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

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Readily available R8SiO12 frameworks react selectively with aqueous Et3NOH to afford discrete incompletely-condensed silsesquioxanes: reaction of R8SiO12 (2a, R = c-C6H11; 2b, R = Bu) with Et3NOH first produces endo-D2-R8SiO11(OH)2 (3a, R = c-C6H11; 3b, R = Bu), which reacts further with Et3NOH to produce endo-D2-R8SiO11(OH)4 (5a and 5b) and endo-D2-R8SiO10(OH)2 (4a, R = c-C6H11; 4b, R = Bu); the reactions of Et3NOH with Me8SiO12 (2c), (c-C6H11)3SiO12 (2d) and (c-C6H11)3Si(OH)SiO12 (2d) also produce the corresponding trisilanol (i.e. endo-D2-R8SiO9(OH)3 (4a, R = c-C6H11; 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 [RSiO3/2]n frameworks, such as (c-C6H11)6Si6O9 (1) and (c-C6H11)3Si8O12 (2a), can be selectively cleaved by strong acids provides access to many useful, 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 R8SiO12 can be achieved directly with complete retention of stereochemistry at Si to afford endo disilanol with structure 3. Under more vigorous conditions, cleavage of additional Si–O–Si linkages occurs to produce tetrasilanol with structure 4 and trisilanol with structure 5.

The reaction of 2a with aqueous Et3NOH in THF occurs over a period of several hours at room temperature. The first product to appear in the 29Si NMR spectrum was D2-symmetric disilanol 3a, which was identified by its characteristic 29Si NMR resonances at δ = −60.1, −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 Et3NOH,5a the 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 C2-symmetric trisilanol 5a, which exhibits three resonances at δ = −60.1, −67.2, and −69.4 (3:1:3) in the 29Si NMR spectrum.5 The second product, which exhibits four 29Si 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]1+ and 1139.37 [M + Na]1+ in its electrospray mass spectrum, is most consistent with C2-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).5 The balance of the reaction mixture exhibited a very broad featureless 29Si 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.5,16

A number of other R8SiO12 frameworks react similarly with Et3NOH. For example, the reactions of 2d and 2e with aqueous Et3NOH (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 SiO32− 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 Et3NOH with (Bu)3SiO12 (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-C6H11)3SiO12 (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.5 Similar results are observed with (vinyl)3SiO12, (cyclopentyl)3SiO12 and (Et)3SiO12. Even Me8SiO13 (2e), which is notoriously difficult to functionalize because of its very low solubility in organic solvents,19 reacts with aqueous Et3NOH to produce an incompletely-condensed framework with spectroscopic features expected for Me8Si3O9(OH)3 (5c).19 The isolated yield is relatively low (< 10%), but the fact that inexpensive and readily available 2e can be used to produce incompletely-condensed fragments of discrete polyhedral silsesquioxanes has important


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

The susceptibility of R6Si2O12 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 inorganic/organic polymers.2

Like many polyhedral silsesquioxanes, trisilanol as endo-Cy7[(c-C5H9)Si3O9(OH)]2. Crystal data for 5b obtained by recrystallization from toluene-acetonitrile: C35H76O12Si7 M = 791.44, monoclinic, space group P21/n, α = 14.089(3), b = 21.336(5), c = 14.750(3) Å, α = γ = 90°, β = 100.119(4), V = 4368.17(17) Å3, T = 158 K, Z = 4, ρ_{calc} = 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° < 2θ < 57.5°; of the 45556 collected reflections, 10644 are independent, and these were used for the refinement of 424 parameters; R1 = 0.166, wR2 = 0.468 with R1 = \sum F^2 - |F|^2/\sum |F|^2 and wR2 = (\sum wF^2 - F^2)^2/\sum wF^2)^1/2. CCDC 182/1444.

Selected characterization data for 791.16 [M + H]^+ , 80%); 813.08 [M + Na]^+ , 100%).

1H NMR (99.3 MHz, C6D6, 25 °C) δ = 6.6 Hz, 18 H, CH3), 1.21 (d, J = 6.6 Hz, 18 H, CH3). 1.17 (d, J = 6.6 Hz, 6 H, CH2), 0.97 (d, J = 7.1 Hz, 6 H, CH2), 0.95 (d, J = 7.1 Hz, 6 H, CH2), 0.92 (d, J = 7.0 Hz 2 H, CH2), 39C[1H] NMR (125.8 MHz, C6D6, 25 °C) δ 25.7 (s, CH3), 25.6 (s, CH3), 25.5 (s, CH3) 24.1, 24.05, 24.0 (s, 3:1:3 for CH3), 23.4, 23.0, 22.6 (s, 3:1:3 for CH3) MS (ESI, 100% MeOH) m/z: 496.96 ([M + H]^+ , 100%); 518.86 ([M + Na]^+ , 75%).

Notes and references

1 Preparation of Cy7Si3O9(OH)2 (5a): A solution of Cy7Si3O12 (500 mg, 0.46 mmol) and 35% aqueous Et4NOH (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 Et2O and dried over anhydrous MgSO4. Filtration and partial evaporation of the solvent afforded crude 5a as colorless 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-Cy7[(c-C5H9)Si3O9(OH)]2. Crystal data for 5b obtained by recrystallization from toluene-acetonitrile: C35H76O12Si7 M = 791.44, monoclinic, space group P21/n, α = 14.089(3), b = 21.336(5), c = 14.750(3) Å, α = γ = 90°, β = 100.119(4), V = 4368.17(17) Å3, T = 158 K, Z = 4, ρ_{calc} = 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° < 2θ < 57.5°; of the 45556 collected reflections, 10644 are independent, and these were used for the refinement of 424 parameters; R1 = 0.166, wR2 = 0.468 with R1 = \sum F^2 - |F|^2/\sum |F|^2 and wR2 = (\sum wF^2 - F^2)^2/\sum wF^2)^1/2. CCDC 182/1444.


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