HIGH YIELD ROUTES TO HEXA(DIMETHYLSILYLOXY)SILSESQUIOXANE AND HEXA(BROMODIMETHYLSILYLOXY)SILSESQUIOXANE

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Summary

Convenient high yield routes to both hexa(dimethylsilyloxy)silsesquioxane, $\text{Si}_6\text{O}_{15}(\text{SiMe}_2\text{H})_6$, and hexa(bromodimethylsilyloxy)silsesquioxane, $\text{Si}_6\text{O}_{15}(\text{SiMe}_2\text{Br})_6$, via the ionic salt $(\text{NEt}_4)_6\{\text{Si}_6\text{O}_{15}\} \cdot 30\text{H}_2\text{O}$ are described.

Introduction

Examination of the structures adopted by zeolites and related materials shows that the channels and cavities comprise closed polyhedra made up of silicon/aluminium and oxygen atoms. The smallest such unit observed in zeolites is the cubane $[\text{Si}_8\text{O}_{12}]$ cage (I) although much larger polyhedra also occur. Closed vertex sphaerosilicates of the general formula $(\text{XSiO}_{1.5})_n$ ($n \geq 6$; X = reactive functional group) are ideal candidates as precursors for the construction of three-dimensional polymeric architectures [1,2]. Whereas the cubane $[\text{Si}_8\text{O}_{12}]$ cage is isotropic, the $[\text{Si}_6\text{O}_9]$ cage is anisotropic and should, therefore, lead to microporous polymeric materials with rather different characteristics. Unfortunately, suitable high yield routes to molecular precursors possessing these frameworks are not available. In this paper we report convenient, high yield routes to both hexa(dimethylsilyloxy)silsesquioxane, $\text{Si}_6\text{O}_{15}(\text{SiMe}_2\text{H})_6$, and hexa(bromodimethylsilyloxy)silsesquioxane, $\text{Si}_6\text{O}_{15}(\text{SiMe}_2\text{Br})_6$, via the ionic salt $(\text{NEt}_4)_6\{\text{Si}_6\text{O}_{15}\}$.

Results and discussion

The first double three ring silicate cage compounds, $(\text{CH}_3)_6\text{Si}_6\text{O}_9$ and $(\text{C}_2\text{H}_5)_6\text{Si}_6\text{O}_9$, were first synthesised in 1955 by Sprung and Guenther [3,4], with the homologous compounds, $(\text{C}_7\text{H}_{15})_6\text{Si}_6\text{O}_9$, $(\text{C}_8\text{H}_{17})_6\text{Si}_6\text{O}_9$, *iso*- $\text{C}_9\text{H}_{19})_6\text{Si}_6\text{O}_9$ [5,6], $(\text{C}_6\text{H}_{11})_6\text{Si}_6\text{O}_9$ [7,8], and $(\text{C}_6\text{H}_5)_6\text{Si}_6\text{O}_9$ [9,10] being synthesised in the following years. The general method of preparation is by the hydrolysis of the corresponding alkyltrichlorosilane or alkyl(trisalkoxy)silane. In 1970, Smolin [11] synthesised and determined the X-ray structure of the $\{\text{Si}_6\text{O}_{15}^{6-}\}$ anion as the $[\text{Ni}(\text{en})_3]^{2+}$ salt by reacting an ethylenediamine solution of nickel hydroxide with a 2.5% solution of silica in ethylenediamine. The structure showed that the cage is distorted so that most of the OSiO bond angles are very close to the tetrahedral angle.

In the seventies many studies of acidified sodium monosilicate solutions by ^{29}Si gave evidence that double three ring silicates are also present in these systems [12-18]. Subsequent investigations of silicate solutions containing the tetraethylammonium cation showed that this had a stabilizing effect on the double three ring silicate system [19-23]. It was found that using the tetraethylammonium cation in a silicate solution favours the formation of double three ring silicates to more than 95% if the optimum concentration range of Si and the optimum $\text{Si}:\{\text{NEt}_4\}$ ratio is chosen [19]. Similar results were also obtained by Groenen [24] investigating water/DMSO solutions of different tetraethylammonium/silicate ratios. The trimethylsilyl ester of the $\{\text{Si}_6\text{O}_{15}^{6-}\}$ anion, $[(\text{CH}_3)_3\text{Si}]_6\text{Si}_6\text{O}_{15}$, has been obtained and structurally characterised by Hoebbel [25].

