

Synthesis of 2,2,4,4,6,6,8,8-Octakis(3-hydroxypropyl)cyclotetrasiloxane

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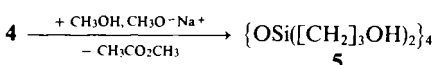
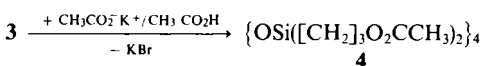
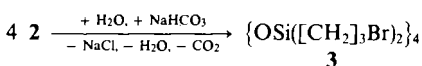
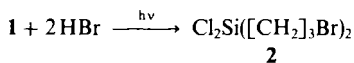
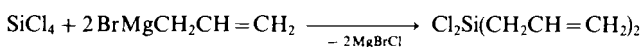
Hydrophilic polysiloxanes are of great interest for contact-lens materials. 2,2,4,4,6,6,8,8-Octakis(3-hydroxypropyl)cyclotetrasiloxane was therefore synthesized.

The initial strategy involved a double Grignard reaction of the 3-hydroxypropyl group (protected as its trimethylsilyl ether) with SiCl_4 yielding dichlorobis(3-trimethylsilyloxypropyl)silane. This was to be hydrolyzed to the cyclosiloxane, followed by cleavage of the protecting group. However, even the synthesis of the Grignard reagent was unsuccessful, and the corresponding organolithium compound yielded a mixture of di-, tri- and tetrasubstituted products, which could not be separated by fractional distillation. Therefore, the 3-hydroxypropyl-substituted compound was synthesized in a multistep sequence, starting from diallyldichlorosilane¹⁾ (**1**). 2,2,4,4,6,6,8,8-Octaallylcyclotetrasiloxane was obtained by hydrolyzing **1**. The attempt to treat **1** with diborane^{2,3)} followed by peroxhydrolysis in alkaline solution was unsuccessful, and the formation of 1,3-propanediol indicated an Si–C cleavage.

Bis(3-bromopropyl)dichlorosilane (**2**) was formed by the addition of gaseous HBr to **1** under irradiation⁴⁾. Hydrolysis⁵⁾ of **2** yielded 2,2,4,4,6,6,8,8-octakis(3-bromopropyl)cyclotetrasiloxane (**3**). Alkaline hydrolysis of **3** was unsuccessful; the reaction with potassium acetate/acetic acid⁶⁾ yielded 2,2,4,4,6,6,8,8-octakis(3-acetoxypropyl)cyclotetrasiloxane (**4**).

Both alkaline and acidic ester hydrolysis were unsuccessful in cleavage of the ester, as also were the reducing conditions with LiAlH_4 by Kropf et al.⁷⁾ An alcoholysis reaction by Henecka et al.⁸⁾, using methanol/sodium methoxide, yielded 2,2,4,4,6,6,8,8-octakis(3-hydroxypropyl)cyclotetrasiloxane (**5**), which was dried for 3 days under a high vacuum.

5 is the first member of a new class of compounds, the hydrophilic diorganofunctional cyclosiloxanes. **5** shows an uncommon solubility – miscible in any proportion with water and with methanol – insoluble in acetone, chloroform, diethyl ether, and other typical organic solvents. Polymerization by a ring-opening reaction with H_2SO_4 or with ammonium peroxodisulfate did not occur.



Experimental

General: ¹H-NMR: Bruker AM 270 SY. – IR: Perkin-Elmer 580 B. – MS: Varian MAT 711. – **1** was synthesized following a procedure by Scott et al.¹⁾ in a Grignard reaction proceeding from allyl bromide and SiCl_4 in absolute diethyl ether.

Bis(3-bromopropyl)dichlorosilane (2): 9.5 g (0.05 mol) of **1** was placed in a 100-ml Erlenmeyer quartz flask. Gaseous HBr was introduced for 40 min under irradiation with a quartz mercury-vapour lamp⁴⁾ ($\lambda_{\text{max}} = 366, 546, \text{ and } 577 \text{ nm}$). The flask was cooled in an ice-bath. The reaction was followed by ¹H NMR. The solution was then distilled under high vacuum over a spinning band column (30 cm), b. p. 98°C/1 Pa; yield 14.3 g (83%). – IR (film): $\tilde{\nu} = 3020 \text{ cm}^{-1}$ (w, CH_2Br), 2970–2860 (s, CH_2), 1440 (m, CH_2), 1410 (w, CH_2), 770–700 (s, C–Br; w, CH_2). – ¹H NMR (CDCl_3 , 270 MHz): $\delta = 1.30$ (q, 2H, SiCH_2), 2.07 (m, 2H, $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Br}$), 3.45 (t, 2H, CH_2Br). – MS: m/z (%) = 219 (99) [$\text{M}^+ - [\text{CH}_2]_3\text{Br}$], 177 (100) [$\text{M}^+ - [\text{CH}_2]_3\text{Br} - [\text{CH}_2]_3$].

