sumptions of these programs are outlined in the supplementary material. Within the constraints of the particular mechanism, all of the independent events that gave rise to *o*- to *o*-carborane isomerization were defined. For statistical reasons, symmetry-equivalent processes were considered as independent isomerization events. We then described the effect of each isomerization event on the relative positions of the boron atoms in *o*-carborane. A 2-dimensional array of size $n \times 10$ stored the ^{10}B concentrations for each of the 10 boron atoms for each of n independent isomerization events. The starting concentrations were those of the enriched compound: 96.2% for B(3), 20.2% for B(4)-B(12). For each isomerization event the movement of boron atoms within *o*-carborane was recorded by exchanging the appropriate concentrations in that row of the array, even if the concentrations were the same. After each independent isomerization event had occurred once, the ^{10}B concentration for each boron was averaged, and this average was used as the starting value for that boron in each event during the second cycle.

Following each cycle, the average ^{10}B concentration for each boron atom was printed out and the concentrations for the equivalent borons were added to give the intensity of a simulated resonance at that point in the isomerization. These were then compared to the normalized integrals of thermally isomerized 3-(^{10}B)-*o*-carborane as described under Results and Discussion. All of the mechanisms reached equilibrium after repeated cycles, giving rise to *o*-carborane resonances in the ratio 2:2:4:2 for B(9,12), B(8,10), B(4,5,7,11), and B(3,6), respectively. This feature served as a check on the proper functioning of the program's calculations.

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Supplementary Material Available: A summary of rearrangement assumptions used for programming, contents of programs used for simulations, and a sample program output for the cuboctahedral intermediate with triangular face rotation (26 pages). Ordering information is given on any current masthead page.

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A New Route to Alkoxysilanes and Alkoxysiloxanes of Use for the Preparation of Ceramics by the Sol-Gel Technique

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The preparation of $(EtO)_4Si$ from $Ca_3(SiO_4)O$, Ca_2SiO_4, and portland cement, $(EtO)_3SiOSi(OEt)_3$ from $Ca_2Zn(SiO_3)_2O$, $(n\text{-}PrO)_3SiOSi(O\text{-}n\text{-}Pr)_2OSi(O\text{-}n\text{-}Pr)_3$ from $Ca_3(SiO_3)_3$, $[(EtO)_2SiO]_4$ from $Ca_8(SiO_3)_4Cl_8$, and the bicyclic [5.5.1]- and [5.3.3]-isomers of $(EtO)_{10}Si_6O_7$ from $Cu_6(SiO_3)_6 \cdot 6H_2O$ and $Na_4Ca_4(SiO_3)_6$ is described. The route employed in these preparations has two variations. Both can be described in terms of three steps. In one, the synthesized silicate variation, the first step is the conversion of silica or an available silicate to a silicate having an ion with a framework that is the same as that of the product or similar to it. The second is either the conversion of this silicate to a silicic acid that is solvated by an alcohol and has a framework that is the same as or similar to that of the product or the conversion of this silicate to one or more corresponding partially alkoxylated silicic acids. The third is the conversion of the silicic acid or acids to the product. In the second, or the available silicate variation, the first step entails the acquisition of a silicate with the needed framework from natural or other sources and the last two steps involve conversions that are the same as those in the synthesized silicate variation. The procedures and conditions used in the route are discussed.

In the past few years tetraalkoxysilanes have been used frequently for the preparation of ceramics by the sol-gel process.[1-3] Very recently oligomeric alkoxysiloxanes have been considered for this same purpose.[4] Accordingly, good routes to these two types of compounds are of interest.

Here we present a simple new route to them. The route entails the conversion of a silicate to a silicic acid and then to the desired alkoxysilane or alkoxysiloxane.[5]

Two precedents for the route are provided by the conversion of sodium silicate solutions to polymeric alkoxysiloxanes[11] and the conversion with apparent framework retention of chrysotile asbestos, $Mg_3Si_2O_5(OH)_4$, to a polymeric allyloxysiloxane.[12] Another precedent is provided by the conversion to a very small extent (as a result of a byproduct reaction) of pseudowollastonite, $Ca_3(SiO_3)_3$, to $[(i\text{-}PrO)_2SiO]_3$.[13] A more distant precedent is furnished by the conversion of various metal silicates to oligomeric organosiloxysiloxanes.[14]

Experimental Section

$(EtO)_4Si$ from Tricalcium Silicate, $Ca_3(SiO_4)O$. An HCl-ethanol solution (7.54 N, 54.9 mL) was added slowly (9 mL/min) to a stirred, cooled (−10 °C) suspension of monoclinic tricalcium silicate, $Ca_3(SiO_4)O$, (Construction Technology Laboratories, Inc., Skokie, IL; powdered, 15.0 g) in ethanol (500 mL). The resulting mixture was added (~22 mL/min) to a solution of ethanol (500 mL) and toluene (1100 mL) that was being distilled (1 atm) at a moderate rate (~17 mL/min). After the addition had been completed, the distillation was continued until the amount of distillate was substantial (1.83 L). The remainder was filtered, and the solid was washed with pentane (75 mL). The filtrate and washings were combined, and the resulting solution was distilled. An

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[2] *Better Ceramics Through Chemistry*; Brinker, C. J., Clark, D. E., Ulrich, D. R., Eds.; North Holland: New York, 1984.

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[5] Preliminary accounts describing this route have been published,[6-8] and patents pertaining to it have been issued.[9,10]

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appropriate fraction of the distillate (97–100 °C, 80 Torr) was retained (6.07 g).

This fraction was shown to be 95% $(EtO)_4Si$ by gas chromatography. Accordingly, the contained yield of $(EtO)_4Si$ was 5.79 g (42%).

