Facile, High-Yield Synthesis of Functionalized Spherosilicates: Precursors of Novel Organolithic Macromolecular Materials

Organolithic macromolecular materials (OMM's) are hybrids composed of silicate and organic moieties.[1-8] Recently, we reported[9] the successful implementation of a new strategy for the synthesis of OMM's that involves the use of functionalized spherosilicates[10] as "molecular building blocks".[11] This allows us to control the structure of both the silicate and the organic component of the OMM. However, progress in synthesizing and characterizing new OMM's has been hampered by the fact that the procedure used to synthesize the functionalized spherosilicates[10] involves many steps, some with very low yields, and is unsuitable for making large quantities of these materials.

We have now developed a facile one-pot procedure that gives pure $[Si_8O_{20}](Si(CH_3)_3)_8$ (**1**),[12] $[Si_8O_{20}](Si(CH_3)_2CHCH_2)_8$ (**2**),[10] and $[Si_8O_{20}](Si(CH_3)_2CH_2Cl)_8$ (**3**)[10] in high yields. All three of these compounds have a cubic spherosilicate core of composition $[Si_8O_{20}]$. In compound **1**, each of the terminal oxygen atoms of this core are capped by trimethylsilyl, $-Si(CH_3)_3$, groups, as shown in Figure 1. In compounds **2** and **3**, the capping groups are $-Si(CH_3)_2CHCH_2$ and $-Si(CH_3)_2CH_2Cl$, respectively.

In the experimental procedure, which is described in detail below, three solutions S1,[13] S2,[14] and S3[15] are mixed sequentially and the product is extracted from the reaction mixture with an immiscible hydrocarbon solvent.

The first solution, S1, contains silicon ($[Si] \approx 0.65$ M) that is present almost exclusively (98%) as the spherosilicate anion, $[Si_8O_{20}]^{8-}$. The composition of this solution was first described by Groennen et al. in 1986.[16]

The second solution, S2, contains both a silylating agent ($YSi(CH_3)_2OSi(CH_3)_2Y + HCl$; $Y = -CH_3, -CHCH_2, -CH_2Cl$) and a dehydrating agent (2,2-dimethoxypropane). Its use, as described below, is a novel feature of our synthesis that simplifies the entire procedure[12] and makes it more economical by reducing the amounts of organosilane reagents required.[17]

The third solution, S3, is a variant of the well-known trimethylsilylating mixture first described by Tamas et al. in 1977.[18]

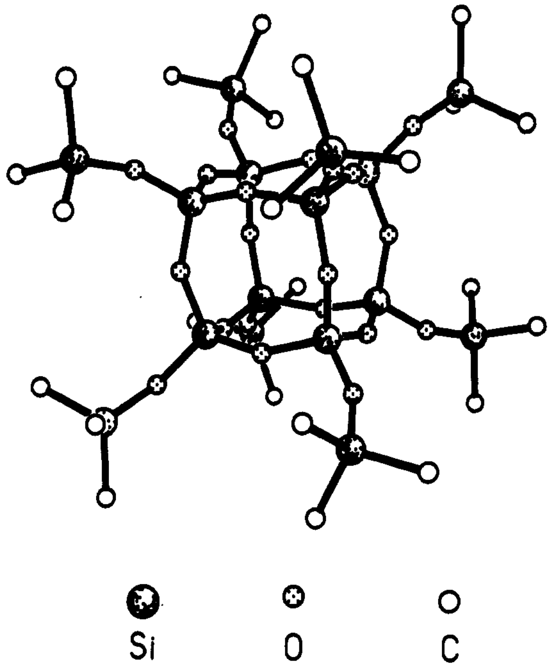

Figure 1. Ball-and-stick representation of the structure of $[Si_8O_{20}](SiCH_3)_3)_8$. In compounds **2** and **3** the $-Si(CH_3)_3$ groups capping the $[Si_8O_{20}]$ core are replaced by $-Si(CH_3)_2CHCH_2$ and $-Si(CH_3)_2CH_2Cl$ groups, respectively.

