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

Gerhard Koßmehl* and Andrea Fluthwedel

Institut für Organische Chemie der FU Berlin,
Takustraße 3, D-1000 Berlin 33

Received August 11, 1989

Key Words: Cyclotetrasiloxanes, octafunctional, watersoluble

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 diallyldichlorosilane[1] (**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 peroxohydrolysis 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 irradiation[4]. Hydrolysis[5] 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 acid[6] 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.

$$SiCl_4 + 2\,BrMgCH_2CH{=}CH_2 \xrightarrow[-\,2\,MgBrCl]{} \underset{\mathbf{1}}{Cl_2Si(CH_2CH{=}CH_2)_2}$$

$$\mathbf{1} + 2\,HBr \xrightarrow{h\nu} \underset{\mathbf{2}}{Cl_2Si([CH_2]_3Br)_2}$$

$$4\ \mathbf{2} \xrightarrow[-\,NaCl,\ -\,H_2O,\ -\,CO_2]{+\,H_2O,\ +\,NaHCO_3} \underset{\mathbf{3}}{\{OSi([CH_2]_3Br)_2\}_4}$$

$$\mathbf{3} \xrightarrow[-\,KBr]{+\,CH_3CO_2^-K^+/CH_3\,CO_2H} \underset{\mathbf{4}}{\{OSi([CH_2]_3O_2CCH_3)_2\}_4}$$

$$\mathbf{4} \xrightarrow[-\,CH_3CO_2CH_3]{+\,CH_3OH,\,CH_3O^-Na^+} \underset{\mathbf{5}}{\{OSi([CH_2]_3OH)_2\}_4}$$

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 lamp[4] (λ_{max} = 366, 546, and 577 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 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): δ = 1.30 (q, 2H, $SiCH_2$), 2.07 (m, 2H, $SiCH_2CH_2CH_2Br$), 3.45 (t, 2H, CH_2Br). – MS: *m/z* (%) = 219 (99) [M^+ – $[CH_2]_3Br$], 177 (100) [M^+ – $[CH_2]_3Br$ – $[CH_2]_3$].

$C_6H_{12}Br_2Cl_2Si$ (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 ice 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 ([D_6]acetone, 270 MHz): δ = 0.83 (m, 2H, $SiCH_2$), 1.9 (m, 2H, $SiCH_2CH_2CH_2Br$), 3.5 (m, 2H, CH_2Br).

$C_{24}H_{48}Br_8O_4Si_4$ (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 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 (C_2D_5OD, 270 MHz): δ = 0.66 (q, 2H, $SiCH_2$), 1.71 (q, 2H, $SiCH_2CH_2CH_2OH$), 2.04 (s, 2H, CH_2O_2C), 4.04 (t, 3H, O_2CCH_3). – MS: *m/z* (%) = 884 (23) [M^+ – $[CH_2]_3O_2CCH_3$], 740 (10) [M^+ – $[CH_2]_3O_2CCH_3$ – $OCCH_3$], 596 (12) [M^+ – 3 $[CH_2]_3O_2CCH_3$ – 2 $OCCH_3$], 553 (32) [M^+ – 3 $[CH_2]_3O_2CH_3$ – 3 $OCCH_3$], 511 (15) [M^+ – 3 $[CH_2]_3O_2CCH_3$ – 3 $OCCH_3$ – $[CH_2]_3$], 493 (14) [M^+ – 3 $[CH_2]_3O_2CCH_3$ – 3 $OCCH_3$ –

0009–2940/89/1212–2413 $ 02.50/0

$[CH_2]_3 - H_2O]$, 452 (26) $[M^+ - 4\,[CH_2]_3O_2CCH_3 - 3\,OCCH_3]$, 451 (81) $[M^+ - 3\,[CH_2]_3O_2CCH_3 - 3\,OCCH_3, - 2\,[CH_2]_3 - H_2O]$, 410 (37) $[M^+ - 4\,[CH_2]_3O_2CCH_3 - 3\,OCCH_3 - [CH_2]_3]$, 409 (100) $[M^+ - 4\,[CH_2]_3O_2CCH_3 - 4\,OCCH_3]$, 367 (44) $[M^+ - 4\,[CH_2]_3O_2CCH_3 - 4\,COCH_3 - [CH_2]_3]$, 349 (31) $[M^+ - 4\,[CH_2]_3O_2CCH_3 - 4\,OCCH_3 - [CH_2]_3 - H_2O]$, 325 (46) $[M^+ - 4\,[CH_2]_3O_2CCH_3 - 4\,OCCH_3 - 2\,[CH_2]_3]$, 307 (19) $[M^+ - 4\,[CH_2]_3O_2CCH_3 - 4\,OCCH_3 - 2\,[CH_2]_3 - H_2O]$.