$(EtO)_4Si$ from γ-Calcium Orthosilicate, γ-Ca_2SiO_4. γ-Calcium orthosilicate, γ-Ca_2SiO_4 (Cerac, Inc., Milwaukee, WI; powdered, 11.0 g), was treated in a fashion similar to that used for the treatment of the $Ca_3(SiO_4)O$ in the previous synthesis (HCl–ethanol solution, 8.01 N, 33.5 mL).

The product (4.34 g) was shown by gas chromatography to be 99.8% $(EtO)_4Si$. The contained yield of product was thus 4.33 g (33%).

$(EtO)_4Si$ from Portland Cement. Portland cement (Maryneal zero C_3A Type III, Lone Star Industries, Inc., Houston, TX; 15.0 g)[15] was likewise treated in a fashion similar to that used for the treatment of the $Ca_3(SiO_4)O$ in the first synthesis (HCl–ethanol solution, 7.61 N, 54.5 mL).

By gas chromatography the product (4.77 g) was shown to be 94% $(EtO)_4Si$. The contained yield of $(EtO)_4Si$ was accordingly 4.48 g (41% with the assumption that the silicon content of the cement was the same as that typical for this cement, 9.91%).

Hardystonite, $Ca_2Zn(SiO_3)_2O$, from Wollastonite, $CaSiO_3$.[16] A mixture of wollastonite, $CaSiO_3$ (Mexico,[18] −200 mesh, 50.0 g), and ZnO (17.5 g) was heated in a Pt dish in air at ~1100 °C for 40 h. After being crushed to a powder, the mixture formed was heated at the same temperature for 50 h. The resulting solid was freed of brown particles by hand sorting and by sieving (200-mesh screen). The product was shown to be hardystonite by X-ray diffractometry (64.0 g, 95%).[19]

Hardystonite is readily soluble in dilute HCl.

$(EtO)_3SiOSi(OEt)_3$ from Hardystonite, $Ca_2Zn(SiO_3)_2O$. An HCl–ethanol solution (7.48 N, 56.3 mL) was added slowly (11 mL/min) to a stirred suspension of hardystonite, $Ca_2Zn(SiO_3)_2O$ (prepared as described above, −200 mesh, 20.0 g), in ethanol (500 mL). The resulting mixture was stirred for 13 min (intermittantly applied cold water bath) and filtered. The filtrate was cooled (ice bath) and then was added slowly (~12 mL/min) to a mixture of ethanol (500 mL) and toluene (1000 mL) that was being distilled (1 atm) at a moderate rate (~13 mL/min). After the addition had been completed, the distillation was continued until the amount of distillate was substantial (1.75 L). The remainder was decanted, and the decantate was concentrated with a rotary evaporator (50 °C bath). The concentrate was fractionally distilled, and an appropriate fraction of the distillate (91–95 °C, 2.5 Torr) was retained (6.53 g).

By gas chromatography this fraction was shown to be 97% $(EtO)_3SiOSi(OEt)_3$. Thus, the contained yield of $(EtO)_3SiOSi(OEt)_3$ was 6.31 g (29%).

Pseudowollastonite, $Ca_3(SiO_3)_3$, from Wollastonite, $CaSiO_3$. The work of Yamanaka and Mori furnished a precedent for this synthesis.[20] Wollastonite, $CaSiO_3$ (Mexico,[18] small pieces), was heated in a Pt dish at ~1265 °C for 75 h. The resulting solid was crushed and sieved (150-mesh screen). The product was shown to be pseudowollastonite with X-ray powder diffractometry:[21] IR (Nujol mull) 1100 (s, sh), 1070 (s), 990 (vs), 940 (vs), 925 (s, sh), 720 (s), 570 (m), 435 (s), 310 (s), 250 (m) cm^{-1}; XRD d (I/I_0) 5.91 (8), 5.67 (17), 5.07 (7), 4.36 (18), 3.82 (5), 3.77 (6), 3.42 (39), 3.28 (13), 3.23 (95), 2.81 (63), 2.70 (9), 2.52 (7), 2.45 (19), 2.37 (5), 2.35 (9), 2.22 (6), 2.18 (6), 2.12 (9), 2.12 (4), 2.05 (7), 2.00 (34), 1.99 (66), 1.98 (100), 1.94 (6), 1.85 (4), 1.84 (21), 1.83 (16), 1.76 (7), 1.71 (9), 1.69 (18), 1.62 (26), 1.61 (11), 1.57 (4), 1.55 (6), 1.55 (7), 1.54 (8), 1.53 (15), 1.52 (5), 1.48 (22), 1.47 (22), 1.46 (9), 1.45 (8), 1.44 (8), 1.42 (6), 1.41 (17), 1.40 (17) Å.

Pseudowollastonite is slowly soluble in dilute HCl.

$(n\text{-PrO})_3SiOSi(O\text{-}n\text{-}Pr)_2OSi(O\text{-}n\text{-}Pr)_3$ from Pseudowollastonite, $Ca_3(SiO_3)_3$. An HCl–1-propanol solution (80.2 mL, 5.90 N) and 1-propanol (20 mL) were successively added to a stirred suspension of pseudowollastonite, $Ca_3(SiO_3)_3$ (prepared as described above, −150 mesh, 25.0 g), in 1-propanol (1.20 L). The mixture was distilled (1 atm) until a substantial amount (1.07 L) of distillate had been collected. After the remaining mixture had been filtered, the retained solid was washed with pentane (250 mL) and the filtrate and washings were combined and concentrated in a filter flask under vacuum (room temperature). The concentrate (52 mL) was mixed with a solution made up of 1-propanol (250 mL) and an HCl-1-propanol solution (4.05 mL, 5.90 N), and the resulting solution was distilled (1 atm) until a substantial amount of distillate (269 mL) had been collected. The mixture remaining was twice subjected to a procedure in which it was diluted with pentane, filtered, and concentrated with a rotary evaporator (65 °C bath). After the concentrate from the second concentration step had been bulb-to-bulb distilled (122–196 °C bath, 0.01 Torr), the distillate was fractionally distilled and an appropriate fraction of the distillate (128–144 °C, 0.2 Torr) was retained (8.10 g).