The actual synthesis is performed by first adding solution S1 (20 mL, 13 mmol of Si) dropwise, over a period of 20 min, to a flask containing solution S2. The mixture (S1 + S2) is then stirred for an additional 15 min. During these 35 min the reaction of H_2O in S1 and $(H_3CO)_2C(CH_3)_2$ in S2 leads to the formation of methanol and acetone while the $[Si_8O_{20}]^{8-}$ anion is partially silylated.[19] The low-boiling components of this mixture are removed by using a rotary evaporator (water aspirator, ~20 °C bath) over a period of 20 min. Solution S3 is then added to the biphasic residue to complete the silylation reaction[17] and the resultant mixture stirred for 15 min. *n*-Pentane (20 mL) and distilled H_2O (40 mL) are then added. After being stirred for 5 min, the two layers are separated and the volatile components of the nonaqueous layer are removed under vacuum.[20] The white almost dry residue (1.77 g, 96% yield[21] for **1**; 1.76 g, 89% yield for **2**; 2.1 g, 92% yield for **3**) is washed with CH_3OH (3 mL, 1.0% H_2O) and then recrystallized from acetonitrile[22] to give the pure compounds[23] **1** (1.50 g, 81%), **2** (1.18 g, 59%), and **3** (1.07 g, 47%).

The reactions as described above could be easily scaled up to provide much larger quantities of these compounds. Such easy accesses to them should make it possible to synthesize a wide range of OMM's that are designed to exhibit desirable properties.[9]

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(12) Compound **1** was first synthesized in 1971 (75% yield) from $((H_3C)_4N)_8[Si_8O_{20}]\cdot xH_2O$: (a) Hoebbel, Von D.; Wieker, W. *Z. Anorg. Allg. Chem.* **1971**, *384*, 43–52. (b) Smolin, Yu. I.; Shepelev, Yu. F.; Pomes, R. *Khim. Silik. Oksidov* **1982**, 68–85.

(13) Solution S1: [H_2O (20 mL) + $(H_3C)_4NOH$ (25% aqueous, 20 mL) + $(H_3CO)_4Si$ (8.1 mL)] + $(H_3C)_2SO$ (42.0 mL); OH:Si = 1:1; (H_2O, H_3COH):$(H_3C)_2SO$ = 1:1; [Si] = 0.65 M.

(14) Solution S2: $(H_3CO)_2C(CH_3)_2$ (70 mL) + HCl (~10 M, 3.0 mL) + $YSi(CH_3)_2OSi(CH_3)_2Y$ (10 mL) ($Y = -CH_3$ for **1**, $-CHCH_2$ for **2**, and $-CH_2Cl$ for **3**).

(15) Solution S3: [$(H_3C)_2NCHO$ (20 mL) + $YSi(CH_3)_2OSi(CH_3)_2Y$ (10 mL)] + $Y(CH_3)_2SiCl$ (5 mL) ($Y = -CH_3$ for **1**, $-CHCH_2$ for **2**, and $-CH_2Cl$ for **3**).

(16) Groennen, E. J.; Kortbeck, A. G. T. G.; Mackay, J.; Sudmeijer, O. *Zeolites* **1986**, *6*, 403–411.

(17) Compound **1** has been generated in good yields on an analytical scale by adding solution S1 directly to solution S3;[16] however, the use of solution S2 as an intermediate results in a 50-fold reduction in the amounts of organosilane reagents required.

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(19) Stirring this mixture overnight leads to complete silylation, but large amounts of side products such as $[Si_8O_{21}](Si(CH_3)_2Y)_{10}$, identified by mass spectrometry, are generated.

(20) Approximately 75–80% of the organosilane reagents can be recovered at this stage.

(21) Based on the amount of $[Si_8O_{20}]^{8-}$ used.

(22) Recrystallization by slow evaporation of solvent with about 1 mL of mother liquor discarded.

(23) Structure and purity established by comparison of mass spectra and ^1H, $^{13}C\{^1H\}$, and $^{29}Si\{^1H\}$ NMR spectra with those of the same compounds synthesized via another route.[10]

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