$C_{40}H_{72}O_{20}Si_4$ (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 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): δ = 0.64 (m, 2H, $SiCH_2$), 1.64 (m, 2H, $SiCH_2CH_2CH_2OH$), 3.52 (t, 2H, CH_2OH), 4.85 (s, 1H, OH). – MS: **5** was not thermostable.

$C_{24}H_{56}O_{12}Si_4$ (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.

[257/89]

Dieses Heft wurde am 5. Dezember 1989 ausgegeben.

© VCH Verlagsgesellschaft mbH, D-6940 Weinheim, 1989 – Printed in the Federal Republic of Germany.

Verantwortlich für den Inhalt: Prof. Dr. Heinrich Nöth, München (Teil A), Prof. Dr. Henning Hopf, Braunschweig (Teil B). Redaktion: Dr. Robert Temme, Weinheim.

VCH Verlagsgesellschaft mbH (Geschäftsführer: Hans Dirk Köhler), Pappelallee 3, Postfach 101161, D-6940 Weinheim.

Anzeigenleitung: R. J. Roth, Weinheim.

Die Wiedergabe von Gebrauchsnamen, Handelsnamen, Warenbezeichnungen und dgl. in dieser Zeitschrift berechtigt nicht zu der Annahme, daß solche Namen ohne weiteres von jedermann benutzt werden dürfen. Vielmehr handelt es sich häufig um gesetzlich geschützte eingetragene Warenzeichen, auch wenn sie nicht als solche gekennzeichnet sind.

Alle Rechte, insbesondere die der Übersetzung in andere Sprachen, vorbehalten. Kein Teil dieser Zeitschrift darf ohne schriftliche Genehmigung des Verlages in irgendeiner Form – durch Photokopie, Mikrofilm oder irgendein anderes Verfahren – reproduziert oder in eine von Maschinen, insbesondere von Datenverarbeitungsmaschinen verwendbare Sprache übertragen oder übersetzt werden. – All rights reserved (including those of translation into other languages). No part of this issue may be reproduced in any form – by photoprint, microfilm, or any other means – nor transmitted or translated into a machine language without the permission in writing of the publishers. – Von einzelnen Beiträgen oder Teilen von ihnen dürfen nur einzelne Vervielfältigungsstücke für den persönlichen oder sonstigen eigenen Gebrauch hergestellt werden. Die Weitergabe von Vervielfältigungen, gleichgültig zu welchem Zweck sie hergestellt werden, ist eine Urheberrechtsverletzung. – Der Inhalt dieses Heftes wurde sorgfältig erarbeitet. Dennoch übernehmen Autoren, Herausgeber, Redaktion und Verlag für die Richtigkeit von Angaben, Hinweisen und Ratschlägen sowie für eventuelle Druckfehler keine Haftung. – This journal was carefully produced in all its parts. Nevertheless, authors, editors and publisher do not warrant the information contained therein to be free of errors. Readers are advised to keep in mind that statements, data, illustrations, procedural details or other items may inadvertently be inaccurate.

Valid for users in the USA: The appearance of the code at the bottom of the first page of an article in this journal (serial) indicates the copyright owner's consent that copies of the article may be made for personal or internal use, or for the personal or internal use of specific clients. This consent is given on the condition, however, that the copier pay the stated percopy fee through the Copyright Clearance Center, Inc., for copying beyond that permitted by Sections 107 or 108 of the U.S. Copyright Law. This consent does not extend to other kinds of copying, such as copying for general distribution, for advertising or promotional purposes, for creating new collective work, or for resale. For copying from back volumes of this journal see »Permissions to Photo-Copy: Publisher's Fee List« of the CCC.

In der Zeitschrift werden keine Rezensionen veröffentlicht; zur Besprechung eingehende Bücher werden nicht zurückgesandt.

Satz und Druck: Krebs-Gehlen Druckerei, Hemsbach/Bergstraße.
Printed on acid-free paper / Gedruckt auf säurefreiem Papier