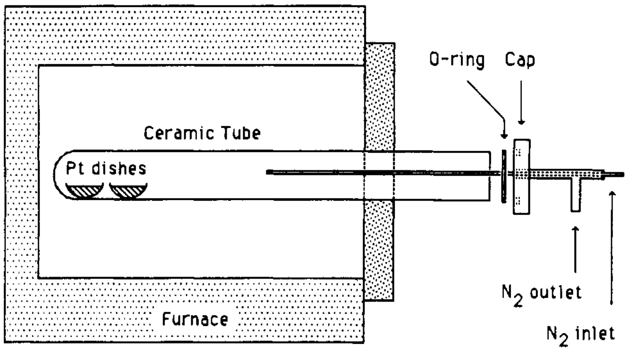

Figure 1. Apparatus used to heat silicate mixtures.

This fraction was shown by gas chromatography and gas chromatography–mass spectroscopy to be 94% $(n\text{-PrO})_3SiOSi(O\text{-}n\text{-}Pr)_2OSi(O\text{-}n\text{-}Pr)_3$: FTIR (neat) 2964 (s), 2938 (s), 2880 (s), 1465 (m), 1393 (w), 1264 (w), 1154 (m, sh), 1104 (vs), 1088 (vs), 1024 (s), 853 (m), 749 (m) 500 (m) cm^{-1}; GC–MS m/z [peak, relative intensity] 529 [$(M - OC_3H_7)^+$, 7], 235 [$((HO)_7Si_3O_2)^+$, 100], 217 [$(M - OC_3H_7 - 7C_3H_6 - H_2O)^+$, 49]. The contained yield of product was accordingly 7.58 g (18%).

$(n\text{-PrO})_3SiOSi(O\text{-}n\text{-}Pr)_2OSi(O\text{-}n\text{-}Pr)_3$ is a mobile, colorless liquid. It is stable to handling in air and to storage in a closed container.

$Ca_8(SiO_3)_4Cl_8$ from Wollastonite, $CaSiO_3$. A mixture of wollastonite, $CaSiO_3$ (Mexico,[18] powdered, 60.0 g), and $CaCl_2{\cdot}2H_2O$ (152 g) contained in two Pt dishes was placed in a horizontal, capped, test-tube-shaped ceramic vessel (8.4 × 83 cm) near the closed end of the vessel. With N_2 flowing through the vessel, the part of the assembly containing the mixture was heated slowly to 775 °C and held at this temperature for 16.5 h. During this step the N_2 flow was kept at a moderate rate until the rapid evolution of H_2O ceased, and then it was reduced to a slower rate (Figure 1). The resultant material was removed, crushed with a mortar and pestle in a N_2-filled glovebag, washed with methanol (450 mL) in air, and dried under vacuum at 100 °C. The product was shown by X-ray powder diffractometry to be $Ca_8(SiO_3)_4Cl_8$ (113 g, 97%):[21] IR (Nujol mull) 1063 (s), 1022 (s), 920 (s), 640 (m), 563 (m), 486 (m) cm^{-1}; XRD d (I/I_0) 7.57 (7), 7.05 (6), 5.35 (7), 4.67 (8), 3.98 (6), 3.78 (13), 3.52 (5), 3.38 (6), 3.33 (21), 2.99 (6), 2.94 (5), 2.83 (4), 2.74 (100), 2.68 (17), 2.61 (19), 2.50 (9), 2.39 (86), 2.34 (21), 2.32 (18), 2.15 (9), 2.13 (22), 2.10 (9), 2.09 (8), 1.99 (7), 1.92 (9), 1.89 (5), 1.84 (9), 1.79 (13), 1.77 (10), 1.73 (9), 1.71 (36), 1.69 (19), 1.67 (18) Å.

$Ca_8(SiO_3)_4Cl_8$ is a white solid. It is stable to handling in air and to storage in a closed container and is readily soluble in dilute HCl.

If air rather than N_2 is used in the high-temperature part of the synthesis, the yield of product is, as expected,[22] substantially reduced. Impurities in the wollastonite can lead to discoloration of the Pt ware.

$Ca_8(SiO_3)_4Cl_8$ from α-Quartz, SiO_2. The work of Chukhlantsev[22] and Wieker and co-workers[23] provided a precedent for this synthesis. A mixture of α-quartz, SiO_2 (Alfa Products, Danvers, MA; −325 mesh, 9.00 g), $CaCO_3$ (15.0 g), and $CaCl_2{\cdot}2H_2O$ (44.1 g) was treated, except for the heating step, in a fashion similar to that used for the treatment of the reaction mixture in the previous synthesis. In the heating step the reaction mixture was slowly heated to 820 °C, held at this temperature for 24 h, cooled to 770 °C, and held at this temperature for 48 h. The identity of the product was verified by powder X-ray diffractometry (33.7 g, 99%).[22]

Because the powder pattern of the product had several impurity lines that were not in the wollastonite-derived product, it was judged to be less

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(15) A generous gift of Lone Star Industries, Inc.

(16) Hardystonite has been synthesized previously by the devitrification of a glass having a stoichiometry the same as that of hardystonite.[17]

(17) Kolesova, V. A.; Ismatov, A. A.; Toropov, N. A. *Inorg. Mater. (Engl. Transl.)* **1969**, *5*, 1350; *Izv. Akad. Nauk SSSR, Neorg. Mater.* **1969**, *5*, 1594.

