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Syntheses of highly-functionalized polyhedral oligosilsesquioxanes

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Abstract

The hydrolytic condensation of p-$ClCH_2C_6H_4SiCl_3$ in aqueous acetone affords [p-$ClCH_2C_6H_4SiO_{3/2}]_8$ (**1**), a synthetically useful precursor for the syntheses of octafunctional polyhedral oligosilsesquioxanes [p-$XCH_2C_6H_4SiO_{1.5}]_8$,including **2** (X = I), **3** (X = OH), **4** (X = ONO_2), **5** (X = OAc), **6** (X = p-nitrobenzoyl), and **7** (X = methylterephthaloyl).

Polyhedral oligosilsesquioxanes (POSS) are an interesting class of organosilicon oligomers that can be synthesized by the hydrolytic condensation of trifunctional organosilicon monomers [1]. Despite the fact that these materials have been known for more than 40 years [2], relatively few applications have been developed [1], presumably because most POSS synthesized thus far lack sufficient functionality for most chemical applications [3]. This paper describes the syntheses of several highly functionalized, *para*-substituted-phenyl POSS possessing octameric "T8" frameworks. The focus of the present work is the synthesis of pure octafunctional materials, which represent the greatest synthetic challenge, but which are inherently much easier to rigorously characterize.

Experimental

p-$ClCH_2C_6H_4SiCl_3$ was obtained from Petrarch Systems and used without further purification. Tetrahydrofuran (THF) was distilled from dark purple solutions of potassium benzophenone ketyl. Acetonitrile was dried over CaH_2 and vacuum distilled (25° C, 10^{-3} torr) immediately prior to use. All other reagent grade chemicals and solvents were used without further purification.

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NMR spectra were recorded on Bruker WM-250 (^{1}H, 250.1 MHz; ^{13}C, 62.5 MHz; ^{29}Si, 49.7 MHz), General Electric QE-300 (^{1}H 300.15 MHz; ^{13}C 75.04 MHz) or GN-500 (^{1}H, 500.1 MHz; ^{13}C, 125.03 MHz; ^{29}Si, 99.36 MHz) NMR spectrometers. All chemical shifts are reported in units of δ (ppm downfield from tetramethylsilane), but were most often measured relative to (residual) ^{1}H or ^{13}C resonances in the deuterated solvents: $CDCl_3$ (δ 7.260 for ^{1}H, δ 77.000 for ^{13}C), C_6D_6 (δ 7.150 for ^{1}H, δ 128.000 for ^{13}C), acetone-d_6 (δ 2.040 for ^{1}H, δ 29.700 for ^{13}C). CH_x assignments in ^{13}C NMR spectra were based on standard DEPT experiments at 125 MHz. Infrared spectra were recorded in pressed KBr pellets on a Perkin–Elmer PE-281 IR spectrophotometer. Melting points were measured using a Mel-Temp melting point apparatus and are uncorrected.

Preparation of $[p\text{-}ClCH_2C_6H_4SiO_{3/2}]_8$ *(1)*

p-(Chloromethyl)phenyltrichlorosilane (32.5 g, 0.125 mol) was added cautiously and with vigorous stirring to 200 ml of 85% acetone/water (v/v) in a 500 ml round-bottomed flask. The mixture was refluxed for two days, cooled to room temperature, then filtered to collect approximately one gram of microcrystalline **1**. Further crops of **1** were obtained from the filtrate over two months at room temperature to give a total yield of 1.33 g (0.935 mmol, 6.0%). Although the product obtained after washing with acetone is analytically pure, recrystallization can be performed by dissolving **1** in the minimum of CH_2Cl_2, tripling the volume with acetone, and cooling to $-30\,^\circ$C overnight. For several reactions performed on 1/10 the above scale the product yields were as high as 15%. m.p. > 400 °C (dec). ^{1}H NMR (300.15 MHz, $CDCl_3$, 25 °C) δ 7.725 (d, $J = 8.2$ Hz, 2H), 7.405 (d, $J = 8.1$ Hz, 2H), 4.570 (s, 2H). ^{13}C NMR (75.04 MHz, $CDCl_3$, 25 °C) δ 140.15 (*C*-CH_2), 134.56 (CH), 129.81 (*C*-Si), 128.08 (CH), 45.90 (CH_2). ^{29}Si NMR (49.7 MHz, $CDCl_3$, 25 °C) $\delta - 78.45$. IR (KBr) 3015vw, 2960vw, 1610m, 1560m, 1400m, 1270m, 1200m, 1120s, 1020s, 835w, 825w, 740m, 700s, 680s cm^{-1}. Anal. Calcd. (found) (%) for $C_{56}H_{48}Cl_8O_{12}Si_8$: C, 47.32 (47.47); H, 3.40 (3.36).

