Synthesis of Hexasilsesquioxanes Bearing Bulky Substituents: Hexakis((1,1,2-trimethylpropyl)silsesquioxane) and Hexakis(*tert*-butylsilsesquioxane)

Masafumi Unno, Shamsul Bahri Alias, Hitoshi Saito, and Hideyuki Matsumoto*

Department of Applied Chemistry, Faculty of Engineering, Gunma University, Kiryu, Gunma 376, Japan

Received September 15, 1995[⊗]

Summary: The hexasilsesquioxanes $(RSiO_{1.5})_6$ *(**1**, R = 1,1,2-trimethylpropyl; **2**, R = tert-butyl) were synthesized by a new method: condensation of the corresponding silanetriol,* $RSi(OH)_3$*, or 1,1,3,3-tetrahydroxydisiloxane,* $(HO)_2RSiOSiR(OH)_2$*, using dicyclohexylcarbodiimide (DCC) as a dehydrating reagent in DMSO or DMF.*

Introduction

As a continuing study on the synthesis and properties of silicon polyhedral compounds,[1] we have been interested in the construction of a strained spherical silsesquioxane bearing bulky substituents. Most of the previous works on spherical silsesquioxanes have dealt with the synthesis and structure determination of octasilsesquioxanes $(RSiO_{1.5})_8$[2a,b] and related compounds.[2c] For the smaller compounds of the family, hexasilsesquioxanes, no members other than hexakis(cyclohexylsilsesquioxane) and silicates[3] are, however, known. Although the synthesis of hexakis(cyclohexylsilsesquioxane) was first reported in 1965,[4a] its X-ray structure was determined only in 1994 by Molloy and et al.[4c] Their synthetic method was similar to that of the previous reports.[4a,b] Thus an acetone solution of cyclohexyltrichlorosilane was treated with water for 4 months to give hexakis(cyclohexylsilsesquioxane) in 10% yield. As in other cases,[2] synthesis of silsesquioxanes by the hydrolysis of trichlorosilanes is straightforward but requires a long reaction time. Here we report the synthesis of the hexasilsesquioxanes $(RSiO_{1.5})_6$ (**1**, R = 1,1,2-trimethylpropyl, denoted Thex or thexyl hereafter; **2**, R = *tert*-butyl) with shorter reaction time and higher yield. The following new method is presented: condensation of the corresponding silanetriols or 1,1,3,3-tetrahydroxydisiloxane using dicyclohexylcarbodiimide (DCC) as a dehydration reagent.

Results and Discussion

Usually with bulky substituents, silanetriol and 1,1,3,3-tetrahydroxydisiloxane are stable to condensation and can be isolated.[5−7] So far, the crystal structures of cyclohexylsilanetriol,[5a] $(Me_3Si)_3CSi(OH)_3$,[5b] $(Me_3Si)_3SiSi(OH)_3$,[5b] *t*-$BuSi(OH)_3$,[6] and $(HO)_2(t\text{-}Bu)SiOSi(t\text{-}Bu)(OH)_2$[7] have been reported. In view of these preceding results, we have attempted to prepare hexasilsesquioxanes by dehydrative condensation of the corresponding silanetriol or tetrahydroxydisiloxane. Preparation of $ThexSi(OH)_3$ (**3**) was effected by following the procedure previously reported by Takiguchi.[8] Thus, by reaction of $ThexSiCl_3$ with aniline and water, **3** was obtained in 64% yield. Tetrahydroxydisiloxane $(HO)_2ThexSiOSiThex(OH)_2$ (**4**) was also prepared from $ThexSiCl_3$ using the method of Sommer and Tyler.[9] The reaction of $ThexSiCl_3$ with KOH/SiO_2 in EtOH gave **4** in 47% yield. The identification of **3** and **4** was made by spectroscopic methods (^1H, ^{13}C, and ^{29}Si NMR, IR, and MS). Both **3** and **4** are remarkably stable and can be handled without problems. They show good solubility in dimethyl sulfoxide (DMSO) and dimethylformamide (DMF). Preparation and identification of *t*-$BuSi(OH)_3$ (**5**) and $(HO)_2(t\text{-}Bu)SiOSi(t\text{-}Bu)(OH)_2$ (**6**) were accomplished by following the methods of Roesky et al.[6] and Lickiss et al.[7]