(18) Purchased from Ward's Natural Science Establishment, Inc., Rochester, NY.

(19) JCPDS International Center for Diffraction Data, Swarthmore, PA, File 12-453.

(20) Yamanaka, T.; Mori, H. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1981**, *B37*, 1010.

(21) JCPDS International Center for Diffraction Data, Swarthmore, PA, File 31-300.

(22) Chukhlantsev, V. G. *Dokl. Phys. Chem. (Engl. Transl.)* **1979**, *246*, 530; *Dokl. Akad. Nauk SSSR* **1979**, *246*, 1187.

(23) Winkler, A.; Ziemer, B.; Wieker, W. *Z. Anorg. Allg. Chem.* **1983**, *504*, 89.

pure. Data from experiments carried out during the development of this synthesis showed that it requires more vigorous reaction conditions than does the wollastonite-based synthesis.

$[(EtO)_2SiO]_4$[24] from $Ca_8(SiO_3)_4Cl_8$. An HCl–ethanol solution (101 mL, 9.12 N) was added slowly (20 mL/min) to a slurry of $Ca_8(SiO_3)_4Cl_8$ (prepared from wollastonite as described above, powdered, 100 g) in a solution of ethanol (1.60 L) and toluene (1.80 L), and the resulting mixture was distilled (1 atm) until a substantial amount of distillate (2.74 L) had been collected. The remainder was filtered, and the retained solid was washed with pentane (200 mL). The filtrate and washings were combined, and the solution formed was concentrated to an oil with a rotary evaporator (60 °C bath). This oil was mixed with ethanol (250 mL), toluene (250 mL), and an HCl–ethanol solution (6.0 mL, 9.12 N) and was slowly distilled (1 atm) until a considerable amount of distillate (388 mL) had been collected. The residue was concentrated with a rotary evaporator (65 °C bath) and then fractionally distilled. An appropriate fraction was retained (38.5 g) (boiling range and pressure data for the corresponding fraction of a similar run are 130–134 °C, 0.1 Torr).

This fraction was shown by gas chromatography, gas chromatography–mass spectroscopy, and ^{29}Si NMR spectroscopy to be 86% $[(EtO)_2SiO]_4$: FTIR (neat) 2979 (s), 2931 (s), 2895 (s), 1485 (w), 1445 (m), 1393 (s), 1368 (m), 1298 (m), 1157–1070 (vs, b), 975 (s), 800 (s), 724 (w), 636 (s), 461 (s) cm^{-1}; GC–MS *m/z* [peak, relative intensity] 491 [$(M - OC_2H_5)^+$, 41], 277 [$((HO)_5Si_4O_5)^+$, 100]; ^{29}Si NMR (39.7 MHz, $CDCl_3$, $Cr(acac)_3$)) δ −95.06 (s). The contained yield of product was thus 33 g (56%).

$[(EtO)_2SiO]_4$ is a mobile, colorless liquid. It is stable to handling in air and to storage in a closed container.

$[5.5.1](EtO)_{10}Si_6O_7$ and $[5.3.3](EtO)_{10}Si_6O_7$ from Dioptase, $Cu_6(SiO_3)_6{\cdot}6H_2O$. An HCl–ethanol solution (7.99 N, 58.4 mL) was added slowly (8 mL/min) to a suspension of dioptase, $Cu_6(SiO_3)_6{\cdot}6H_2O$ (Congo,[18] powdered, 35.0 g) in ethanol (1.00 L) and toluene (1.00 L). The resulting mixture was distilled (1 atm) until a considerable amount (1.79 L) of distillate had been collected. The remainder was filtered, and the retained solid was washed with pentane (75 mL). After the filtrate and washings had been combined, the solution formed was reduced to a concentrate (30 g) with a rotary evaporator (55 °C bath), and the concentrate was mixed with ethanol (250 mL), toluene (250 mL), and an HCl–ethanol solution (7.99 N, 2.3 mL). The resulting mixture was distilled (1 atm) until a substantial amount (387 mL) of distillate had been collected. The residue was doubly distilled (160–185 °C bath, ~0.01 Torr), and the distillate from the second distillation was retained (13.0 g).

By gas chromatography, gas chromatography–mass spectrometry, and ^{29}Si NMR spectroscopy, the distillate was shown to contain 43% $[5.5.1](EtO)_{10}Si_6O_7$: GC–MS *m/z* [peak, relative intensity] 685 [$(M - OC_2H_5)^+$, 6], 415 [$((HO)_7Si_6O_8)^+$, 100]; ^{29}Si NMR (39.7 MHz, $CDCl_3$, $Cr(acac)_3$, isomer mixture) δ −95.56, −101.55. The contained yield of this isomer was thus 5.5 g (20%).

In addition, the distillate was shown to contain 29% $[5.3.3](EtO)_{10}Si_6O_7$: GC–MS *m/z* [peak, relative intensity] 685 [$(M - OC_2H_5)^+$, 12], 415 [$((HO)_7Si_6O_8)^+$, 100]; ^{29}Si NMR (39.7 MHz, $CDCl_3$, $Cr(acac)_3$, isomer mixture) δ −94.69, −96.65, −101.27. The contained yield of this isomer was accordingly 3.8 g (14%).

The product was a clear, pale yellow, somewhat viscous liquid. It was stable to handling in air and to storage in a closed container.

