjata, S. Rubinsztajn, Makromol. Chem. Rapid Commun. 9 (1988) 469.

[5] J. Kurjata, J. Chojnowski, Makromol. Chem. 194 (1993) 3271.

[6] J. Chojnowski, J. Kurjata, Macromolecules 27 (1994) 2302.

[7] J. Chojnowski, J. Kurjata, S. Rubinsztajn, M. Ścibiorek, M. Zeldin, J. Inorg. Organomet. Polym. 2 (1992) 387.

[8] A.A. Zhdanov, M.M. Levitsky, in: Uspekhi v oblasti sinteza elementoorganicheskikh polimerov [Progress in the Synthesis of Organoelement Polymers], Nauka, Moscow, 1988, p. 192 (in Russian).
[9] K.A. Andrianov, A.I. Chernyavskii, N.N. Makarova, Izv. Akad. Nauk SSSR, Ser. Khim. (1979) 1835 [Bull. Acad. Sci. USSR Div. Chem. Sci. 28 (1979) (English translation)].
[10] M. Ishikawa, M. Watanabe, J. Iyoda, H. Ikeda, M. Kumada, Organometallics 1 (1982) 317.
[11] F.K. Mitter, G. Pollhammer, E. Hengge, J. Organomet. Chem. 314 (1986) 1.
[12] F.K. Mitter, E. Hengge, J. Organomet. Chem. 332 (1987) 47.
[13] E. Hengge, P.K. Jenkner, Z. Anorg. Allg. Chem. 560 (1988) 27.
[14] E. Hengge, P. Gspaltl, A. Spielberger, J. Organomet. Chem. 479 (1994) 165.