Preparation of $[p\text{-}ICH_2C_6H_4SiO_{3/2}]_8$ *(2)*

A suspension of **1** (200 mg, 0.141 mmol) and NaI (4.00 g, 26.7 mmol) in THF (20 ml) was refluxed for 10 h *in the dark*. After cooling to room temperature, the solids were removed by vacuum filtration and washed with CH_2Cl_2. Rotary evaporation of the solvent left a moist solid, which was extracted with 3 × 10 ml CH_2Cl_2. Rotary evaporation of solvent and recrystallization from CH_2Cl_2/acetone afforded a virtually quantitative yield (300 mg) of **2** as white, light-sensitive, microcrystals. m.p. > 400 °C (dec). ^{1}H NMR (300.15 MHz, $CDCl_3$, 25 °C) δ 7.642 (d, $J = 8.0$ Hz, 2H), 7.386 (d, $J = 8.0$ Hz, 2H), 4.431 (s, 2H). ^{13}C-NMR (75.04 MHz, $CDCl_3$, 25 °C) δ 142.06 (*C*-CH_2), 134.64 (CH), 129.30 (*C*-Si), 128.28 (CH), 4.97 (CH_2). ^{29}Si-NMR (49.7 MHz, $CDCl_3$, 25 °C) $\delta - 77.5$. IR (KBr) 3020vw, 2960vw, 1600m, 1400m, 1240m, 1200m, 1120s, 1020m, 840w, 820w, 690s cm^{-1}. Anal. Calcd. (found) (%) for $C_{56}H_{48}I_8O_{12}Si_8$: C, 31.24 (31.44); H, 2.25 (2.26).

Preparation of $[p\text{-}HOCH_2C_6H_4SiO_{3/2}]_8$ *(3)*

DANGER: *Mixtures of perchlorates, particularly heavy metal perchlorates (e.g.,* $AgClO_4$*), and organic compounds have been known to detonate. Although the authors* *have not experienced any explosions, they strongly recommend that this procedure be performed behind a protective barrier and only by experienced technicians educated in the use and hazards of perchlorates.* (See: Schilt, A.A. Perchloric Acid and Perchlorates; G. Frederick Smith Chemical Company: Columbus, Ohio, 1979, for leading references on the hazards of perchlorates.)

An acetone solution of $AgClO_4 \cdot H_2O$ (200 mg, 0.888 mmol) was added to a suspension of **2** (200 mg, 0.093 mmol) in 10 ml of 90% aqueous acetone. The precipitation of AgI began immediately and was complete after stirring for 2 h. Saturated brine (0.5 ml) was added to precipitate any unreacted silver ions, then the solids were removed by vacuum filtration and washed with acetone. Rotary evaporation of the filtrate to approximately 5 ml and the addition of water (5 ml) precipitated a fine white powder. The powder was dissolved in acetone, filtered through a thin pad of silica, concentrated to approximately 5 ml, and re-precipitated as an analytically pure white powder by the addition of $CHCl_3$. Yield: 112 mg (95%). m.p. > 400 ° C. ^1H NMR (500.1 MHz, acetone-d_6, 25 ° C) δ 7.78 (d, $J = 8$ Hz, 2H), 7.42 (d, $J = 8$ Hz, 2H), 4.645 and 4.632 (d, 2H for CH_2OH and CH_2OD). 4.25 (OH). ^{13}C-NMR (125.7 MHz, acetone-d_6, 25 ° C) δ 146.10 and 146.09 (C-CH_2), 134.15 (CH), 128.34 (C-Si), 126.33 (CH), 63.76 and 63.64 (for CH_2OH and CH_2OD). ^{29}Si-NMR (49.7 MHz, acetone-d_6, 25 ° C) δ −78.5. IR (KBr) 3330s, br, 3080, 3020w, 2900w, 1630w, 1610m, 1400s, 1190s, 1120vs, 1020s, 840w, 810s, 730w, 700s, 640w cm^{-1}. Anal. Calcd. (found) (%) for $C_{56}H_{56}O_{20}Si_8$: C, 52.80 (52.00); H, 4.43 (4.41).

