

A new route to incompletely-condensed silsesquioxanes: base-mediated cleavage of polyhedral oligosilsesquioxanes

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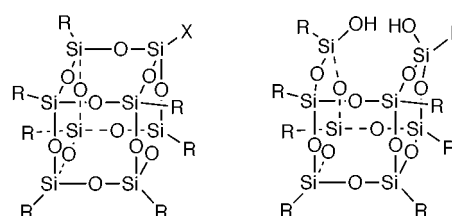
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Readily available $R_8Si_8O_{12}$ frameworks react selectively with aqueous Et_4NOH to afford discrete incompletely-condensed silsesquioxanes: reaction of $R_8Si_8O_{12}$ (**2a**, $R = c-C_6H_{11}$; **2b**, $R = Bu^i$) with Et_4NOH first produces *endo*- D_2 - $R_8Si_8O_{11}(OH)_2$ (**3a**, $R = c-C_6H_{11}$; **3b**, $R = Bu^i$), which reacts further with Et_4NOH to produce *endo*- C_2 - $R_8Si_8O_{10}(OH)_4$ (**5a** and **5b**) and *endo*- C_3 - $R_7Si_7O_9(OH)_3$ (**4a**, $R = c-C_6H_{11}$; **4b**, $R = Bu^i$); the reactions of Et_4NOH with $Me_8Si_8O_{12}$ (**2c**), $(c-C_6H_{11})_7(H)Si_8O_{12}$ (**2d**) and $(c-C_6H_{11})_7(OH)Si_8O_{12}$ (**2e**) also produce the corresponding trisilanols (*i.e.* *endo*- C_3 - $R_7Si_7O_9(OH)_3$ (**4a**, $R = c-C_6H_{11}$; **4c**, $R = Me$).

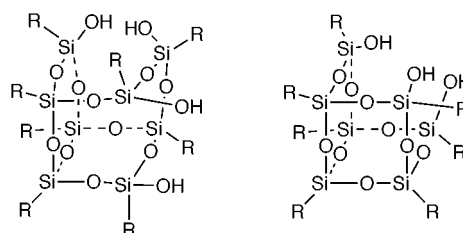
Incompletely condensed polyhedral silsesquioxanes are versatile precursors to a wide range of Si/O and Si/O/M frameworks.^{1–7} For many years, the pool of incompletely condensed silsesquioxanes available in synthetically useful quantities was limited to a small number of compounds available *via* hydrolytic condensation of trifunctional silanes possessing relatively bulky organic groups.^{8–15} Recently however, our discovery that fully-condensed $[RSiO_{3/2}]_n$ frameworks, such as $(c-C_6H_{11})_6Si_6O_9$ (**1**) and $(c-C_6H_{11})_8Si_8O_{12}$ (**2a**), can be selectively cleaved by strong acids provides access to many useful new incompletely-condensed frameworks.^{16–18} In this paper, we report that base catalyzed cleavage of polyhedral silsesquioxanes can be similarly selective. For the first time, cleavage of a single Si–O–Si linkage in $R_8Si_8O_{12}$ can be achieved directly with complete retention of stereochemistry at Si to afford *endo* disilanols with structure **3**. Under more vigorous conditions, cleavage of additional Si–O–Si linkages occurs to produce tetrasilanols with structure **4** and trisilanols with structure **5**.

The reaction of **2a** with aqueous Et_4NOH in THF occurs over a period of several hours at room temperature. The first product to appear in the ^{29}Si NMR spectrum was D_2 -symmetric disilanol **3a**, which was identified by its characteristic ^{29}Si NMR resonances at $\delta -60.4$, -67.2 , and -69.8 (2:2:4).¹⁶ When the reaction is performed at 25 °C for 1 h with 1.1 molar equivalents of 35% aqueous Et_4NOH , **3a** is obtained as the only reaction product in *ca.* 80% yield (along with 20% of unreacted **2a**). At longer reaction times, resonances for **3a** are gradually replaced by resonances for two additional products. One of these products is C_3 -symmetric trisilanol **5a**, which exhibits three resonances at $\delta -60.1$, -67.7 , and -69.4 (3:1:3) in the ^{29}Si NMR spectrum.⁹ The second product, which exhibits four ^{29}Si resonances at $\delta -59.3$, -61.5 , -69.8 and -71.3 (2:2:2:2), as well as prominent peaks at m/z 1117.36 $[M + H]^+$ and 1139.37 $[M + Na]^+$ in its electrospray mass spectrum, is most consistent with C_2 -symmetric tetrasilanol **4a**. For a typical reaction performed in THF at 25 °C, the ratio of unreacted **2a**:**3a**:**4a**:**5a** was 26:34:17:23 after 9 h and 6:18:26:50 after 15 h. When the reaction was performed in refluxing THF or methyl isobutyl ketone, all of the starting material was consumed within 3 h to produce **5a** in 47% crude yield (23% isolated yield).[†] The balance of the product mixture exhibited a very broad featureless ^{29}Si NMR spectrum typical of silsesquioxane resins. Samples of **3a** and **5a** prepared by the above procedure were identical in all respects to authentic samples prepared by other means.^{9,16}



