Practical methods for synthesizing four incompletely condensed silsesquioxanes from a single $R_8Si_8O_{12}$ framework

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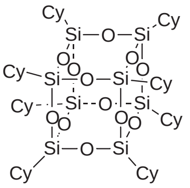
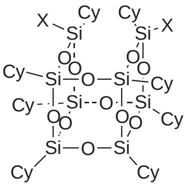
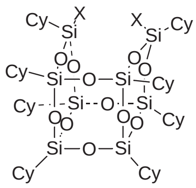
The reaction of $(c\text{-}C_6H_{11})_8Si_8O_{12}$ 1 with triflic acid (TfOH) can produce two different ditriflates with the formula $(c\text{-}C_6H_{11})_8Si_8O_{11}(OTf)_2$, which can be hydrolyzed selectively to four different incompletely condensed silsesquioxane frameworks with the formula $(c\text{-}C_6H_{11})_8Si_8O_{11}(OH)_2$ (2, 4, 7 and 8).

Incompletely condensed silsesquioxanes have attracted broad interest as models for silica surfaces,[1–3] ligands for main group, transition-metal and lanthanide elements,[4–6] building blocks for network solids,[7,8] and precursors to new families of silsesquioxane-containing polymers.[9,10] Our recent discovery that a single Si–O–Si linkage in a fully-condensed $R_8Si_8O_{12}$ framework (*i.e.* **1**) can be cleaved selectively by strong acids [*e.g.* HBF_4–BF_3 or TfOH (triflic acid)] provides an important new method for preparing incompletely condensed frameworks (*e.g.* **2** and **4**),[11] but there are still strong incentives for devising practical routes to silsesquioxanes with reactive SiOH groups. Here, we report an improved method for synthesizing **2**, as well as the discovery of an interesting acid-induced rearrangement reaction of **1** that provides access to two other incompletely condensed frameworks (*i.e.* **7** and **8**).


1 Cy = c-C_6H_{11}


2 X = OH
3 OTf

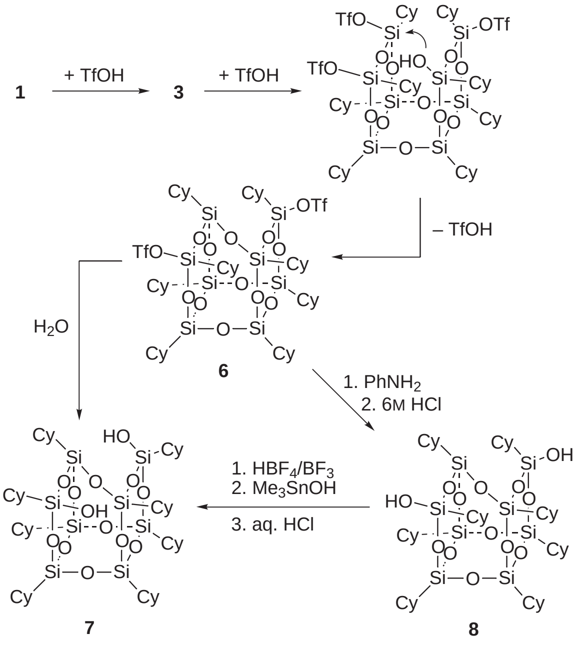

4 X = OH
5 NHPh

The reaction of **1** with TfOH (5 equiv., 25 °C, C_6H_6, 30 min) occurs rapidly upon mixing to afford quantitative NMR yields of a C_{2v}-symmetric ditriflate derived from cleavage of a single Si–O–Si linkage (*e.g.* **3**).[11] This ditriflate reacts with a variety of nucleophiles to afford products resulting from substitution of triflate with complete inversion of stereochemistry at Si.[12] When water[11] or aniline[12] are used as nucleophiles in large excess, **4** or **5** can be obtained in high yield. Disilanol **4** is hydrolytically stable, but **5** reacts very slowly with water to afford several products resulting from hydrolysis of Si–N bonds, including disilanol **2**. Both the rate and selectivity of hydrolysis can be greatly increased by performing the reaction with 6 M HCl. Under these conditions, high yields of **2** are obtained within a few minutes of mixing.‡ This route to **2** is far superior to our previously reported method[11] based on Me_3Sn-OH-mediated hydrolysis of fluoride-substituted frameworks, and it allows both **2** and **4** to be prepared from a common intermediate (*i.e.* **3**) which can be obtained in high yield from a readily available $R_8Si_8O_{12}$ framework.