$Na_4Ca_4(SiO_3)_6$ from α-Quartz, SiO_2.[26] A mixture of Na_2CO_3 (40.6 g), $CaCO_3$ (76.8 g), and α-quartz, SiO_2 (Alfa Products, −325 mesh, 69.1 g), was heated in two Pt dishes in air at ~1080 °C for 7 h, crushed and reheated at ~1080 °C in a Pt dish for 8.5 h, and recrushed and reheated at ~1080 °C for 6.5 h. The resulting solid was heated at ~1240 °C for 49 h. The product was shown by powder X-ray diffractometry to be $Na_4Ca_4(SiO_3)_6$ (128 g, 94%):[27] IR (Nujol mull) 1035 (s, b), 915 (vs, b), 730 (m), 700 (w), 630 (m), 615 (m), 535 (m), 450 (s), 290 (m) cm^{-1}; XRD d (I/I_0) 12.21 (4), 9.05 (4), 7.45 (8), 5.32 (5), 5.22 (4), 4.86 (8), 4.39 (12), 3.95 (7), 3.73 (45), 3.42 (10), 3.36 (34), 3.31 (67), 3.15 (4), 3.09 (5), 3.02 (14), 2.94 (3), 2.78 (5), 2.70 (17), 2.67 (86), 2.62 (100), 2.57 (8), 2.53 (12), 2.52 (7), 2.49 (5), 2.47 (8), 2.38 (4), 2.35 (15), 2.28 (7), 2.23 (10), 2.20 (10), 2.18 (5), 2.14 (17), 2.09 (6), 2.06 (9), 2.03 (6), 2.02 (5), 2.00 (10), 1.98 (5), 1.96 (9), 1.90 (6), 1.87 (95), 1.84 (10), 1.81 (14), 1.80 (14), 1.77 (5), 1.76 (3), 1.75 (10), 1.72 (4), 1.70 (12), 1.68 (7), 1.65 (21), 1.63 (7), 1.62 (7), 1.60 (7), 1.58 (9), 1.57 (5), 1.55 (28) Å.

$Na_4Ca_4(SiO_3)_6$ is a white, nonhygroscopic, stable solid. It is soluble in dilute HCl.

$[5.5.1](EtO)_{10}Si_6O_7$ and $[5.3.3](EtO)_{10}Si_6O_7$ from $Na_4Ca_4(SiO_3)_6$. $Na_4Ca_4(SiO_3)_6$ (prepared as described above, powdered, 50.0 g) was treated in a fashion similar to that used for the treatment of the dioptase in the previous synthesis (HCl–ethanol solution, 6.71 N, 133 mL).

The product (35.6 g) was shown by gas chromatography, gas chromatography–mass spectrometry, and ^{29}Si NMR spectroscopy to contain 46% $[5.5.1](EtO)_{10}Si_6O_7$: GC–FT IR (Ar matrix) 2984 (m), 2936 (w), 2905 (w), 1445 (w), 1397 (w), 1370 (w), 1300 (w), 1161 (m), 1105 (vs), 984 (m), 971 (m, sh), 817 (m), 801 (m) cm^{-1}. In addition it was shown to contain 28% $[5.3.3](EtO)_{10}Si_6O_7$: GC–FT IR (Ar matrix) 2983 (m), 2935 (m), 2904 (m), 1485 (w), 1445 (w), 1397 (m), 1369 (w), 1300 (w), 1162 (s), 1106 (vs), 982 (m), 969 (m), 815 (m, sh), 799 (m) cm^{-1}. Accordingly, the contained yield of $[5.5.1](EtO)_{10}Si_6O_7$ was 16.2 g (31%) and the contained yield of $[5.3.3](EtO)_{10}Si_6O_7$ was 10.1 g (20%).

The product was a clear, colorless, somewhat viscous liquid. It was stable to handling in air and to storage in a closed container.

Instrumentation. A Varian Vista 4600 gas chromatograph (Varian Associates, Inc., Palo Alto, CA) equipped with a flame-ionization detector was used to collect the gas chromatograms. The chromatograph was fitted with a DB-5 FSOT column (15 m × 0.32 mm, J & W Scientific, Inc., Rancho Cordova, CA) and was interfaced to a Varian Vista 401 chromatography data station. Perkin-Elmer IR 598 (Perkin-Elmer Corp., Norwalk, CT) and Mattson Cygnus 25 (Mattson Instruments, Inc., Madison, WI) infrared spectrophotometers were used to record the conventional infrared spectra. For the gas chromatography–infrared spectra, a Mattson Sirius 100 Fourier transform infrared spectrophotometer coupled with a Perkin-Elmer Sigma 2000 capillary gas chromatograph was used. The column employed was a DB-5 FSOT column (30 m × 0.32 mm). For the mass spectra, a Hewlett-Packard 5970 A Series mass-selective detector (Hewlett-Packard Co., Palo Alto, CA) interfaced with a Hewlett-Packard 5790 A Series gas chromatograph was used. In some determinations the chromatograph was fitted with an SE-54 (G.E. Silicone Products Department, Waterford, NY) FSOT capillary column (40 m × 0.25 mm, Supelco, Inc., Bellefonte, PA) and in others with a SPB-5 FSOT capillary column (60 m × 0.25 mm, Supelco). A Philips APD 3520 auto diffractometer (Philips Electronic Instruments, Inc., Mahwah, NJ) equipped with an XRG 3100 X-ray generator was used to collect the powder data. The generator was operated at 40 kV and 30 mA. The Cu Kα radiation produced was passed through a graphite monochromator. Counter techniques were used to determine the positions and intensities of the lines.