2a $R = X = c-C_6H_{11}$
b $R = X = Bu^i$
c $R = X = Me$
d $R = c-C_6H_{11}$; $X = H$
e $R = c-C_6H_{11}$; $X = OH$

3a $R = c-C_6H_{11}$
b $R = Bu^i$
c $R = Me$



4a $R = c-C_6H_{11}$
b $R = Bu^i$

5a $R = c-C_6H_{11}$
b $R = Bu^i$
c $R = Me$

A number of other $R_8Si_8O_{12}$ frameworks react similarly with Et_4NOH . For example, the reactions of **2d** and **2e** with aqueous Et_4NOH (1.1 equiv., THF, reflux, 1 h) both afford **5a** in good (>50%) yield. These results clearly demonstrate that Si centers possessing H or OH groups are much more readily extracted from the Si_8O_{12} framework than Si centers possessing relatively bulky, electron-rich cyclohexyl groups.

We have only begun to explore the scope and generality of base-mediated silsesquioxane cleavage reactions, but it is already clear that this approach will provide access to a large number of useful new compounds, including many incompletely-condensed frameworks with substituents other than cycloalkyl groups. For example, the reaction of Et_4NOH with $(Bu^i)_8Si_8O_{12}$ (**2b**) appears to produce isobutyl analogs of **3**, **4** and **5**. This reaction is approximately an order of magnitude faster than the reaction of $(c-C_6H_{11})_8Si_8O_{12}$ (**2a**), and it eventually produces a good isolated yield of **5b**,[‡] which was identified on the basis of compelling multinuclear NMR data and a single-crystal X-ray diffraction study.[§] Similar results are observed with $(vinyl)_8Si_8O_{12}$, $(cyclopentyl)_8Si_8O_{12}$ and $Et_8Si_8O_{12}$. Even $Me_8Si_8O_{12}$ (**2c**), which is notoriously difficult to functionalize because of its very low solubility in organic solvents,¹⁹ reacts with aqueous Et_4NOH to produce an incompletely-condensed framework with spectroscopic features expected for $Me_7Si_7O_9(OH)_3$ (**5c**).[¶] The isolated yield is relatively low (<10%), but the fact that inexpensive and readily available **2c** can be used to produce incompletely-condensed fragments of discrete polyhedral silsesquioxanes has important

implications for many potential applications—particularly the use of polyhedral silsesquioxanes as precursors to hybrid inorganic/organic polymers.²

The susceptibility of $R_8Si_8O_{12}$ frameworks to base-catalyzed redistribution and non-selective degradation is well established,^{20,21} but the results described above are unprecedented, apparently quite general and of considerable practical importance: it is now possible to prepare synthetically useful quantities of incompletely-condensed silsesquioxanes by selectively removing Si atoms from fully condensed $R_8Si_8O_{12}$ frameworks. Our efforts to expand the scope of this methodology—including our efforts to use spherosilicates as feedstocks—will be reported in due course.

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Note added in Proof: The reactions of **2a** and **2b** with Et_4NOH have been optimized to produce high isolated yields of disilanols **3a** (77%) and **3b** (98%). Similarly selective cleavage reactions have also been achieved with $R_8Si_8O_{12}$ with $R = c-C_5H_9$ and vinyl.²²

Notes and references

† Preparation of $Cy_7Si_7O_9(OH)_3$ (**5a**): A solution of $Cy_8Si_8O_{12}$ (500 mg, 0.46 mmol) and 35% aqueous Et_4NOH (0.2 mL, 0.49 mmol) was refluxed in THF (5 mL) for 4 h then neutralized with dilute aqueous HCl. Evaporation of the volatiles afforded a white solid, which was dissolved in Et_2O and dried over anhydrous $MgSO_4$. Filtration and partial evaporation of the solvent afforded **5a** as a white microcrystalline solid in 23% yield. The product is indistinguishable from authentic **5a** prepared via the hydrolytic condensation of $CySiCl_3$.

