Methods for effecting monofunctionalization of $(CH_2{=}CH)_8Si_8O_{12}$

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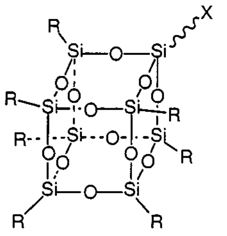
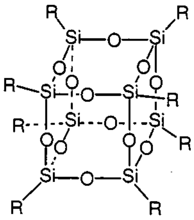
A new method is described for effecting selective monofunctionalization of $CH_2{=}CH)_8Si_8O_{12}$ 2: reaction of 2 with triflic acid (TfOH) produces $(TfOCH_2CH_2)(CH_2{=}CH)_7Si_8O_{12}$ 3, which reacts with nucleophiles (*e.g.* H_2O or 2-mercaptopyridine) to produce $(XCH_2CH_2)(CH_2{=}CH)_7Si_8O_{12}$ (4 X = OH, 5 X = SC_5H_4N); acylation of 4 with *p*-$O_2NC_6H_4COCl$ affords (*p*-$O_2NC_6H_4CO_2$-$CH_2CH_2)(CH_2{=}CH)_7Si_8O_{12}$ 6; catalytic hydrogenation of 4 affords $(HOCH_2CH_2)$ $Et_7Si_8O_{12}$ 7.

Polyhedral oligosilsesquioxanes (POSS) have recently attracted interest as building blocks for hybrid inorganic/organic materials.[1–5] Many families of POSS monomers are now known, but some of the most promising monomers are cube-octameric frameworks with a single polymerizable pendant group (*e.g.* **1**).[6,7] As part of a general effort to identify cost-effective ways for manufacturing POSS monomers on a large scale, we have been exploring potential methods for preparing POSS monomers from inexpensive $R_8Si_8O_{12}$ frameworks.[8–10] Here, we outline a new strategy for preparing POSS monomers from $(CH_2{=}CH)Si_8O_{12}$ **2**. This strategy, which involves addition of triflic acid (TfOH) to a C=C bond of the vinylsilsesquioxane, produces an attractive precursor for the preparation of cube-octameric POSS monomers containing seven vinyl or ethyl groups and one unique pendant group.



1 X = polymerizable pendant group



2 R = vinyl

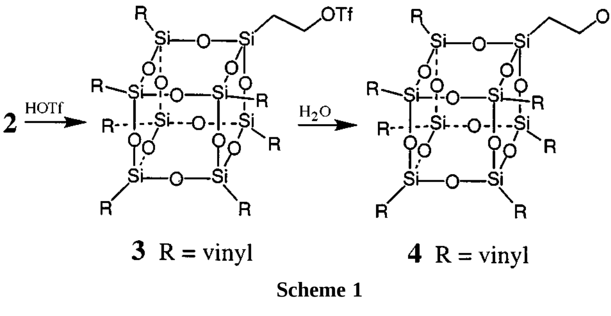
Vinylsilsesquioxane **2**, which is readily available from the hydrolytic condensation of $(CH_2{=}CH)SiCl_3$,[11,12] undergoes a wide variety of useful transformations, including free-radical addition reactions,[13] catalytic hydrogenation,[14] Diels–Alder reactions,[15] epoxidation[4] and olefin metathesis.[8] With eight potentially reactive vinyl groups, reactions of **2** often produce complicated product mixtures. Under the right conditions, however, reactions of **2** can be quite selective for the functionalization of a single vinyl group.