The preparation of the $\{\text{Si}_6\text{O}_{15}^{6-}\}$ anion as the tetraethylammonium salt has previously been described by Hoebbel [26] by reacting silica gel with an aqueous NEt_4OH

solution (N:Si ratio 1:1) for 3 days from which crystalline $(\text{NEt}_4)_6\{\text{Si}_6\text{O}_{15}\} \cdot 57\text{H}_2\text{O}$ could be recovered by crystallisation. A more convenient and shorter preparation of $(\text{NEt}_4)_6\{\text{Si}_6\text{O}_{15}\}$ (I) is by the hydrolysis of $\text{Si}(\text{OEt})_4$ in an aqueous tetraethylammonium hydroxide solution (N:Si ratio 1:1):

The product was obtained in near quantitative yield as a polyhydrate after removal of the water and the ethanol formed. The ^{29}Si nmr spectrum (saturated D_2O solution) exhibits a single resonance at -87.48ppm due to the silicon atoms of the $\{\text{Si}_6\text{O}_{15}\}$ cage (*cf. ca.* -88ppm [19]), with only small peaks at -69ppm due to a small amount of monosilicate (*ca.* 2-3%), -77.32 due to disilicate (*ca.* 2%), and -79.80ppm due to the cyclic $\{\text{Si}_3\text{O}_9\}$ silicate (*ca.* 2-3%).

The quite strained $\{\text{Si}_6\text{O}_{15}\}^{6-}$ cage is labile towards hydrolysis and condensation reactions. However, this may be overcome by silylation with dimethylchlorosilane in a dimethylformamide/heptane mixture giving the hexa(dimethylsilyloxy)-substituted cage $\text{Si}_6\text{O}_{15}(\text{SiMe}_2\text{H})_6$ (II) which is significantly less labile and is very soluble in organic solvents:

The nmr spectra confirm the identity of the silylated cage. The ^1H nmr spectrum of (II) exhibits a septet centred at 4.73ppm for the Si-H hydrogens due to coupling with six methyl hydrogens and a doublet at 0.255ppm flanked by satellites due to ^{29}Si coupling $\{2J(^{29}\text{Si}-^1\text{H}) = \text{ca. } 7\text{Hz}\}$ in the ratio 1:6 $\{^3J(^1\text{H}-^1\text{H}) = 2.5\text{Hz}\}$. The ^{29}Si nmr spectrum exhibits a singlet resonance at -98.94ppm due to the cage silicon atoms and a doublet of partially resolved septets for the SiMe_2H silicon atoms centred at 0.31ppm due to coupling with both types of hydrogen atom $\{^1J(^{29}\text{Si}-^1\text{H}) = 210.7\text{Hz}, 2J(^{29}\text{Si}-^1\text{H}) = 7.5\text{Hz}\}$. The ^{29}Si solid state nmr spectrum of $\text{Si}_6\text{O}_{15}(\text{SiMe}_2\text{H})_6$, however, is much more complex. The

resonance for the cage silicon atoms, which is a single resonance in the ^{29}Si solution nmr spectrum, becomes five resonances at -98.32, -98.74, -99.15, -99.88 and -100.54ppm in the solid state spectrum, indicative of considerable distortion of the cage due to crystal packing effects. The SiMe_2H silicon atoms show four resonances at 0.43, -0.06, -0.83 and -1.83ppm. The uncoupled ^{13}C solution nmr spectrum shows the expected coupling of the methyl and Si-H hydrogens with the methyl carbon atoms to give a quartet of doublets at $\delta = 0.025\text{ppm}$ $\{^2J(^{13}\text{C}-^1\text{H}) = 11.95\text{Hz}, ^1J(^{13}\text{C}-^1\text{H}) = 119.5\text{Hz}\}$. In contrast, the ^{13}C solid state nmr spectrum exhibits only a single peak at 0.85ppm for the $\text{Si}(\text{CH}_3)_2\text{H}$ methyl group carbon atoms.

In the infrared $\text{Si}_6\text{O}_{15}(\text{SiMe}_2\text{H})_6$ exhibits characteristic $\nu(\text{Si-H})$, $\nu_{\text{anti}}(\text{Si-O})$, and $\delta(\text{OSiO})$ vibrations at 2142, 1174 and 1095, and 551 cm^{-1} , respectively. The mass spectrum is very simple with clusters of peaks at $m/e = 762(\pm 2)$ due to the parent ion with gain and loss of up to two hydrogens, and at $m/e = 746(\pm 2)$ due to loss of a methyl group from these fragments. Other minor peaks due to the loss of exocage methylsiloxy fragments are also observed, however none due to the fragmentation of the cage structure itself are apparent. The strong peaks at m/e 74 and 60 are due to $\text{Me}_2\text{SiH}_2^+$ and Me_3SiH^+ , respectively.