When **1** is reacted with a larger excess of TfOH (10 equiv., 25 °C, C_6H_6, 3 h), cleavage of additional Si–O–Si linkages is observed, but the major product is not a tetratriflate derived from cleavage of the second Si–O–Si linkage. Instead, this reaction produces large amounts (*ca.* 70%) of a new C_2-symmetric framework with two Si–OTf groups. If cleavage of the second Si–O–Si linkage by TfOH and intramolecular displacement of a triflate group both occur with complete inversion of stereochemistry at Si, the mechanism proposed in Scheme 1 predicts that this new ditriflate is **6**.§ This ditriflate reacts with H_2O or aqueous $NaHCO_3$ to afford **7**;¶ hydrolysis of the ditriflate *via* sequential reaction with excess aniline and 6 M HCl affords **8**. The structures of **7** and **8** were established by comparison to authentic samples prepared by alternative methods. Disilanol **8** is available in 15–20% yield *via* the slow (3–36 months) hydrolytic condensation of $CySiCl_3$.[3] Disilanol **7** can be independently synthesized *via* sequential reactions of **8** with HBF_4–BF_3, Me_3SnOH and aqueous HCl. The stereochemical consequences of these reactions are well established and known to invert the stereochemistry of SiOH groups on silsesquioxane frameworks.[11,13,14]

The formation of **6** during the reaction of **1** with TfOH is surprising because it requires formation of an Si_5O_5 ring under conditions where Si_4O_4 rings are cleaved selectively and Si–OH groups are quickly converted into Si–OTf groups by an excess of TfOH. It is difficult to rationalize the high selectivities observed in these reactions. Nevertheless, it is abundantly clear that Si–O–Si cleavage by strong acids can be extremely selective and that the formation of new Si–O–Si linkages can be competitive.

In conclusion, the reaction of **1** with TfOH can produce two different ditriflates (**3** and **6**), which can be hydrolyzed selectively to four different incompletely condensed silsesquioxane frameworks (**2**, **4**, **7** and **8**). These results represent an important advance in the chemistry of discrete silsesquioxanes



Scheme 1

because **1** is available in high yield *via* base-catalyzed hydrolytic condensation of $CySi(OMe)_3$[15] and catalytic hydrogenation of readily available $Ph_8Si_8O_{12}$.[16,17] Our efforts to expand the generality of these reactions, as well as the reaction chemistry of **3** and **6** will be reported in due course.

These studies were supported by the National Science Foundation and Phillips Laboratory (Edwards AFB).

Notes and References

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‡ Disilanol **2** was prepared in quantitative yield by adding an excess of 6 M HCl to a solution of **5** in THF. The product obtained after evaporation of the THF and a standard aqueous work-up with Et_2O as an extraction solvent was identical in all respects to an authentic sample of **2** prepared according to ref. 11.

§ The ditriflate tentatively assigned as **6** was prepared by reacting **1** (102 mg, 0.094 mmol) and TfOH (83 μl, 0.943 mmol) at 25 °C for 3 h according to the procedure described for the synthesis of **3**.[11] Repeated attempts to crystallize the crude product were unsuccessful because the ditriflate is extremely water sensitive and highly soluble in all solvents with which it does not react. The crude product obtained after evaporation of the solvent is *ca.* 70% pure (by ^{13}C and ^{29}Si NMR spectroscopy) and should be used immediately to avoid decomposition. Selected characterization data: $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 25 °C), δ 27.35–25.26 (CH_2), 23.24, 23.00, 22.95, 22.66 (s CH, 1 : 1 : 1 : 1). $^{29}Si\{^1H\}$ NMR (99 MHz, $CDCl_3$, 25 °C), δ −62.82, −64.84, −67.25, −68.02 (1 : 1 : 1 : 1). A C_2-symmetric structure with the opposite orientation of Cy and OTf groups is equally consistent with all of our spectroscopic and analytical data. Although this structure it is considered unlikely on the basis of mechanistic considerations, it should not be ruled out until the structure of **6** is confirmed by a single-crystal X-ray diffraction study.

¶ For **7**: ^1H NMR (500 MHz, $CDCl_3$, 25 °C), δ 2.38 (br s, 2 H), 1.73 (br m, 40 H), 1.24 (br m, 40 H), 0.42 (br m, 8 H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 25 °C), δ 27.45, 27.40, 27.37, 26.76, 26.70, 26.60, 26.52, 26.45, 26.42 (for CH_2), 23.46, 23.29, 23.27, 22.15 (1 : 1 : 1 : 1 for CH). $^{29}Si\{^1H\}$ NMR (99 MHz, $CDCl_3$, 25 °C): δ −57.47, −66.18, −67.24, −67.76 (1 : 1 : 1 : 1). MS (70 eV, 200 °C, relative intensity): *m*/*z* 1015 ($[M - Cy]^+$, 100%), 932 ($[M - 2Cy]^+$, 15%), 466 ($[M - 2Cy]^{2+}$, 35%). Anal. Calc. for $C_{48}H_{90}O_{13}Si_8$ (found): C, 52.42 (52.40); H, 8.25 (8.05)%. Mp by DSC: 233.5 °C.

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Received in Bloomington, IN, USA, 8th April 1998; 8/02670J