

The First Octasilacubane System: Synthesis of Octakis-(*t*-butyldimethylsilyl)pentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octasilane

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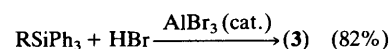
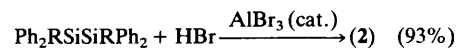
The first octasilacubane, octakis-(*t*-butyldimethylsilyl)pentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octasilane, was synthesised in one step by condensation of 2,2,3,3-tetrabromo-1,4-di-*t*-butyl-1,1,4,4-tetramethyltetrasilane or 1,1,1-tribromo-2-*t*-butyl-2,2-dimethyldisilane with sodium in toluene.

The synthesis of an octasilacubane is one of the most attractive challenges in organosilicon chemistry, since such a strained cage framework of silicon atoms might possess unprecedented physical and chemical properties. Recently, Nagase and his co-workers have predicted that the parent octasilacubane would be markedly less strained than the corresponding carbon compound.¹ However, no octasilacubane has been synthesised hitherto. In continuation of our investigation of the chemistry of polycyclosilanes consisting of fused four-membered rings^{2,3} we commenced a study of the construction of an octasilacubane, and found that the bulky *t*-butyldimethylsilyl group can confer kinetic stability on the cubic silicon skeleton.[†] We now describe the synthesis of octakis-

(*t*-butyldimethylsilyl)pentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octasilane (1), the first octasilacubane derivative to be reported.

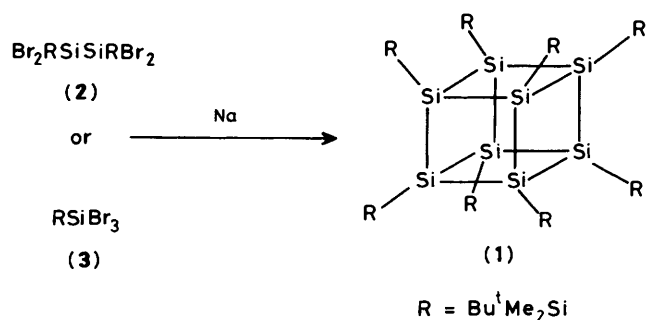
The persilyloctasilacubane (1) could be obtained by condensation of 2,2,3,3-tetrabromo-1,4-di-*t*-butyl-1,1,4,4-tetramethyltetrasilane (2)[‡] or 1,1,1-tribromo-2-*t*-butyl-2,2-dimethyldisilane (3)[‡] with sodium in toluene (Scheme 1). Thus, treatment of (2) (30.0 g, 49.6 mmol) with sodium sand (5.0 g, 218 mmol) in toluene (400 ml) at 90 °C for 7 h under argon, followed by filtration and evaporation afforded (1) (7.8 g,

[‡] The tetrabromotetrasilane (2) and the tribromodisilane (3) can be prepared by the reactions:



These new compounds were characterised by i.r., n.m.r., and mass spectra and elemental analyses.

[†] Kinetic stabilisation due to trialkylsilyl groups such as Me₃Si, EtMe₂Si, and Et₃Si has been successfully utilized for the synthesis of cyclotri- and cyclotetra-silanes.⁴⁻⁶ Also, the potential of a silyl group for stabilizing the tetrasilatetrahedrane skeleton has been suggested in the emblem of the 8th International Symposium on Organosilicon Chemistry, St. Louis, July, 1987.



Scheme 1

55% crude yield) as a reddish-yellow solid. Recrystallization from methylcyclohexane provided bright yellow prisms. § A similar condensation of (3) led to the formation of (1) in 72% yield.

Compound (1) is air-sensitive, being converted into a colourless solid upon exposure to the atmosphere for several days at room temperature, but is indefinitely stable in an inert atmosphere. It is moderately soluble in aliphatic and aromatic solvents. Identification was based on the following evidence. ¶ The mass spectrum showed the correct molecular mass; field desorption (observed isotopic pattern coefficients of molecular ions): m/z 1144 (85%), 1145 (98), 1146 (100), 1147 (94), 1148 (73), 1149 (41), 1150 (7), and 1151 (4). Diagnostic of the

§ This compound exhibits thermochromism; colourless at -196°C , orange at 280°C (glassy solid), and pale yellow at 400°C (semi-solid).

¶ An attempt to obtain good elemental analytical figures met with failure owing to the formation of silicon carbide; a micro-combustion analysis afforded a lower value for C than that calculated for $\text{C}_{48}\text{H}_{120}\text{Si}_{16}$, but a satisfactory result for H, and left residual ash.

persilicubane structure was the simplicity of the n.m.r. spectra. The $^{29}\text{Si}\{^1\text{H}\}$ spectrum ($\text{C}_6\text{D}_5\text{CD}_3$; Me_4Si) showed two resonances, at $\delta -35.03$ and $+5.60$ p.p.m., indicating the presence of only two different silicon environments. The former resonance is assignable to the ring silicon atoms and the latter to the substituents. The $^{13}\text{C}\{^1\text{H}\}$ n.m.r. spectrum (C_6D_6 ; Me_4Si) consisted of only three lines, at $\delta -0.57$ (2C), $+20.74$ (1C), and $+30.07$ (3C), assigned to methyl, methyne, and t-butyl carbon, respectively. The ^1H n.m.r. spectrum (C_6D_6 ; Me_4Si) showed only two singlets, at $\delta +0.57$ (3H, Me) and $+1.28$ (9H, Bu^t). The i.r. spectrum (KBr) showed no absorption bands due to Si-H and Si-O-Si bonds. The u.v. spectrum (3-methylpentane) tailed off into the visible region: $\log \epsilon$ 2.9 at 400 nm and 2.5 at 450 nm.

Studies on the electronic properties and reactions of the octasilicubane as well as X-ray structural analysis are being undertaken.

This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture.

Received, 18th April 1988; Com. 8/01481G

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