Synthesis of Hexakis(alkylgermasesquioxane)s from Alkyl(chloro)ethoxygermanes and Their Formation Mechanism

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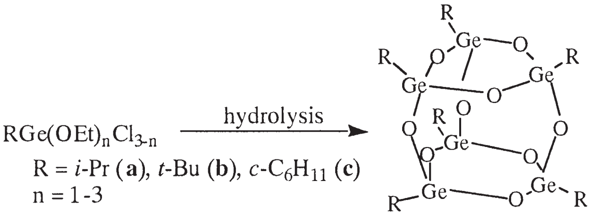
Alkyl(chloro)ethoxygermanes were hydrolyzed with water to give 1,3,5-trialkyl-1,3,5-trichlorocyclotrigermoxanes. Hydrolysis of 1,3,5-trichlorocyclotrigermoxanes gave 5,7-dichloro-1,3,5,7,9,11-hexaalkyltricyclo[7.3.1.1^{3,7}]-hexagermoxanes. The tricylic *anti*-form ladder hexagermoxanes reacted with water to afford hexakis(alkylgermasesquioxane)s. These cage and ladder germoxanes were identified by spectrospcopic and X-ray diffraction methods.

Organosilsesquioxanes with the formula $(RSiO_{1.5})_n$ containing Si-O bonds as a main chain have been of considerable interest because of their unusual structures and properties, and as new materials.[1] Matsumoto, Unno, and co-workers,[2] and other groups[3–7] reported the synthesis of cage, ladder, and sheet-like oligomers and polymers of $(RSiO_{1.5})_n$ and established their structures by X-ray analysis. They are found to be organometallic analogues of silicate anions, $(Si_nO_{2.5n})^{n-}$. The modified silicate can be used as pre-ceramic building blocks,[8] organolithic macromolecular materials,[9] heterogeneous silica-supported metal catalyst,[10] potential photoresists,[11–13] and so on. While the organosilsesquioxanes have been amply investigated, there have been few reports on organogermasesquioxanes.[14] We describe herein the synthesis of hexakis(alkylgermasesquioxane)s by hydrolysis of alkyl(chloro)ethoxygermanes and cyclic germoxanes as intermediates of the cage germoxanes, and determination of these structures by X-ray diffraction methods.

The alkyl(chloro)ethoxygermanes, $RGe(OEt)_nCl_{3-n}$ ($R =$ *i*-Pr, $n = 0$; $R =$ *t*-Bu, $n = 0$–3; $R =$ *c*-C_6H_{11}, $n = 0$) reacted with aqueous NaOH solution in xylene at 130–140 °C for 3 h. The concentration of the reaction mixture by evaporation of xylene followed by crystallization from pentane gave colorless crystals with a composition of hexakis(alkylgermasesquioxane)s, $(RGe)_6O_9$, **1a–c** in 60–98% yields.



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The germasesquioxane **1a–c** was fully established by spectroscopic and X-ray diffraction methods. As a typical example, a molecular structure of hexakis(*iso*propylgermasesquioxane), $(i\text{-}PrGe)_6O_9$, **1a** is shown in Figure 1.[15] The average Ge–O bond length is 1.755 Å in six- and eight-membered rings. The average O–Ge–O and Ge–O–Ge bond angles are 108° and 130.5°, respectively. All these values are within the normal range,

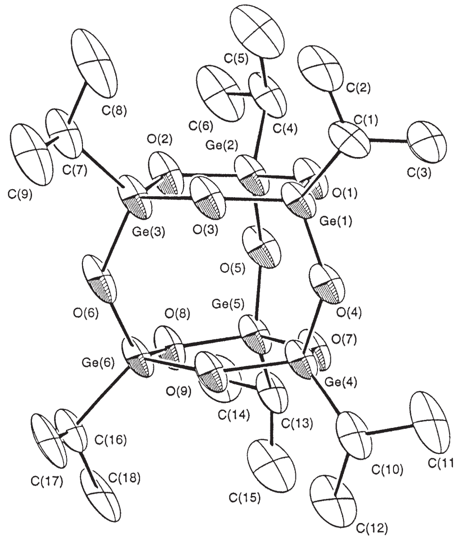
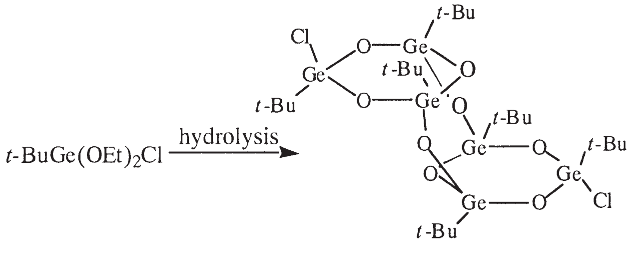