Preparation of $[p\text{-}O_2NOCH_2C_6H_4SiO_{3/2}]_8$ (4)

Anhydrous acetonitrile (20 ml) was vacuum distilled (25 ° C, 10^{-3} mm Hg) into a flask containing **2** (200 mg, 0.0930 mmol) and $AgNO_3$ (220 mg, 1.30 mmol). The mixture was stirred for 2 h at room temperature, saturated brine (0.5 ml) was added, and the solids removed by vacuum filtration. Rotary evaporation of the volatiles, CH_2Cl_2 (3 × 10 ml) extraction, and rotary evaporation afforded a white solid, which was recrystallized from CH_2Cl_2/acetone to give 140 mg (93%) of **2** as analytically pure white microcrystals. m.p. > 400 ° C (dec). ^1H NMR (300.15 MHz, $CDCl_3$, 25 ° C) δ 7.761 (d, $J = 7.9$ Hz, 2H), 7.423 (d, $J = 7.9$ Hz, 2H), 5.434 (s, 2H). ^{13}C NMR (75.04 MHz, $CDCl_3$, 25 ° C) δ 135.25 (C-CH_2), 134.59 (CH), 130.69 (C-Si), 128.33 (CH), 74.23 (CH_2). ^{29}Si NMR (49.7 MHz, $CDCl_3$, 25 ° C) δ −78.6. IR (KBr) 3040vw, 2900vw, 1635s, 1400m, 1280s, 1200m, 1120vs, 1020w, 860s, 810m, 760w, 740w, 700w cm^{-1}.

Preparation of $[p\text{-}AcOCH_2C_6H_4SiO_{3/2}]_8$ (5)

A solution of **3** (30 mg, 0.0236 mmol) in acetic anhydride (5 ml) was stirred overnight at 50 ° C. Evaporation of the volatiles (25 ° C, 10^{-3} mm Hg) gave a white solid, which was dissolved in $CHCl_3$, filtered through a thin pad of silica, and rotary evaporated to afford a quantitative yield of **5** (38 mg) as white microcrystals. m.p. 258–262 ° C. ^1H NMR (250 MHz, $CDCl_3$, 25 ° C) δ 7.729 (d, $J = 8$ Hz, 2H), 7.356 (d, $J = 8$ Hz, 2H), 5.108 (s, 2H) 2.104 (s, 3H). ^{13}C NMR (125.03 MHz, $CDCl_3$, 25 ° C) δ 170.77, 138.76, 134.42, 129.71, 127.50, 65.95, 20.97. ^{29}Si NMR (49.7 MHz, $CDCl_3$, 25 ° C) δ −78.3. IR (KBr) 2950w, 1740s, 1610m, 1380m, 1240s, 1195m, 1110s, 1020m, 800m, 700m cm^{-1}.