For the synthesis of silsesquioxanes, dicyclohexylcarbodiimide (DCC) was used as a dehydrating reagent. We used DMSO or DMF as solvent because of the good solubility of the starting silanols. This procedure required slightly forcing conditions, but the reaction was complete in several days. Thus after 72 h at 120 °C, **3** reacted with DCC in DMSO to give hexakis(thexylsilsesquioxane) ($Thex_6Si_6O_9$, **1**) in 41% yield. Purification of **1** was easily effected by the workup as follows. The reaction mixture was poured in hexane and water and separated to remove DMSO, remaining DCC, and dicyclohexylurea. Then the organic phase was concentrated and triturated from acetone to give pure **1**. The other fractions of the workup process were carefully analyzed, and only incompletely condensed silanols were observed. In DMF, **1** was obtained in 34% yield. A similar reaction occurred with **4**, and **1** was obtained in 38% yield in DMSO and 38% yield in DMF. With *tert*-butyl-substituted compounds, the reaction proceeded in like manner and the desired hexakis(*tert*-butylsilsesquioxane) ($t\text{-}Bu_6Si_6O_9$, **2**) was obtained in 26% yield from **5** and 25% yield from **6**. As in the case of **1**, no other silsesquioxanes (T_8 or T_{10}) were obtained. The reaction pathway is shown in Scheme 1.

[⊗] Abstract published in *Advance ACS Abstracts,* March 15, 1996.

[1] (a) Matsumoto, H.; Higuchi, K.; Kyushin, S.; Goto, M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1354. (b) Unno, M.; Higuchi, K.; Ida, M.; Shioyama, H.; Kyushin, S.; Matsumoto, H.; Goto, M. *Organometallics* **1994**, *13*, 4633. (c) Unno, M.; Shioyama, H.; Ida, M.; Matsumoto, H. *Organometallics* **1995**, *14*, 4004.

[2] (a) Dittmar, U.; Hendan, B. J.; Floerke, U.; Marsmann, H. C. *J. Organomet. Chem.* **1995**, *489*, 185 and references cited therein. (b) Baney, R. H.; Itoh, M.; Sakakibara, A.; Suzuki, T. *Chem. Rev.* **1995**, *95*, 1409. (c) Feher, F. J.; Rahimian, K.; Budzichowski, T. A.; Ziller, Z. W. *Organometallics* **1995**, *14*, 3920 and references cited therein.

[3] (a) Smolin, Y. I. *Kristallografiya* **1970**, *15*, 31. (b) Smolin, Y. I.; Shepelev, Y. F.; Ershov, A. S.; Hoebbel, D.; Wieker, W. *Kristallografiya* **1984**, *29*, 712. (c) Hoebbel, D.; Engelhardt, A.; Samoson, A.; Ujszaszy, K.; Smolin, Y. I. *Z. Anorg. Allg. Chem.* **1987**, *552*, 236.

[4] (a) Brown, J. F.; Vogt, L. H. *J. Am. Chem. Soc.* **1965**, *87*, 4313. (b) Feher, F. J.; Newman, D. A.; Walzer, J. F. *J. Am. Chem. Soc.* **1989**, *111*, 1741. (c) Behbehani, H.; Brisdon, B. J.; Mahon, M. F.; Molloy, K. C. *J. Organomet. Chem.* **1994**, *469*, 19.

[5] (a) Ishida, H.; Koenig, J. L.; Gardner, K. C. *J. Chem. Phys.* **1982**, *77*, 5748. (b) Al-Juaid, S. S.; Buttrus, N. H.; Damja, R. I.; Derouiche, Y.; Eaborn, C.; Hitchcock, P. B.; Lickiss, P. D. *J. Organomet. Chem.* **1989**, *371*, 287 and references cited therein.

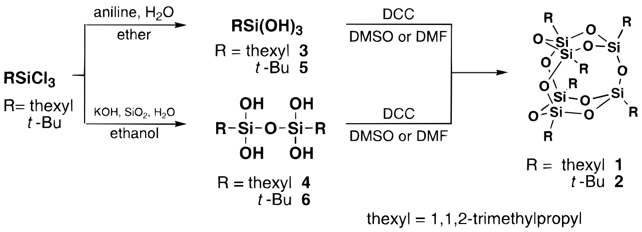
[6] Winkhofer, N.; Roesky, H. R.; Noltemeyer, M.; Robinson, W. T. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 599.

[7] Lickiss, P. D.; Litster, S. A.; Redhouse, A. D.; Wisener, C. J. *J. Chem. Soc., Chem. Commun.* **1991**, 173.

[8] Takiguchi, T. *J. Am. Chem. Soc.* **1959**, *81*, 2359.

[9] Sommer, L. H.; Tyler, L. J. *J. Am. Chem. Soc.* **1954**, *76*, 1030.