The hydrido cage $\text{Si}_6\text{O}_{15}(\text{SiMe}_2\text{H})_6$ may be converted to the corresponding hexabromo compound $\text{Si}_6\text{O}_{15}(\text{SiMe}_2\text{Br})_6$ (III) by the catalytic bromination by allyl bromide both as solvent and reagent at 60° for 3.5h under nitrogen using $\text{Rh}(\text{acac})_3$ as catalyst:

As with (II), (III) may be fully characterised by nmr. The ^1H nmr spectrum exhibits only a single resonance at 0.69ppm for the methyl hydrogens, and no resonance is observed at 4.73ppm indicating that all the $\text{Si}_6\text{O}_{15}(\text{SiMe}_2\text{H})_6$ has been consumed. The ^{29}Si solid state spectrum exhibits a singlet resonance at -100.94ppm for the cage silicon atoms and also a partially resolved septet centred at 6.59ppm for the SiMe_2Br silicon atoms $\{^2J(^{29}\text{Si}-^1\text{H}) = 7.5\text{Hz}\}$. The ^{13}C spectrum exhibits the expected quartet at 5.45ppm $\{^1J(^{13}\text{C}-^1\text{H}) = 122.0\text{Hz}\}$. In the infrared, the characteristic $\nu(\text{Si-H})$ band of $\text{Si}_6\text{O}_{15}(\text{SiMe}_2\text{H})_6$ is completely absent, and the spectrum exhibits $\nu(\text{Si-O})_{\text{anti}}$ bands at 1121, 1071 and 1020 cm^{-1} and a $\delta(\text{OSiO})$ band at 524 cm^{-1} . A mass spectrum could not be obtained because of the very high molecular mass.

Experimental

Preparation of $(\text{NEt}_4)_6\text{Si}_6\text{O}_{15} \cdot 30\text{H}_2\text{O}$

A 35% aqueous solution of NEt_4OH (40ml, 95.2mmol) was placed in a polyethylene bottle, followed by $\text{Si}(\text{OEt})_4$ (20ml, 89.6mmol) and stirred overnight. The solvent was reduced under vacuum to give 25.6g (99.1%) of $(\text{NEt}_4)_6\text{Si}_6\text{O}_{15} \cdot 30\text{H}_2\text{O}$ (Found: C, 33.21; H, 10.69; N, 4.72%. $\text{C}_{48}\text{H}_{180}\text{N}_6\text{Si}_6\text{O}_{45}$ requires: C, 33.31; H, 10.51; N, 4.86%).

Preparation of $\text{Si}_6\text{O}_{15}[\text{SiMe}_2\text{H}]_6$

To a vigorously stirred mixture of dimethylchlorosilane (100ml, 0.92mol), heptane (500ml) and dimethylformamide (200ml) cooled with an ice bath was added $(\text{NEt}_4)_6\text{Si}_6\text{O}_{15} \cdot 30\text{H}_2\text{O}$ (14g, 8.07mmol) over a period of *ca.* 30min. After addition of all the $(\text{NEt}_4)_6\text{Si}_6\text{O}_{15} \cdot 30\text{H}_2\text{O}$ the mixture was stirred for an additional 30min and then allowed to warm to room temperature. Ice-water (1l) was added and the mixture stirred for 15min. The upper organic layer was separated and washed three times with water (150ml) until neutral. The organic solvent was removed under reduced pressure and the colourless residue recrystallised from acetonitrile to give $\text{Si}_6\text{O}_{15}[\text{SiMe}_2\text{H}]_6$ (3.11g, 50.4%) M.p. 239°. (Found: C, 18.82; H, 5.85% $\text{C}_{12}\text{H}_{42}\text{Si}_{12}\text{O}_{15}$ requires: C, 18.87; H, 5.56%). Infrared data: 2963w, 2922vw, 2142m, 1256m, 1174m,sh, 1095s, 899s, 834w, 768w, 755w,sh, 725vw,sh, 648vw, 627vw, 551m cm^{-1} .

Preparation of $\text{Si}_6\text{O}_{15}[\text{SiMe}_2\text{Br}]_6$

A solution of $\text{Si}_6\text{O}_{15}[\text{SiMe}_2\text{H}]_6$ (2.5g, 3.27mmol), dry, oxygen-free allyl bromide (10ml) and $\text{Rh}(\text{acac})_3$ (acac = acetylacetonate) (0.15mg) was heated at 60° for 3.5h under a nitrogen atmosphere. The allyl bromide was removed under reduced pressure to give $\text{Si}_6\text{O}_{15}[\text{SiMe}_2\text{Br}]_6$ (4.02g, 98.9%) M.p. 298°. (Found: C, 11.47; H, 3.07% $\text{C}_{12}\text{H}_{36}\text{Br}_6\text{Si}_{12}\text{O}_{15}$ requires: C, 11.65; H, 2.94%). Infrared data: 2961w, 2920vw, 1260m, 1121m sh, 1071s, 1020m sh, 895vw sh, 851m, 818m, 801m, 744vw, 698vw, 676w, 658 vw sh, 608, 592vw sh, 524w cm^{-1} .

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