Discussion

Structures of Silicon-Containing Reactants and Products. The structures of the sole or predominant silicate ions in the silicate reactants are all well established. Thus, the silicate ion in γ-calcium orthosilicate, Ca_2SiO_4,[28] and in monoclinic tricalcium silicate, $Ca_3(SiO_4)O$,[29] is the orthosilicate ion; the predominant silicate ion in portland cement is also the orthosilicate ion;[30] the silicate ion in hardystonite, $Ca_2Zn(SiO_3)_2O$, is the disilicate ion;[31] the ion in pseudowollastonite, $Ca_3(SiO_3)_3$, is the cyclotrisilicate ion;[20] that in $Ca_8(SiO_3)_4Cl_8$ is the cyclotetrasilicate ion;[32] that in dioptase, $Cu_6(SiO_3)_6{\cdot}6H_2O$, and $Na_4Ca_4(SiO_3)_6$ is the cyclohexasilicate ion;[33-35] and that in wollastonite, $CaSiO_3$, is the infinite linear silicate ion.[36] The structure of the silica reactant, α-quartz, is also well established and is an infinite, three-dimensionally cross-linked structure.[37]

The structures of the silicate ions in the silicate reactants and of α-quartz are shown in Figure 2. The structures of the alk-

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(24) $[(EtO)_2SiO]_4$ is a known compound.[25]

(25) Marsmann, H. C.; Meyer, E.; Vongehr, M.; Weber, E. F. *Makromol. Chem.* **1983**, *184*, 1817.

(26) $Na_4Ca_4Si_6O_{18}$ has been prepared earlier by the crystallization of a melt having a stoichiometry the same as that of $Na_4Ca_4Si_6O_{18}$.[27]

(27) Dent Glasser, L. S.; Mileson, J. S. *J. Am. Ceram. Soc.* **1968**, *51*, 55.

(28) Udagawa, S.; Urabe, K.; Natsume, M.; Yano, T. *Cem. Concr. Res.* **1980**, *10*, 139.

(29) Nishi, F.; Takéuchi, Y.; Maki, I. *Z. Kristallogr.* **1985**, *172*, 297.

(30) Guinier, A.; Regourd, M. In *Proceedings of the Fifth International Symposium on the Chemistry of Cement*; The Cement Association of Japan: 1969; Vol. 1, Part I, p 1.

(31) Louisnathan, S. J. *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.* **1969**, *130*, 427.

(32) Golovastikov, N. I.; Kazak, V. F. *Sov. Phys.—Crystallogr. (Engl. Transl.)* **1977**, *22*, 549; *Kristallografiya* **1977**, *22*, 962.

(33) Ribbe, P. H.; Gibbs, G. V.; Hamil, M. M. *Am. Mineral.* **1977**, *62*, 807.

(34) Belov, N. V.; Maksimov, B. A.; Nozik, Yu. Z.; Muradyan, L. A. *Sov. Phys.—Dokl. (Engl. Transl.)* **1978**, *23*, 215; *Dokl. Akad. Nauk SSSR* **1978**, *239*, 842.

(35) Ohsato, H.; Takéuchi, Y.; Maki, I. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1986**, *42*, 934.

(36) Ohashi, Y. *Phys. Chem. Mineral.* **1984**, *10*, 217.

(37) Wright, A. F.; Lehmann, M. S. *J. Solid State Chem.* **1981**, *36*, 371.

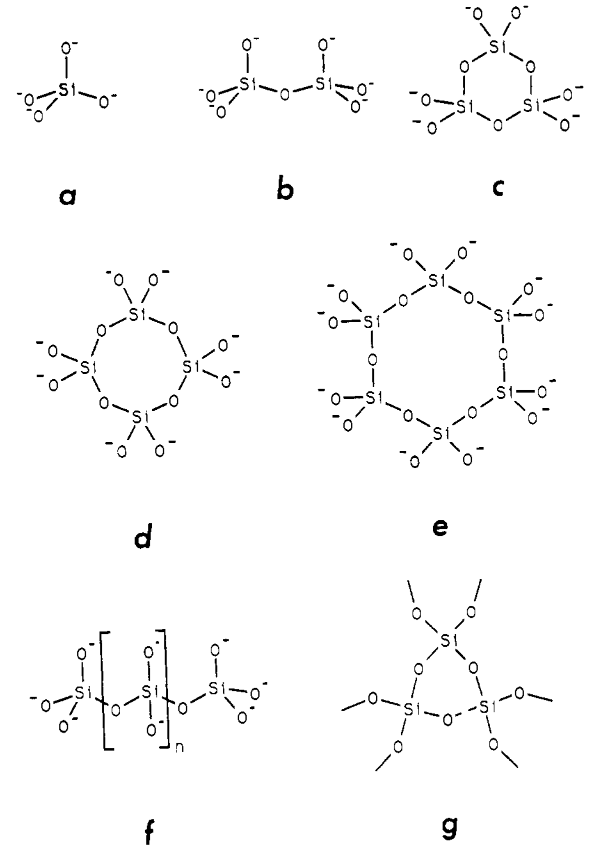

Figure 2. Structures of the (a) SiO_4^{4-}, (b) $(SiO_3)_2O^{6-}$, (c) $(SiO_3)_3^{6-}$, (d) $(SiO_3)_4^{8-}$, (e) $(SiO_3)_6^{12-}$, and (f) $(SiO_3)_n^{2n-}$ ions and structure of (g) quartz, SiO_2.

oxysilane and alkoxysiloxane products are shown in Figure 3.

Operational Description of Alkoxysilane and Alkoxysiloxane Route. The alkoxysilane and -siloxane route described here has two variations. In one, the synthesized silicate variation, the first step is the conversion of silica or an available silicate to a silicate with an ion having a framework that is the same as the framework of the desired alkoxysilane or alkoxysiloxane or is similar to it. The second step is the conversion of this silicate to a silicic acid that is solvated by an alcohol and has a framework that is the same as that of the product or is similar to it or the conversion of the silicate to one or more corresponding partially alkoxylated silicic acids. The third step is the conversion of the silicic acid or acids to the desired product. In the second variation of the route, the available silicate variation, the last two steps are the same. The first step is the acquisition of a silicate with the needed framework from natural, industrial, or laboratory supply sources.