Figure 1. An ORTEP representation of the structure of **1a** (hydrogen atoms are omitted for clarity). Selected bond length (Å) and angles (°): Ge1–O4 1.746(4), Ge1–O3 1.758(4), Ge1–O1 1.763(4), Ge1–C1 1.916(5), O4–Ge1-O3 107.95(18), O4–Ge1–O1 108.27(17), O3–Ge1–O1 107.26(17), O4–Ge1–C1 111.2(2).

showing that this molecule is strain-free.

The *tert*-butyl(chloro)diethoxygermane, *t*-$BuGe(OEt)_2Cl$ prepared by *tert*-butyltrichlorogermane, *t*-$BuGeCl_3$ and ethanol in the presence of pyridine at room temperature for 2 weeks, was carefully hydrolyzed with water in ethanol at 5 °C for 6 h. The reaction mixture was concentrated by evaporation of ethanol. The residue was stirred in benzene at 5 °C and the generated solids were filtered off. The concentration of the organic layer by evaporation of benzene followed by recrystallization from hexane gave only 5,7-dichloro-1,3,5,7,9-hexa-*tert*-butyltricyclo[7.3.1.1^{3,7}]octagermoxane, $(t\text{-}BuGe)_6O_8Cl_2$ **2** in 29% isolated yield.



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The ^1H NMR spectrum of **2** displayed two *tert*-butyl signals at 1.29 and 1.32 ppm in 1 : 2 ratio. The ^{13}C NMR showed four signals at 25.9, 26.5, 30.5, and 34.7 ppm. These NMR data indicated that germoxane **2** was a symmetrical structure. The structure was established by X-ray crystallography.[16] The molecular structure is shown in Figure 2 as an *anti*-form ladder germoxane. The average Ge–O bond length is 1.76 Å in six- and eight-membered rings. The average O–Ge–O bond angle is 107°; the average Ge–O–Ge is 126.5°. The structural parameters of **2** (e.g., Ge–O bond lengths, Ge–O–Ge angles, O–Ge–O angels) are similar to those for **1**.[14,15]

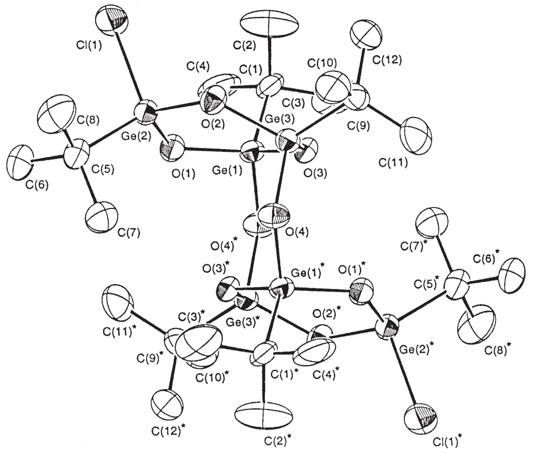
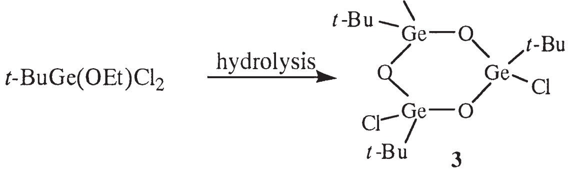


Figure 2. An ORTEP representation of the structure of **2** (hydrogen atoms are omitted for clarity). Selected bond length (Å) and angles (°): Ge1–O4$^{\#1}$ 1.751(3), Ge1–O3 1.765(3), Ge1–O1 1.780(3), Ge1–C1 1.947(4), Ge2–O1 1.746(3), Ge2–O2 1.755(3), Ge2–C5 1.946(4), Ge2–Cl1 2.1739(12), O4$^{\#1}$–Gel–O3 107.39(13), O4$^{\#1}$–Ge1–O1 106.43(13), O3–Ge1–O1 107.68(13), O4$^{\#1}$–Ge1–C1 109.80(15), O3–Ge1–C1 112.05(16), O1–Ge1–C1 113.18(16).