‡ Preparation of $Bu^i_7Si_7O_9(OH)_3$ (**5b**): A solution of $Bu^i_8Si_8O_{12}$ (400 mg, 0.46 mmol) and 35% aqueous Et_4NOH (0.2 mL, 0.49 mmol) was refluxed in THF (5 mL) for 4 h then neutralized with dilute aqueous HCl. Evaporation of the volatiles afforded a resinous white material, which was dissolved in Et_2O and dried over anhydrous $MgSO_4$. Filtration and evaporation of the solvent afforded crude **5b** as a tacky white solid. Recrystallization from toluene–acetonitrile gave pure **5b** as colorless crystals. Yield 142 mg (39%). Selected characterization data: Anal. Calc. for $C_{28}H_{66}Si_7O_{12}$ (found): C, 42.49 (42.62); H, 8.41 (8.52)%. $^{29}Si\{^1H\}$ NMR (99.3 MHz, C_6D_6 , 25 °C) δ –58.5, –66.9, –68.3 (s, 3:1:3); 1H NMR (500 MHz, C_6D_6 , 25 °C) δ 7.0 (br s, 3 H, OH), 2.21 (m, 7 H, –CH–), 1.24 (d, $J = 6.6$ Hz, 18 H, CH_3), 1.21 (d, $J = 6.6$ Hz, 18 H, CH_3), 1.17 (d, $J = 6.6$ Hz, 6 H, CH_3), 0.97 (d, $J = 7.1$ Hz, 6 H, CH_2), 0.95 (d, $J = 7.1$ Hz, 6 H, CH_2), 0.92 (d, $J = 7.0$ Hz, 2 H, CH_2), $^{13}C\{^1H\}$ NMR (125.8 MHz, C_6D_6 , 25 °C) δ 25.7 (s, CH_3), 25.6 (s, CH_3), 25.5 (s, CH_3), 24.1, 24.05, 24.0 (s, 3:1:3 for CH_2), 23.4, 23.0, 22.6 (s, 3:1:3 for CH). MS (ESI, 100% MeOH): m/z 791.16 $[M + H]^+$, 80%; 813.08 $[M + Na]^+$, 100%.

§ Like many polyhedral silsesquioxanes, trisilanol **5b** crystallizes from many solvent systems as well formed but poorly diffracting (even at 158 K) crystals. Attempts to obtain a high quality set of diffraction data were unsuccessful, but a marginal set of data was eventually collected from a

large crystal obtained from toluene–acetonitrile. Although the quality of the structure does not warrant a discussion of metrical data, it clearly identifies the trisilanol as *endo*- C_3 - $[(c-C_4H_9)_7Si_7O_9(OH)_3]$. Crystal data for **5b** obtained by recrystallization from toluene–acetonitrile: $C_{28}H_{66}O_{12}Si_7$, $M = 791.44$, monoclinic, space group $P2_1/n$, $a = 14.089(3)$, $b = 21.336(5)$, $c = 14.750(3)$ Å, $\alpha = \gamma = 90^\circ$, $\beta = 100.119(4)^\circ$, $V = 4365.1(17)$ Å³, $T = 158$ K, $Z = 4$, $\rho_{calcd} = 1.204$ Mg m^{–3}, $\mu = 0.268$ mm^{–1}, $F(000) = 1712$, $\lambda = 0.71073$ Å, crystal dimensions $0.60 \times 0.60 \times 0.40$ mm, $3.40^\circ \leq 2\theta \leq 57.5^\circ$; of the 45556 collected reflections, 10644 are independent, and these were used for the refinement of 424 parameters; $R_1 = 0.166$, $wR_2 = 0.468$ with $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR_2 = (\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2)^{0.5}$. CCDC 182/1444.

¶ Selected characterization data for **5c**: $^{29}Si\{^1H\}$ NMR (99.3 MHz, C_6D_6 , 25 °C) δ –56.8, –64.5, –67.4 (3:1:3); MS (ESI, 100% MeOH) m/z : 496.96 $[M + H]^+$, 100%; 518.86 $[M + Na]^+$, 75%.

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