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

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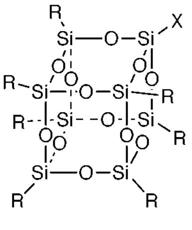
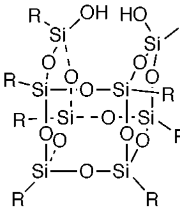
Readily available $R_8Si_8O_{12}$ frameworks react selectively with aqueous Et_4NOH to afford discrete incompletely-condensed silsesquioxanes: reaction of $R_8Si_8O_{12}$ (2a, R = c-C_6H_{11}; 2b, R = Bu^i) with Et_4NOH first produces *endo-D_2*-$R_8Si_8O_{11}(OH)_2$ (3a, R = c-C_6H_{11}; 3b, R = Bu^i), 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-$C_6H_{11})_7(OH)Si_8O_{12}$ (2d) 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**.

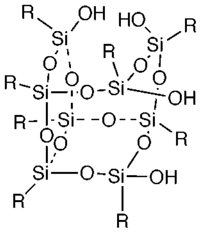
The reaction of **2a** with aqueous Et_4NOH in THF occurs over a period of several hours at room temperature. The first product to appear in the ^{29}Si NMR spectrum was D_2-symmetric disilanol **3a**, which was identified by its characteristic ^{29}Si NMR resonances at δ −60.4, −67.2, and −69.8 (2 : 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 δ −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 δ −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]



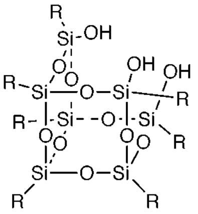
2a R = X = c-C_6H_{11}
b R = X = Bu^i
c R = X = Me
d R = c-C_6H_{11}; X = H
e R = c-C_6H_{11}; X = OH



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, $\alpha = \gamma = 90°$, β = 100.119(4)°, V = 4365.1(17) Å^3, T = 158 K, Z = 4, ρ_{calcd} = 1.204 Mg m^{-3}, μ = 0.268 mm^{-1}, $F(000)$ = 1712, λ = 0.71073 Å, crystal dimensions 0.60 × 0.60 × 0.40 mm, $3.40° \leqslant 2\theta \leqslant 57.5°$; 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 $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR_2 = (\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2)^{0.5}$. 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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