$\text{C}_6\text{H}_{12}\text{Br}_2\text{Cl}_2\text{Si}$ (343.0) Calcd. C 21.01 H 3.53

Found C 20.64 H 3.62

2,2,4,4,6,6,8,8-Octakis(3-bromopropyl)cyclotetrasiloxane (3): 23.0 g (1.300 mol) of **2** and 30.0 g (0.360 mol) of NaHCO_3 in 150 ml of diethyl ether were placed in a 250-ml round-bottomed flask equipped with a reflux condenser, dropping funnel, and thermometer. 16.0 g (0.047 mol) of **2** was added dropwise, with stirring, at –5 to 0°C. After gas generation had ceased, the mixture was stirred at room temp. for 30 min, filtered, and the organic layer dried with Na_2SO_4 . After evaporating the solvent, a clear viscous liquid was obtained; yield 12.5 g (84%). – ¹H NMR ($[\text{D}_6]$ acetone, 270 MHz): $\delta = 0.83$ (m, 2H, SiCH_2), 1.9 (m, 2H, $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Br}$), 3.5 (m, 2H, CH_2Br).

$\text{C}_{24}\text{H}_{48}\text{Br}_8\text{O}_4\text{Si}_4$ (1152.3) Calcd. C 25.02 H 4.20

Found C 23.83 H 4.17

2,2,4,4,6,6,8,8-Octakis(3-acetoxypropyl)cyclotetrasiloxane (4): A mixture of 20.0 g (0.200 mol) of potassium acetate in 30 ml of acetic acid was heated to reflux, and 15.3 g (0.013 mol) of **3**, dissolved in 20 ml of acetic acid, was added. After heating the mixture for 24 h at reflux, it was filtered under vacuum and the solvent evaporated. The residue was dissolved in diethyl ether. After filtration, the residue was washed with diethyl ether (3 × 25 ml). The solvent was evaporated, and the syrupy oil was dried under high vacuum for 2 d; yield 10.4 g (81%). – IR (film): $\tilde{\nu} = 2960 - 2900 \text{ cm}^{-1}$ (s, CH_2 , CH_3), 1750–1730 (s, C=O), 1440 (m, CH_2 , CH_3), 1415 (w, CH_2), 1390–1370 (m, CH_3 ; m, C–O), 1090–1070 (s, Si–O–Si), 700 (m, CH_2). – ¹H NMR ($\text{C}_2\text{D}_5\text{OD}$, 270 MHz): $\delta = 0.66$ (q, 2H, SiCH_2), 1.71 (q, 2H, $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{OH}$), 2.04 (s, 2H, $\text{CH}_2\text{O}_2\text{C}$), 4.04 (t, 3H, O_2CCH_3). – MS: m/z (%) = 884 (23) [$\text{M}^+ - [\text{CH}_2]_3\text{O}_2\text{CCH}_3$], 740 (10) [$\text{M}^+ - [\text{CH}_2]_3\text{O}_2\text{CCH}_3 - \text{OCCH}_3$], 596 (12) [$\text{M}^+ - 3[\text{CH}_2]_3\text{O}_2\text{CCH}_3 - 2\text{OCCH}_3$], 553 (32) [$\text{M}^+ - 3[\text{CH}_2]_3\text{O}_2\text{CCH}_3 - 3\text{OCCH}_3$], 511 (15) [$\text{M}^+ - 3[\text{CH}_2]_3\text{O}_2\text{CCH}_3 - 3\text{OCCH}_3 - [\text{CH}_2]_3$], 493 (14) [$\text{M}^+ - 3[\text{CH}_2]_3\text{O}_2\text{CCH}_3 - 3\text{OCCH}_3 -$