Scheme 1



The ^{29}Si NMR spectra of **1** and **2** show single peaks, indicating a highly symmetrical structure. Chemical shifts were −55.1 ppm for **1** and −54.3 ppm for **2**; both values are in agreement with that of hexakis(cyclohexylsilsesquioxane) (−56.2 ppm, ref 3b). In addition, supporting the symmetrical structures, the ^{1}H and ^{13}C NMR spectra show only one kind of substituent on Si is present. Finally, the mass spectra indicate that these compounds are hexasilsesquioxanes (see Experimental Section). The framework of **1** was also confirmed by X-ray crystallography.[10]

In summary, a new synthetic method for the preparation of cage polysiloxanes utilizing dicyclohexylcarbodiimide was demonstrated. This method opens a new route to more controlled synthesis of cage siloxanes.

Experimental Section

Fourier transform nuclear magnetic resonance spectra were obtained by a JEOL Model α-500 (^{1}H at 500.00 MHz, ^{13}C at 125.65 MHz, and ^{29}Si at 99.25 MHz). Chemical shifts are reported as δ units (ppm) relative to $SiMe_4$, and residual solvents peaks were used for standards. For ^{29}Si NMR, $SiMe_4$ was used as an external standard. EI mass spectrometry was performed with a JEOL JMS-D300. Infrared spectra were measured with a JASCO A-102 spectrometer, and polystyrene film was used for the standard.

Preparation of (1,1,2-Trimethylpropyl)silanetriol (3). Thexyltrichlorosilane[11] (12 g, 55 mmol) in ether (100 mL) was added dropwise to a vigorously stirred emulsion of water (3.2 mL, 0.18 mol) and aniline (17 mL, 0.18 mol) in ether (200 mL) at 0 °C. The mixture was then stirred for 12 h at room temperature. Warm hexane (10 mL) was added, and the mixture was filtered rapidly through a glass filter. The solid obtained from concentration of the filtrate was recrystallized from acetone to give **3** (5.8 g, 64%).

3: colorless crystals; mp 142 °C (sublimed), 165−168 °C (sealed capillary); ^{1}H NMR (DMSO-d_6) δ 0.81 (s, 6H), 0.84 (d, 6H, J = 6.7 Hz), 1.55 (sept, 1H, J = 6.7 Hz), 5.66 (s, 3H); ^{13}C NMR (DMSO-d_6) δ 18.7, 21.2, 24.0, 33.8; ^{29}Si NMR (DMSO-d_6) δ_{Si} −42.4; IR (KBr) ν 3100, 2950, 1470, 1370, 1100, 840 cm^{-1}; MS (70 eV) m/z 164 (M$^+$, 15) 79 (100). Anal. Calcd for $C_6H_{16}SiO_3$: C, 43.87; H, 9.82. Found: C, 43.56; H, 9.86%.

Preparation of 1,3-Bis(1,1,2-trimethylpropyl)-1,1,3,3-tetrahydroxydisiloxane (4). Thexyltrichlorosilane (4.0 g, 18 mmol) was added dropwise to a mixture of ethanol (58 mL), SiO_2 (8.3 g), KOH (50 mg, 0.9 mmol), and water (3 mL) over 45 min at room temperature. The reaction mixture was then heated at reflux for 24 h. Ether was added to the mixture. After filtration, the filtrate was washed with water and the aqueous layer was extracted three times with ether. The combined organic phase was dried and evaporated to give a white solid that was recrystallized from 2-butanone to give **4** (yield 1.3 g, 47%).

4: colorless crystals; mp 164 °C (sublimed), 193−197 °C (sealed capillary); ^{1}H NMR (DMSO-d_6) δ 0.83 (s, 12H), 0.85 (d, J = 6.9 Hz, 12H), 1.62 (sept, J = 6.9 Hz, 2H), 5.63 (s, 4H); ^{13}C NMR (DMSO-d_6) δ 18.6, 20.9, 23.9, 33.4; ^{29}Si NMR (DMSO-d_6) δ_{Si} −51.2; IR (KBr) ν 3250, 2875, 1465, 1385, 1150, 840 cm^{-1}; MS (70 eV) m/z 225 (M$^+$ − thexyl, 38), 155 (100). Anal. Calcd for $C_{12}H_{30}Si_2O_5$: C, 46.41; H, 9.76. Found: C, 46.08; H, 9.73%.