The reaction of **2** with TfOH† (1 equiv., CH_2Cl_2, 25 °C) occurs quickly upon mixing to afford a new silsesquioxane product in good yield (*ca.* 40–45%) (Scheme 1).‡ Based on the known reactivity of $R_8Si_8O_{12}$ frameworks toward TfOH[9,10] and the tendency of some vinylsilanes to undergo protodesilylation or rearrangement,[16] we expected to observe cleavage of Si–O–Si linkages and/or Si–C bonds. Instead, both the ^{13}C and ^{29}Si NMR spectra were consistent with a compound possessing a C_3-symmetric Si_8O_{12} framework, and the ^1H NMR spectrum exhibited an AA′BB′ coupling pattern characteristic of $R_7Si_8O_{12}(CH_2CH_2X)$ frameworks.[17] Based on the reaction stoichiometry and the ^1H chemical shift for the CH_2X group (δ 4.75, t, *J* 12 Hz), this compound was assigned as **3**; this assignment was confirmed by multinuclear NMR data (^{13}C, ^{29}Si, ^{19}F) and a high resolution mass spectrum. To the best of our knowledge, this is the first example of triflic acid addition to a vinylsilane.

Triflate **3** could not be isolated in pure form because it readily co-crystallizes with **2**. However, crude product mixtures containing **3** react with a variety of nucleophiles to afford substitution products that can be easily isolated as pure compounds. For example, hydrolysis of **3** (acetone or dioxane–aqueous Na_2CO_3) produces **4**, which was identified on the basis of compelling multinuclear NMR data, a high resolution mass spectrum, and a preliminary single crystal X-ray diffraction study.§ Reaction of **3** with 2-mercaptopyridine affords **5**.¶ In both cases, separation of the product from unreacted **2**, as well as small amounts of products derived from functionalization of more than one vinyl group (*vide infra*), can be accomplished by flash chromatography on SiO_2.

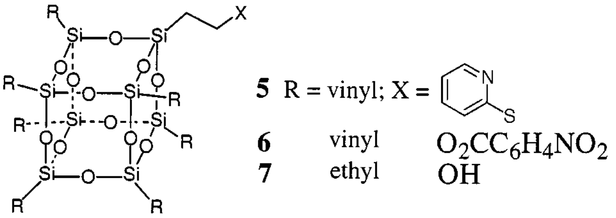
In contrast to most compounds containing $SiCH_2CH_2OH$ groups, **4** does not undergo facile base-catalyzed elimination of ethylene to produce SiOH groups. It is also resistant to acid-catalyzed dehydration. This unexpected stability, which is probably due to a strong preference for *trans*-diaxial orientation of the Si_8O_{12} framework and OH group, allows **4** to be used as a precursor to a wide range of potentially useful compounds. For example, both acylation of **4** to **6** (*p*-$O_2NC_6H_4COCl$, CH_2Cl_2–pyridine, 50 °C, 8 h) and the catalytic hydrogenation of **4** to **7** (10% Pd/C, 100 psig H_2, Et_2O, 25 °C, 20 h) occur in quantitative NMR yield.¶

Unlike TfOH-induced Si–O–Si cleavage reactions of $R_8Si_8O_{12}$, which can afford high yields of a single product at complete conversion, functionalization of POSS pendant groups is normally selective for monofunctionalization[18] only at low conversion ($<10\%$ based on $R_8Si_8O_{12}$). At higher conversion the monofunctionalization reaction no longer enjoys a large statistical advantage and the formation of many polyfunctional products is usually observed. For the reaction of **2** with TfOH described above, the selectivity for monofunctionalization is *ca.* 85–90% as judged by multinuclear NMR spectra and EI mass spectra obtained on crude product mixtures. Under these conditions, difunctionalized products are



3 R = vinyl **4** R = vinyl

Scheme 1



also produced in yields of *ca.* 10–15% (based on the amount of **2** consumed). Higher selectively for monofunctionalization can be achieved by performing the reaction to lower conversion, but larger amounts of unreacted **2** must be recovered and the absolute mass yield of **3** is correspondingly lower. We have not been able to separate or isolate any of the triflates derived from addition of TfOH to vinyl groups on **2**. However, hydrolysis of the crude product mixture cleanly transforms all CH_2CH_2OTf groups into CH_2CH_2OH groups and produces a mixture of alcohols that can be efficiently separated by chromatography. A full account of our efforts to control the extent of functionalization and isolate synthetically useful quantities of polyfunctional products will be reported separately.