The wollastonite–$Ca_8(SiO_3)_4Cl_8$ synthesis of $[(EtO)_2SiO]_4$ provides an example of the synthesized silicate variation. Here, if an unalkoxylated silicic acid is assumed to be the silicic acid intermediate, the appropriate equations are

$$\mathrm{CaSiO_3 + CaCl_2{\cdot}2H_2O \xrightarrow[\Delta]{N_2} Ca_8(SiO_3)_4Cl_8} \tag{1}$$

$$\mathrm{Ca_8(SiO_3)_4Cl_8 + H^+ + EtOH \rightarrow [(HO)_2SiO]_4{\cdot}\mathit{x}EtOH} \tag{2}$$

$$\mathrm{[(HO)_2SiO]_4{\cdot}\mathit{x}EtOH + EtOH \xrightarrow{H^+} [(EtO)_2SiO]_4} \tag{3}$$

An example of the available silicate variation of the route is furnished by the synthesis of $(EtO)_4Si$ from tricalcium orthosilicate. For this example, if again an unalkoxylated silicic acid is assumed to be the silicic acid intermediate, the equations are

$$\mathrm{Ca_3(SiO_4)O + H^+ + EtOH \rightarrow (HO)_4Si{\cdot}\mathit{x}EtOH} \tag{4}$$

$$\mathrm{(HO)_4Si{\cdot}\mathit{x}EtOH + EtOH \xrightarrow{H^+} (EtO)_4Si} \tag{5}$$

It is presumed that the alcohol solvating the silicic acid produced in the second step is held in position largely by hydrogen bonding.

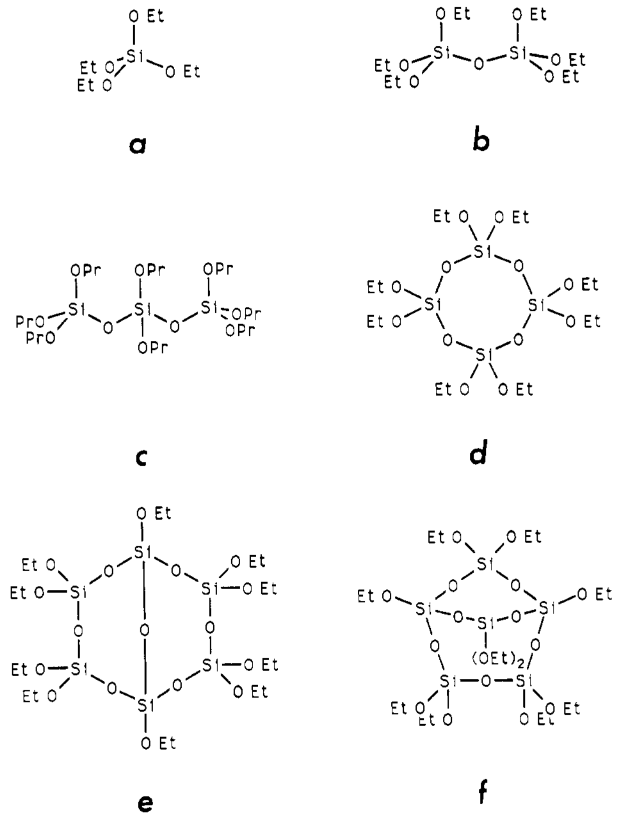

Figure 3. Structures of (a) $(EtO)_4Si$, (b) $(EtO)_3SiOSi(OEt)_3$, (c) $(n\text{-}PrO)_3SiOSi(O\text{-}n\text{-}Pr)_2OSi(O\text{-}n\text{-}Pr)_3$, (d) $[(EtO)_2SiO]_4$, (e) $[5.5.1]\text{-}(EtO)_{10}Si_6O_7$, and (f) $[5.3.3](EtO)_{10}Si_6O_7$.

It also presumed that the conversion of the silicic acid to the product occurs mostly after the temperature has been raised.

Alternative Descriptions of the Route. In polymer chemistry terms the first step of the synthesized silicate variation of the route in the examples given can be described as a depolymerization.[38] If an unalkoxylated silicic acid is assumed as the silicic acid intermediate, the second step of both variations can be described in all cases as a pendent group addition accompanied by a solvation. Finally, the third step of both variations can be described as a pendent group displacement that is catalyzed by acid and assisted by azeotropic dehydration.[39,41]

For instance, the wollastonite–$Ca_8(SiO_3)_4Cl_8$ synthesis of $[(EtO)_2SiO]_4$ can be accounted for as a chain-to-ring depolymerization, a proton addition accompanied by a solvation, and a displacement of a silanol group by an ethoxy group that is catalyzed by acid and assisted by azeotropic dehydration.

$$\mathrm{(SiO_3)_n^{2n-} \xrightarrow[\Delta]{} (SiO_3)_4^{8-} \xrightarrow[EtOH]{H^+} [(HO)_2SiO]_4{\cdot}\mathit{x}EtOH \xrightarrow{EtOH} [(EtO)_2SiO]_4} \tag{6}$$

Likewise, the wollastonite–hardystonite synthesis of $(EtO)_3SiOSi(OEt)_3$ can be accounted for as an oxide ion addition depolymerization, a proton addition accompanied by a solvation, and a displacement of a silanol group by an ethoxy group that is catalyzed by acid and assisted by azeotropic dehydration.

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(38) Examples in which this step can be described as an oligomerization, an isomerization, or an equilibration can be envisioned. For instance, the conversion of a hydroxyorthosilicate to a pyrosilicate would be an example of an oligomerization, the conversion of one cyclosilicate to another would be an example of an isomerization, and the conversion of an orthosilicate and silica to a cyclosilicate would be an example of an equilibration.