$[\text{CH}_2]_3 - \text{H}_2\text{O}$, 452 (26) $[\text{M}^+ - 4 [\text{CH}_2]_3\text{O}_2\text{CCH}_3 - 3 \text{OCCH}_3]$, 451 (81) $[\text{M}^+ - 3 [\text{CH}_2]_3\text{O}_2\text{CCH}_3 - 3 \text{OCCH}_3 - 2 [\text{CH}_2]_3 - \text{H}_2\text{O}]$, 410 (37) $[\text{M}^+ - 4 [\text{CH}_2]_3\text{O}_2\text{CCH}_3 - 3 \text{OCCH}_3 - [\text{CH}_2]_3]$, 409 (100) $[\text{M}^+ - 4 [\text{CH}_2]_3\text{O}_2\text{CCH}_3 - 4 \text{OCCH}_3]$, 367 (44) $[\text{M}^+ - 4 [\text{CH}_2]_3\text{O}_2\text{CCH}_3 - 4 \text{COCH}_3 - [\text{CH}_2]_3]$, 349 (31) $[\text{M}^+ - 4 [\text{CH}_2]_3\text{O}_2\text{CCH}_3 - 4 \text{OCCH}_3 - [\text{CH}_2]_3 - \text{H}_2\text{O}]$, 325 (46) $[\text{M}^+ - 4 [\text{CH}_2]_3\text{O}_2\text{CCH}_3 - 4 \text{OCCH}_3 - 2 [\text{CH}_2]_3]$, 307 (19) $[\text{M}^+ - 4 [\text{CH}_2]_3\text{O}_2\text{CCH}_3 - 4 \text{OCCH}_3 - 2 [\text{CH}_2]_3 - \text{H}_2\text{O}]$.

$\text{C}_{40}\text{H}_{72}\text{O}_{20}\text{Si}_4$ (985.4) Calcd. C 48.76 H 7.37
Found C 46.47 H 7.19

2,2,4,4,6,6,8,8-Octakis(3-hydroxypropyl)cyclotetrasiloxane (5): A methanolic sodium methoxide solution [0.18 g (7.8 mmol) of Na in 20 ml of absol. methanol] was placed in a 100-ml round-bottomed flask equipped with a reflux condenser, dropping funnel, and thermometer, and heated to reflux. 2.63 g (2.7 mmol) of **4**, dissolved in 10 ml of absol. methanol, was added dropwise with stirring. During the addition, the methanol/methyl acetate azeotrope (b.p. 58 to 62°C) was distilled off as it was formed. When the boiling temp. of pure methanol was reached, the residual solvent was evaporated. The residue was mixed with water, neutralized with dil. HCl, and the solvent was evaporated. The residue was extracted with diethyl ether. The residue was filtered and dissolved in methanol. After filtration, the solid was dried for 3 d under high vacuum; yield 1.30 g (74%). — IR (film): $\tilde{\nu} = 3600-3100 \text{ cm}^{-1}$ (s, OH), 2940–2880 (s, CH_2), 1440 (w, CH_2), 1415 (m, CH_2 ; m, OH), 1150–1010 (s, C–OH), 1060 (s, Si–O–Si), 700 (w, CH_2). — ^1H NMR (CD_3OD , 270 MHz): $\delta = 0.64$ (m, 2H, SiCH_2), 1.64 (m, 2H,

$\text{SiCH}_2\text{CH}_2\text{CH}_2\text{OH}$), 3.52 (t, 2H, CH_2OH), 4.85 (s, 1H, OH). — MS: **5** was not thermostable.

$\text{C}_{24}\text{H}_{56}\text{O}_{12}\text{Si}_4$ (529.0) Calcd. C 44.70 H 8.70
Found C 43.08 H 7.98

CAS Registry Numbers

1: 3651-23-8 / 2: 123331-54-4 / 3: 123331-55-5 / 4: 123331-56-6 / 5: 123331-57-7

- ¹⁾ R. E. Scott, K. C. Frisch, *J. Am. Chem. Soc.* **73** (1951) 2599.
- ²⁾ H. C. Brown, G. Zweifel, *Organic Reactions*, vol. 13, p. 1, John Wiley & Sons, Inc., New York 1963.
- ³⁾ H. C. Brown, B. C. Subba Rao, *J. Am. Chem. Soc.* **81** (1959) 6423.
- ⁴⁾ Autorenkollektiv, *Organikum*, 15th, revised edition, p. 623, VEB Deutscher Verlag der Wissenschaften, Berlin 1977.
- ⁵⁾ S. Pawlenko, "Organo-polysiloxane" in *Methoden der organischen Chemie* (Houben-Weyl), 4th, revised edition, vol. 13/5, p. 147, Georg Thieme Verlag, Stuttgart 1980.
- ⁶⁾ J. L. Speier, B. F. Daubert, R. R. Mc Gregor, *J. Am. Chem. Soc.* **71** (1948) 1474.
- ⁷⁾ H. Kropf, J. Thiem, H. Nimz, "Alkohole" in *Methoden der organischen Chemie* (Houben-Weyl), 4th, revised edition, vol. 6/1a/1, p. 272, Georg Thieme Verlag, Stuttgart 1979.
- ⁸⁾ H. Henecka, "Carbonsäureester" in *Methoden der organischen Chemie* (Houben-Weyl), 4th, revised edition, vol. 8, p. 526, Georg Thieme Verlag, Stuttgart 1952.

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