In summary, the addition of triflic acid to vinyl groups of **2** provides the basis for a fundamentally new method for preparing functionalized silsesquioxanes. Frameworks containing seven vinyl or ethyl groups and one unique pendant group are particularly easy to prepare, but both the rich reaction chemistry of vinylsilsesquioxanes and the ease with which multiply functionalized derivatives can be isolated in synthetically useful quantities provide access to a wide range of potentially useful compounds.

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Notes and references

† TfOH = CF_3SO_3H

‡ Triflic acid (TfOH, 1 equiv.) was added to a solution of **2** (188 mg, 0.297 mmol) in CH_2Cl_2. After 3 h at 25 °C, the reaction mixture was diluted with CH_2Cl_2, washed with saturated aqueous Na_2CO_3, dried over $MgSO_4$, and evaporated to afford 180 mg of a white solid. Analysis by NMR spectroscopy (^{1}H, ^{13}C, ^{29}Si) and mass spectrometry indicated that the crude product contains mainly **3** (40–45%), unreacted **2** (50%) and small amounts of products resulting from addition of TfOH to more than one vinyl group. For **3**: ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 6.25–5.75 (m, 21H), 4.73 (t, *J* 12 Hz, 2H, CH_2OTf), 1.50 (t, *J* 12 Hz, 2H, $SiCH_2$). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, 25 °C): δ 137.40, 137.24, 137.03 (rel. int. 3 : 3 : 1 for CH_2), 128.39, 128.29, 128.09 (rel. int. 1 : 3 : 3 for CH), 118.5 (q, *J* 320 Hz, CF_3), 75.15 (CH_2OTf), 14.89 ($SiCH_2$). $^{29}Si\{^{1}H\}$ NMR (99 MHz, $CDCl_3$, 25 °C): δ −71.61, −80.08, −80.14 (rel. int: 1 : 3 : 4). $^{19}F\{^{1}H\}$ NMR (470.13 MHz, $CDCl_3$, 21 °C): δ −139.45. EI (70 eV, 200 °C) exact mass for M^+ (found): *m/z* 781.9020 (781.9041).

§ The hydrolysis of crude **3** was performed in wet acetone–CH_2Cl_2. Analysis (^{1}H, ^{13}C, ^{29}Si NMR) of the crude product obtained after evaporation of the solvent indicated complete conversion of $SiCH_2CH_2OTf$ to $SiCH_2CH_2OH$. Flash chromatography on silica with CH_2Cl_2 afforded **4** as a white solid, which was recrystallized from CH_2Cl_2 at −35 °C. For **4**: ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 6.15–5.90 (m, 21H), 3.85 (t, *J* 7.2 Hz, 2H, CH_2OH), 1.18 (t, *J* 7.2 Hz, 2H, $SiCH_2$). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, 25 °C): δ 137.07, 137.05, 136.95 (rel. int. 3 : 3 : 1 for CH_2), 128.58, 128.56 (rel. int. 4 : 3 for CH), 58.48 (CH_2OH), 17.28 ($SiCH_2$). $^{29}Si\{^{1}H\}$ NMR (99 MHz, $CDCl_3$, 25 °C): δ −68.00, −80.16, −80.36 (rel. int. 1 : 3 : 4). EI (70 eV, 200 °C) exact mass for M^+ (found): *m/z* 649.9528 (649.9520).

Crystal data for **4**: $C_{16}H_{26}O_{13}Si_8$, M = 651.09, rhombohedral, space group $R\bar{3}$, $a = b$ = 13.4510(8), c = 13.9408(12) Å, γ = 120°, V = 2184.4(3) Å^3, T = 158 K, Z = 3, μ = 0.426 mm^{-1}, 4488 reflections collected, 1152 independent reflections with $I > 2\sigma(I)$, R_1 = 0.0811, wR_2 = 0.2285. The CH_2CH_2OH group exhibits $\bar{3}$ disorder because the crystallographic center of inversion is located at the center of the Si_8O_{12} framework.