Synthesis of Hexakis((1,1,2-trimethylpropyl)silsesquioxane) (1) (General Procedure). In a two-necked flask were placed **3** (0.16 g, 1.0 mmol), DCC (0.69 g, 3.3 mmol), and DMSO (5 mL), and the solution was heated to 120 °C for 72 h. Benzene (5 mL) was added to the mixture, and the resulting dicyclohexylurea was removed by filtration. The filtrate was washed with water (20 mL), and the aqueous phase was extracted three times with hexane. The combined organic phase was dried and evaporated. The resulting semisolid was triturated with 5 mL of acetone to give **1** (yield 57 mg, 41%). All the other fractions were concentrated and analyzed; MS showed peaks in the range 0−280 and no molecular peaks more than 300, and NMR and IR spectra indicated that Si−OH groups were included. The structures of these compounds were not further examined.

1: colorless crystals; mp 285−290 °C; ^{1}H NMR (C_6D_6) δ 1.06 (d, 36H, J = 7.1 Hz), 1.14 (s, 36H), 1.82 (sept, 6H, J = 7.1 Hz); ^{13}C NMR (C_6D_6) δ 18.8, 20.8, 24.9, 34.7; ^{29}Si NMR (C_6D_6) δ_{Si} −55.1; IR (KBr) ν 2850, 1460, 1380, 1025 cm^{-1}; MS (70 eV) m/z 822 (M$^+$, 6), 84 (100). Anal. Calcd for $C_{36}H_{78}Si_6O_9$: C, 52.50; H, 9.56. Found: C, 52.23; H, 9.48%.

Syntheses from **3** in DMF, from **4** in DMSO, and from **4** in DMF were carried out in a similar manner.

Synthesis of Hexakis(*tert*-butylsilsesquioxane) (2) (General Procedure). Into a two-necked flask was charged **6** (0.25 g, 1.0 mmol), DCC (0.62 g, 3.0 mmol), and DMSO (5 mL), and the solution was heated to 130 °C for 72 h. The reaction mixture was poured in hexane and water and separated. The organic phase was washed three times with water to remove the remained dicyclohexylurea and DMSO and then dried and evaporated, and the resulting semisolid (0.17 g) was triturated with 5 mL of acetone to give **2** (yield 54 mg, 25%). After filtration of **2**, the filtrate was concentrated. The aqueous layer was extracted with CH_2Cl_2 and concentrated. These fractions were analyzed, and the results (MS, NMR, IR) were similar as in the case of **1**.

2: colorless prisms; mp >320 °C; ^{1}H NMR (C_6D_6) δ 1.22 (s, 54H); ^{13}C NMR (C_6D_6) δ 16.3, 25.6; ^{29}Si NMR (C_6D_6) δ_{Si} −54.3; IR (KBr) ν 2950, 1470, 1390, 1025 cm^{-1}; MS (70 eV) m/z 654 (M$^+$, 9), 599 (16), 543 (13), 487 (11) 73 (100). Anal. Calcd for $C_{24}H_{54}Si_6O_9$: C, 40.64; H, 8.54. Found: C, 39.86; H, 8.33%.

Synthesis from **5** was carried out in a similar manner.

Acknowledgment. This work was supported by a Grant-in-aid on Priority Area of Reactive Organometallics (No. 05236102) from the Ministry of Education, Science, and Culture of Japan. We also thank Shin-Etsu Chemical Co. Ltd. and Chisso Co. Ltd for the gift of silicon reagents.

Supporting Information Available: For **1**, text giving details on the X-ray analysis experiment, tables of anisotropic thermal parameters, atomic coordinates and isotropic thermal parameters, and bond lengths and angles, and figures showing the molecular structure and views of the molecular packing (30 pages). Ordering information is given on any current masthead page.

OM950737A

---

[10] Although the measurements were repeated five times with different crystals, we could not decrease the temperature factors of some of carbon atoms in the substituents. The obtained data showed the disorder of the isopropyl groups of thexyl substituents due to little energy differences between the conformers. Crystal data: $C_{36}H_{78}Si_6O_9$, monoclinic, $P2_1/n$, a = 11.777(2) Å, b = 18.975(3) Å, c = 22.001(2) Å, β = 99.24(1)°, V = 4852(1) Å^3, Z = 4, R = 0.082, R_w = 0.071 (for detailed data, see the Supporting Information).

[11] (a) Tobita, H.; Kawano, Y.; Shimoi, M.; Ogino, H. *Chem. Lett.* **1987**, 224. (b) Kawano, Y.; Tobita, H.; Ogino, H. *J. Organomet. Chem.* **1992**, *428*, 125.