Preparation of $[p\text{-}(p\text{-}O_2NC_6H_4CO)OCH_2C_6H_4SiO_{3/2}]_8$ *(6)*

p-$NO_2C_6H_4COCl$ (210 mg, 1.13 mmol) was added to a solution of **3** (30 mg, 0.0236 mmol) and dry pyridine (1.5 ml) in 5 ml of THF. After stirring overnight at 50 °C the mixture was filtered, the solids were washed with $CHCl_3$ and the volatiles (including the excess *p*-$NO_2C_6H_4COCl$) were removed in vacuo (80 °C, 10^{-3} mm Hg) to afford a nearly quantitative yield of crude **6**. Pale yellow crystals were obtained by dissolving the crude product in $CHCl_3$, filtering through a thin pad of silica, and crystallization by the addition of one volume of acetonitrile and slow evaporation overnight. The isolated yield of crystalline **6** was 46 mg (80%). m.p. 257–259 °C. ^1H NMR (500.1 MHz, $CDCl_3$, 25 °C) δ 8.272 (d, $J = 9$ Hz, 2H), 8.209 (d, $J = 9$ Hz, 2H), 7.769 (d, $J = 8$ Hz, 2H), 7.455 (d, $J = 8$ Hz, 2H), 5.398 (s, 2H). ^{13}C NMR (125.03 MHz, $CDCl_3$ 25 °C) δ 164.43 (CO), 150.66, 138.30, 135.16, 129.972 (C), 134.52, 130.80, 127.75, 123.59 (CH), 67.16 (CH_2). ^{29}Si NMR (49.7 MHz, $CDCl_3$, 25 °C) δ −78.5. IR (KBr) 1730s, 1610w, 1530s, 1350m, 1110s, 1020w, 810w, 720s, 690w cm^{-1}.

Preparation of $[p\text{-}(p\text{-}MeO_2CC_6H_4CO)OCH_2C_6H_4SiO_{3/2}]_8$ *(7)*

p-$ClCOC_6H_4COCl$ (420 mg, 2.07 mmol) was added to a solution of **3** (30 mg, 0.0236 mmol) and dry pyridine (1.5 ml) in 5 ml of THF. After stirring overnight at 50 °C methanol (5 ml) was added and stirring was continued for 2 h. The mixture was filtered, the solids were washed with $CHCl_3$ and the volatiles (including the excess *p*-$ClCOC_6H_4COCl$ as *p*-$MeO_2CC_6H_4Co_2Me$) were removed in vacuo (80 °C, 10^{-3} mmHg) to afford a nearly quantitative yield of crude **7**. Analytically pure material was obtained by dissolving the crude product in $CHCl_3$, filtering through a thin pad of silica, and crystallization by the addition of one volume of acetonitrile and slow evaporation overnight. The isolated yield of crystalline **7** was 55 mg (91%). m.p. 218–222 °C (dec). ^1H NMR (500.1 MHz, $CDCl_3$, 25 °C) δ 8.111 (d, $J = 8.7$ Hz, 2H), 8.081 (d, $J = 8.7$ Hz, 2H), 7.769 (d, $J = 8$ Hz, 2H), 7.451 (d, $J = 8$ Hz, 2H), 5.373 (s, 2H), 3.938 (s, 3H). ^{13}C NMR (125.03 MHz, $CDCl_3$, 25 °C) δ 166.18, 165.53 (CO), 138.54, 134.09, 133.64, 129.85 (C), 134.49, 129.65, 1290.57, 127.58 (CH), 66.75 (CH_2), 52.46 (CH_3). ^{29}Si NMR (99.36 MHz, $CDCl_3$, 25 °C) δ −78.37. IR (KBr) 1760s, 1280s, 1110s, 1020m, 730m cm^{-1}.

Results and discussion

The hydrolytic condensation of *p*-$ClCH_2C_6H_4SiCl_3$ in 90% aqueous acetone (65 °C, 48 h) affords **1**. Typical yields for the reaction are currently somewhat modest 6–15%, but optimization of the reaction, particularly the development of a base-catalyzed equilibrative condensation [4], should provide substantially improved yields. The structure of **1** was unequivocally established by NMR spectroscopy, elemental analysis, a solution molecular weight determination (Signer method) [5], and a single crystal X-ray diffraction study [6*].