CCDC 182/1295. See http://www.rsc.org/suppdata/cc/1999/1289/ for crystallographic files in .cif format.

¶ For **5**: ^{1}H NMR (500.2 MHz, $CDCl_3$, 25 °C): δ 8.38 (m, CH, 1H), 7.63 (m, CH, 1H), 7.24 (s, CH, 1H), 7.10 (m, CH, 1H), 6.1–5.9 (m, $CH{=}CH_2$, 21H), 3.31 (t, CH_2S, 2H), 1.22 (t, CH_2Si, 2H). $^{13}C\{^{1}H\}$ NMR (125.8 MHz, $CDCl_3$, 25 °C): δ 159.4 (s, CH), 148.0 (s, CH), 138.0 (s, CH) 137.308, 137.256, 137.22 (s, $CH{=}CH_2$, rel. int. 3 : 3 : 1), 128.785, 128.765, (s, $CH{=}CH_2$, rel. int. 3 : 4), 122.9 (s, CH), 119.9 (s, CH), 25.44 (s, CH_2S), 12.84 (s, $SiCH_2$). $^{29}Si\{^{1}H\}$ NMR (99.4 MHz, $CDCl_3$, 25 °C): δ −68.8 (s, $SiCH_2CH_2S$), −79.95, −80.00 (s, rel. int. 4 : 3). Mass spectrum (EIMS) *m/z* calc. for $C_{21}H_{29}O_{12}NSSi_8$: $[M]^+$ 742.9565, found 742.9564.

For **6**: ^{1}H NMR (500.2 MHz, $CDCl_3$, 25 °C) δ: 8.26–8.19 (m, $C_6H_4NO_2$, 4H), 6.16–5.84 (m, $SiCH{=}CH_2$, 21H), 4.52 (t, CH_2O, 2H), 1.37 (t, $SiCH_2$, 2H). $^{13}C\{^{1}H\}$ NMR (125.8 MHz, $CDCl_3$, 25 °C): δ 164.55 (s, CO), 150.45 (s, C-quat), 137.398, 137.13 (br, $SiCH{=}CH_2$, rel. int. 3 : 4), 135.72 (s, C-quat), 130.710 (s, CH), 128.45 (s, $SiCH{=}CH_2$), 123.50 (s, CH), 62.269 (s, CH_2O), 12.92 (s, $SiCH_2$). $^{29}Si\{^{1}H\}$ NMR (99.4 MHz, $CDCl_3$, 25 °C): δ −69.0 (s, $SiCH_2CH_2O$), −80.1, −80.3 (s, rel. int. 4 : 3). Mass spectrum (ESMS) *m/z* calc. for $C_{23}H_{29}O_{16}NSi_8$: $[M]^+$ 798.9640, found 798.9640.

For **7**: ^{1}H NMR (500.2 MHz, $CDCl_3$, 25 °C): δ 3.81 (t, *J* 8.0 Hz, CH_2OH, 2H), 1.60 (br, OH, 1H), 1.09 (t, *J* 7.6 Hz, CH_2CH_2OH, 2H), 0.993 (t, $SiCH_2CH_3$, 21H), 0.60 (q, $SiCH_2CH_3$, 14H). $^{13}C\{^{1}H\}$ NMR (125.8 MHz, $CDCl_3$, 25 °C): δ 58.83 (s, CH_2CH_2O), 17.58 (s, CH_2CH_2O), 6.47 (s, $SiCH_2CH_3$), 4.00 (s, $SiCH_2CH_3$). $^{29}Si\{^{1}H\}$ NMR (99.4 MHz, $CDCl_3$, 25 °C): δ −65.6, −65.7, −68.8 (s, rel. int. 3 : 4 : 1). Mass spectrum (EIMS) *m/z* calc. for $C_{16}H_{40}Si_8O_{13}$: $[M - H]^+$ 663.0545, found 663.0487.

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