(39) A toluene–ethanol–water azeotrope (12% water) was formed in all alkoxysilane and alkoxysiloxane syntheses except the $(n\text{-}PrO)_3SiOSi(O\text{-}n\text{-}Pr)_2OSi(O\text{-}n\text{-}Pr)_3$ synthesis. In the latter a 1-propanol–water azeotrope (28% water) was formed.[40]

(40) Horsley, L. H. *Azeotropic Data-III*; Advances in Chemistry 116; American Chemical Society: Washington, DC, 1973; pp 18 and 460.

(41) The mechanistic details of this displacement are unknown.

$$(SiO_3)_n^{2n-} \xrightarrow[\Delta]{O^{2-}} O_3SiOSiO_3^{6-} \xrightarrow[EtOH]{H^+} (HO)_3SiOSi(OH)_3\cdot xEtOH \xrightarrow{EtOH} (EtO)_3SiOSi(OEt)_3 \quad (7)$$

The steps of the synthesis can also be thought of in classical chemical terms. Thus, the first step of the synthesized silicate variation in some instances can be thought of as an acid–base reaction, and the last two steps of both variations generally can be thought of as an acid–base reaction accompanied by a solvation and an esterification. For example, the hardystonite–wollastonite synthesis of $(EtO)_3SiOSi(OEt)_3$ can be viewed as a Lux–Flood acid–base reaction, a Brønsted–Lowry acid-base reaction accompanied by an ethanol solvation, and an ethanol esterification.

Procedures and Conditions. Step 1. The silicate acquisitions made in the examples of the available silicate variation of the route and the silicate syntheses carried out in the examples of the synthesized silicate variation of the route offered no particular difficulties. This and the known existence of a large number of silicates that are reasonably readily obtainable or preparable suggest that the first step in both variations will generally present few problems.

Step 2. The silicates and other reactants used in the second step of the examples of both variations are well suited to the purposes for which they were used. On the basis of the findings from the examples and the requirements of the general approach, it is concluded that the main criteria that the silicates used in the route must meet are (1) the possession of the proper framework, (2) the ability to undergo ready acid attack, and (3) the ability to give reaction products that do not form protective layers on their surfaces. Accordingly, it appears that many silicates can be used in the route. In particular, it appears that a number of calcium silicates and some hydrated silicates can be used.

No acids other than HCl were tried in the route. However, it is believed that other strong acids can serve satisfactorily in the second step.

Exploratory experiments with 2-propanol and 1-butanol showed that these alcohols work well in the route. On the basis of this and the satisfactory functioning of ethanol and 1-propanol in the route, it is concluded that a variety of primary and secondary alcohols can be used in the second step.

In the examples in which pure silicates were used, the silicate-to-alcohol ratios and silicate-to-acid ratios employed while the main part of this step was being carried out were quite low and just under unity, respectively. These ratios were used to help control self-condensation and cleavage of the silicic acids and thus to aid in the formation of the desired products. The low temperatures employed in some of the examples while this step was being carried out were used for the same reason.

Step 3. As with the second step, it appears that strong acids other than HCl can be used in the third step. From the results of the exploratory experiments with 2-propanol and 1-butanol and from the results of the examples, it also appears that, again as with the second step, a variety of primary and secondary alcohols can be used.

The low silicic acid-to-alcohol ratios and high silicic acid-to-HCl ratios employed while the main part of this step was being carried out were used to further help control structural rearrangements of the silicic acid intermediates and to help control rearrangements of the alkoxide products.[42]

Framework Alterations. The ring opening that occurs during the synthesis of $(n\text{-PrO})_3SiOSi(O\text{-}n\text{-Pr})_2OSi(O\text{-}n\text{-Pr})_3$ from pseudowollastonite could occur in either the second step or the third step or in both. It can be attributed to a proton-assisted cleavage of the siloxane ring in the parent silicate enhanced by the strain inherent in the six-membered siloxane ring.

Likewise the rearrangements that take place in the synthesis of the [5.5.1]- and [5.3.3]-isomers of $(EtO)_{10}Si_6O_7$ from dioptase and from $Na_4Ca_4(SiO_3)_6$ also could occur in either the second step or the third step or in both. In the case of the [5.5.1]-isomer the rearrangement can be assigned to a proton-catalyzed silanol–silanol condensation. With the [5.3.3]-isomer, the rearrangement can be ascribed to a proton-assisted ring cleavage followed by two proton-catalyzed ring closures.

In view of what is known about siloxane chemistry, the occurrence of rearrangements like these is not surprising even though mild conditions are used. Their occurrence stresses the need for the use of mild conditions in the route.

Conclusions. The route offers a path to alkoxysilanes and alkoxysiloxanes that is simple and versatile. In addition, it opens a way to alkoxysiloxanes that are not easily available by other means. In many instances it uses readily accessible starting materials[43] and gives nontoxic byproducts. Some of the alkoxysilanes and alkoxysiloxanes to which it leads may be of interest as ceramic precursors.

Acknowledgment. We thank Ralph E. Temple, Dale R. Pulver, and F. W. Gordon Fearon for helpful discussions. In addition, we thank Diamond Shamrock and Dow Corning for financial support.

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(42) The pentane employed in the $(n\text{-PrO})_3SiOSi(O\text{-}n\text{-Pr})_2OSi(O\text{-}n\text{-Pr})_3$ synthesis in the workup subsequent to the third step was used to precipitate the byproduct $CaCl_2$ and thus facilitate its separation.

(43) Quartz comprises 18% by volume of the earth's crust and is the third most abundant mineral in it.[44] Wollastonite is a common mineral and is mined commercially at Willsboro, NY.

(44) Wedepohl, K. H. *Geochemistry*; Holt, Rinehart and Winston: New York, 1971; p 67.