The benzylic chloride moieties in **1** are remarkably inert toward substitution and are generally not amenable to high-yield synthetic manipulations, including simple hydrolysis. Compound **1** does not even react with $AgNO_3$ or $AgClO_4$ in aqueous acetone, THF or acetonitrile, or with freshly prepared moist Ag_2O. It is also uneffected by AgOAc in refluxing HOAc. Although **1** does react with more strongly

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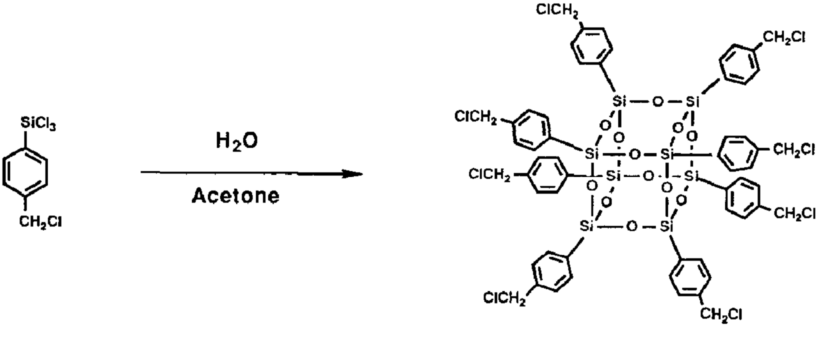
* Reference number with asterisk indicates a note in the list of references.



1

(1)

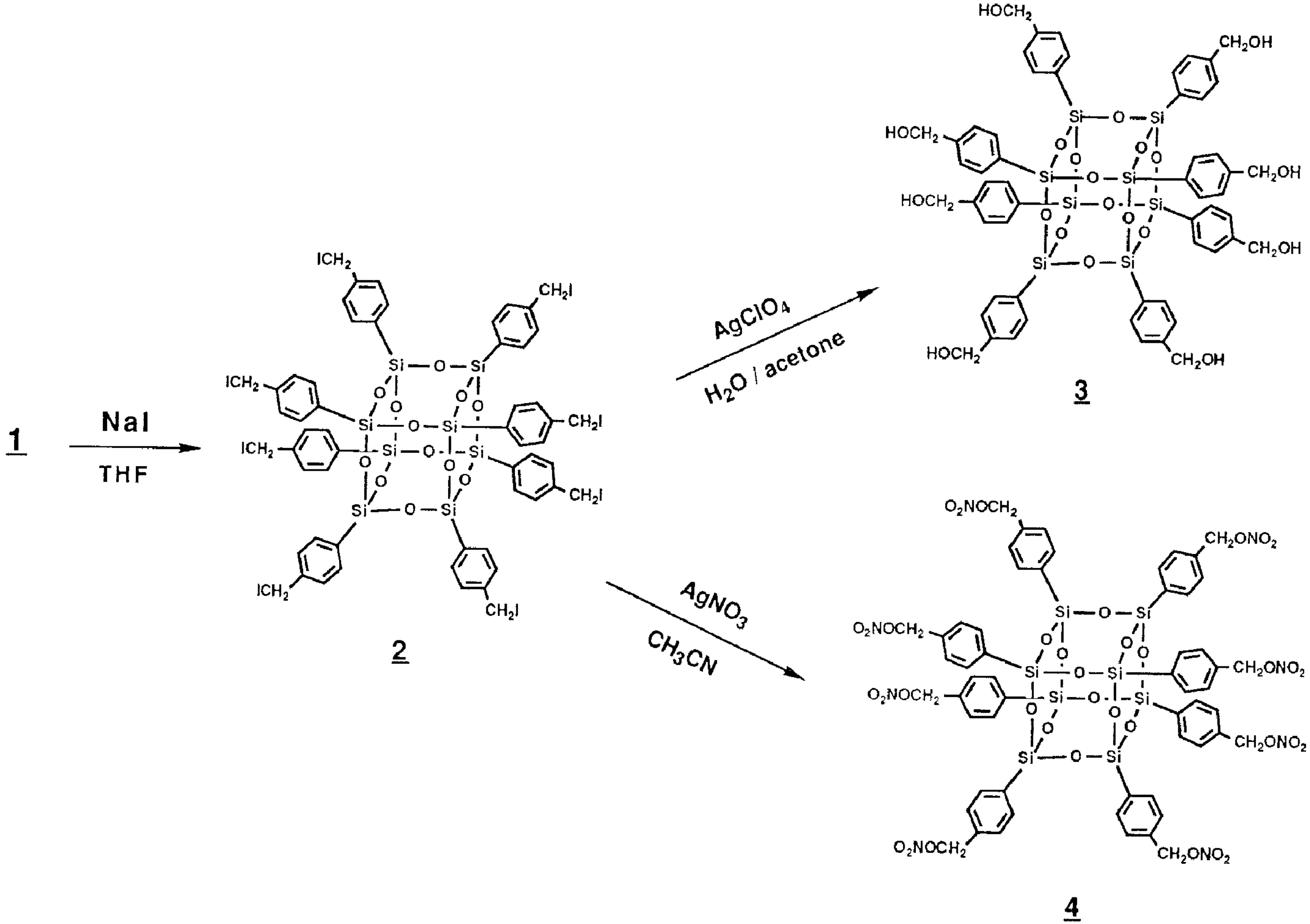
nucleophilic reagents, such as $[C_6H_5CH_2NMe_3]OH$, $[n\text{-}Bu_4N]CN$, and $[n\text{-}Bu_4N]N_3$, basic or strongly nucleophilic reagents usually induce rapid polymerization of the Si_8O_{12} frameworks, rather than the desired substitution, and generally must be avoided.