After hydrolysis of **2** with aqueous NaOH in xylene at 140 °C for 3 h, the cage germasesquioxane **1** was formed in 18% isolated yield together with polygermoxane. The formation of **1** suggests that the germoxane **2** is clearly an intermediate for the formation of **1**.

The *tert*-butyl(dichloro)ethoxygermane, t-BuGe(OEt)Cl_2, prepared by t-BuGeCl_3 and ethanol at room temperature for 2 weeks, was treated with water at 5 °C for 3 h to give **3** as a sole product. The product **3** was isolated by distillation in 31% yield. ^{1}H NMR spectrum of **3** displayed two *tert*-butyl signals at 1.29 and 1.33 ppm in 1 : 2 ratio. ^{13}C NMR of **3** showed four signals at 25.2, 25.5, 35.4, and 39.6 ppm. The fragment peak (M^+-t-Bu) with m/z 487 was observed. The NMR (^{1}H and ^{13}C{^{1}H}) and GC-MS spectra of **3** disclosed it to be 1,3,5-tri-*tert*-butyl-1,3,5-trichlorotrigermoxane. After hydrolysis of **3** for an additional 33 h, the *anti*-form ladder germoxane **2** was formed.



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A reasonable mechanism is that two cyclic germoxanes **3** having probably *cis,trans*-1,3,5-tri-*tert*-butyl-1,3,5-trichlorocyclotrigermoxane geometry join co-facially to form the *anti*-form ladder germoxane **2**, which undergoes isomerization to give the *syn*-type isomer. Dehydration of the *syn*-form germoxane gives the cage germoxane **1**.

In summary, we synthesized cage hexakis(alkylgermasesquioxane), $(RGe)_6O_9$, (R = i-Pr, t-Bu. c-C_6H_{11}) from hydrolysis of RGe$(OEt)_nCl_{3\text{-}n}$ (n = 0–3), and determined its crystal structure. Cyclic and *anti*-form ladder germoxanes as intermediates of the cage germoxanes by careful hydrolysis of RGe$(OEt)_nCl_{3\text{-}n}$ were examined.

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15 Crystal data for **1a**: $C_{18}H_{42}Ge_6O_9$; fw = 838.06; crystal size $0.40 \times 0.20 \times 0.20\,mm^3$; triclinic, space group $P\bar{1}$, $Z = 2$, a = 11.9140(11) Å, b = 12.5490(11) Å, c = 13.2720(15) Å, α = 63.855(4)°, β = 64.205(5)°, γ = 89.764(5)°; V = 1559.3(3) Å^3, D_{calcd} = 1.784 g/cm^3; Goodness of fit = 1.048, R = 0.0388 (R_{all} = 0.0479 for 4280 reflections), R_w = 0.1243 for 3522 reflections with $I > 2\sigma(I)$. Crystallographic data for **1a** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-192754.

16 Crystal data for **2**: $C_{24}H_{54}Cl_2Ge_6O_8$; fw = 977.11; crystal size $0.40 \times 0.30 \times 0.30\,mm^3$; triclinic, space group $P\bar{1}$, $Z = 1$, a = 10.2730(10) Å, b = 10.8580(10) Å, c = 10.9450(10) Å, α = 65.663(5)°, β = 71.909(5)°, γ = 63.960(5)°; V = 986.84(16) Å^3, D_{calcd} = 1.644 g/cm^3; Goodness of fit = 1.133, R = 0.0354 (R_{all} = 0.031 for 2604 reflections), R_w = 0.1188 for 2469 reflections with $I > 2\sigma(I)$. CCDC-192755.