The inertness of **1** toward substitution and hydrolysis was initially somewhat surprising and prompted us to determine the electron-withdrawing capabilities of the Si_8O_{12} framework. Using the well-established [7] correlation between ^{13}C chemical shifts of substituted phenyl compounds and Hammett substituent constants, the electron-withdrawing tendency of the Si_8O_{12} framework was qualitatively established as being approximately equivalent to a trifluoromethyl group (i.e., CF_3). It is, therefore, not surprisingly that substitution, hydrolysis, and oxidation reactions occurring at the benzylic position are quite sluggish.

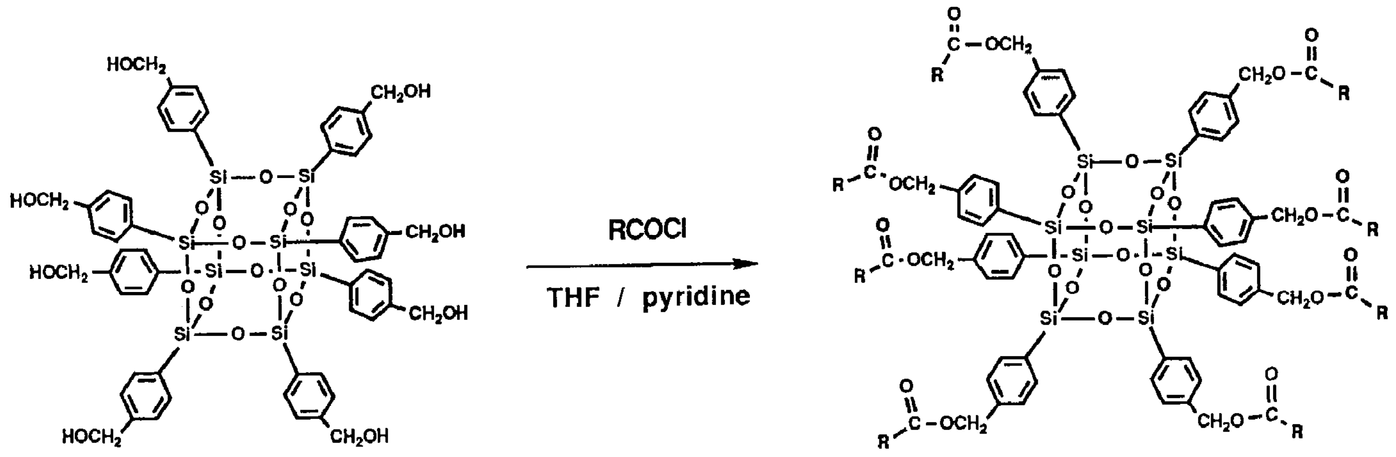
The inertness of **1** prevents it from being used directly to synthesize other functionalized silsesquioxanes, but the eight chlorides in **1** can be quantitatively replaced by iodide to afford **2**. Although **2** is inherently more reactive toward substitution than **1**, it is still remarkably inert for a molecule possessing eight benzylic iodide moieties. Even hydrolysis, which is normally very rapid for benzylic iodides, is surprisingly difficult. Compound **2** can be quantitatively recovered after refluxing overnight in aqueous acetone or THF. Quantitative hydrolysis was eventually effected using $AgClO_4$ (or Ag_2O in dilute aqueous $HClO_4$). Quite remarkably, if there is incomplete substitution of chloride during the synthesis of **2**, the residual chloride is uneffected by $AgClO_4$ [8*].

Although the use of perchlorates is generally undesirable, we have yet to find another reagent that is as efficient at hydrolyzing **2** as $Ag_2O/HClO_4$. The use of aqueous acetone solutions containing silver salts of other normally innocent anions (e.g., $AgNO_3$, AgOTs, AgOTf, etc.) produced large amounts of less reactive substitution products that cannot be easily hydrolyzed. Ag_2O and Ag_2CO_3 are unreactive under conditions that do not destroy the Si_8O_{12} framework, while silver salts with labile fluoride anions (e.g., $AgBF_4$ or $AgPF_6$) induce polymerization. Treatment of **2** with $AgNO_3$ in anhydrous acetonitrile [9] produces quantitative yields of the corresponding nitrate ester, but hydrogenolysis [10] of the N–O bond could not be accomplished without substantial hydrogenolysis of the benzylic $C\text{-}ONO_2$ and/or C–OH moieties.

Efficient procedures for oxidizing **3** to the aldehyde or carboxylic acid stages for further synthetic elaborations have remained elusive. The total insolubility [11*] of alcohol **3** in non-coordinating organic solvents (e.g., chlorocarbons, hydrocarbons)


1
NaI
THF
ICH$_2$
CH$_2$I
2
AgClO$_4$
H$_2$O / acetone
AgNO$_3$
CH$_3$CN
HOCH$_2$
CH$_2$OH
3
O$_2$NOCH$_2$
CH$_2$ONO$_2$
4
Si
O

(2)



(3)

3

5 R = Me

6 $p\text{-}O_2NC_6H_4$

7 $p\text{-}MeO_2CC_6H_4$

that are compatible with many oxidizing agents of choice seriously limits the number of reagents available. The acylation of **3** is, however, very facile and other potentially useful functional groups can be tethered from the Si_8O_{12} framework by the esterification of **3** with bifunctional acyl halides. For example, the reaction of **3** with *p*-nitrobenzoyl chloride gives **6**, while esterification with terephthaloyl chloride and methanolysis affords **7**. Many other such reactions are undoubtedly possible.

In summary, we have developed procedures for the syntheses of highly functionalized polyhedral oligosilsesquioxanes. We have also shown that the simultaneous quantitative manipulation of eight functional groups, although far from trivial, does not present a fundamental problem and that single greatest obstacle to the synthesis of highly-functionalized silsesquioxanes is the preparation of synthetically versatile precursors. The syntheses of **1** provides one such precursor. Forthcoming work from our laboratory will describe other approaches to the syntheses of highly functionalized silsesquioxanes.

Acknowledgements

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6 Chloride **1** crystallizes in the space group $R3$ bar ($a = b = 13.2961$ (25) Å and $c = 32.9743$ (97) Å). The crystallographic inversion center is located at the center of the Si_8O_{12} cube and a crystallographic three-fold rotational axis is aligned along the body diagonal. Although all of the atoms could be located, disordering of the *p*-$ClCH_2C_6H_4$ groups situated along the three-fold axis prevented a satisfactory solution of the structure.

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8 The extent of any reaction reported in this paper can be conveniently monitored by ^1H NMR spectroscopy: resonances for the various *p*-substituted phenyl groups occur at characteristic chemical shifts and are uneffected by the identity of remote functionality on adjacent *p*-substituted phenyl groups. For example, all benzylic groups containing chloride exhibit resonances identical to analytically pure **1**, while those containing iodide exhibit resonances identical to pure **2**. Unless otherwise specified, all reactions reported in this paper give pure (by ^1H NMR) octafunctional products.

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11 Samples of **4** in $CDCl_3$ or C_6D_6 do not give any detectable ^1H NMR signal attributable to **4**, even after 1000 scans at 500 MHz.