The First Bicyclo[2.2.0]hexasilane System: Synthesis of Decaisopropylhexasilabicyclo[2.2.0]hexane

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The first bicyclo[2.2.0]hexasilane, decaisopropylhexasilabicyclo[2.2.0]hexane was synthesized by the co-condensation of 1,1,2,2-tetrachlorodi-isopropyldisilane and 1,2-dichlorotetraisopropyldisilane with lithium in tetrahydrofuran.

Bicyclopolysilanes consisting of small-membered rings are of interest, since fused and strained frameworks of silicon atoms can lead to unique properties. Recently, Masamune and co-workers isolated a bicyclo[1.1.0]tetrasilane, 1,3-di-t-butyl-2,2,4,4-tetrakis(2,6-diethylphenyl)tetrasilabicyclo[1.1.0]butane.[1] No bicyclo[2.2.0]hexasilane system, however, has been reported so far. Our current interest in the chemistry of small-membered cyclopolysilanes[2] has led us to investigate the construction of such a bicyclic skeleton of two annelated four-membered rings. We now report the first synthesis of a bicyclo[2.2.0]hexasilane, decaisopropylhexasilabicyclo-[2.2.0]hexane (**1**).

The bicyclohexasilane (**1**) could be obtained by the co-condensation of the disilanes (**2**) and (**3**) with lithium in tetrahydrofuran (THF) (Scheme 1).

Typically, a solution of (**2**)† (2.39 mmol) and (**3**)[3] (7.18

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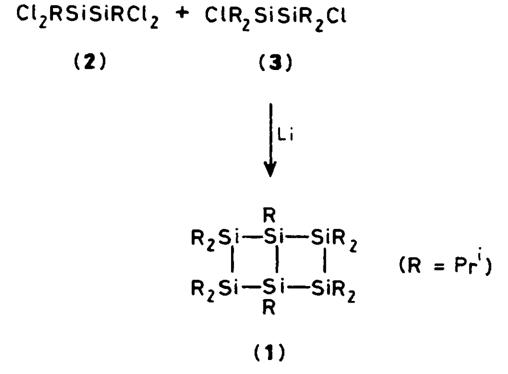
† The tetrachlorodisilane (**2**) (b.p. 80 °C at 13 mmHg) can be prepared by the coupling of Pr^iSiH_2Cl with Li, followed by chlorination with CCl_4–benzoyl peroxide (overall yield, 33%).



Scheme 1. R = Prⁱ.

mmol) in THF (25 ml) was added dropwise to 50 ml of stirred THF containing lithium fine cut (26.4 mmol) at room temperature under nitrogen. The reddish orange mixture was stirred for an additional 15 h. After removal of THF under reduced pressure, the residue was taken up in 200 ml of hexane. The precipitate was filtered off and then the filtrate was passed through a short silica gel column. Liquid chromatography (Lobar RP-18, THF–MeOH, 30:70) gave a semi-solid which was recrystallized from acetone to give colourless crystals of (**1**) (47 mg, 3.3% yield), m.p. 384—395 °C (decomp.).‡

Compound (**1**) is stable to atmospheric oxygen and water.§ It is readily soluble in aliphatic and aromatic hydrocarbons as well as THF, but poorly soluble in MeOH. We assign the bicyclohexasilane structure on the basis of the following evidence. The mass spectrum shows the correct molecular mass (field desorption, parent clusters 598—601), and high resolution confirms the composition $C_{30}H_{70}Si_6$ (obs. 598.4097; calc. 598.4094). The ^{29}Si n.m.r. spectrum (C_6D_6, Me_4Si) shows two resonances at −21.22 and −34.24 p.p.m., indicating two different silicon environments. The former resonance is assignable to the bis(silyl)-substituted silicon atoms and the latter to the tris(silyl)-substituted silicon atoms.¶ The $^{13}C\{^1H\}$ (gated decoupling) n.m.r. spectrum (C_6D_6, Me_4Si) exhibits seven lines at δ 14.82(2C), 16.07(4C), 17.53(4C), 21.43(4C), 22.38(4C), 23.20(8C), and 24.18(4C), falling into two groups from δ 14.8 to 17.6 and from δ 21.4 to 24.2, assigned to the methyne and methyl carbons, respectively. ‖ The corresponding resonances for the monocycle $(Pr^i{}_2Si)_4$ (**4**) consist of two

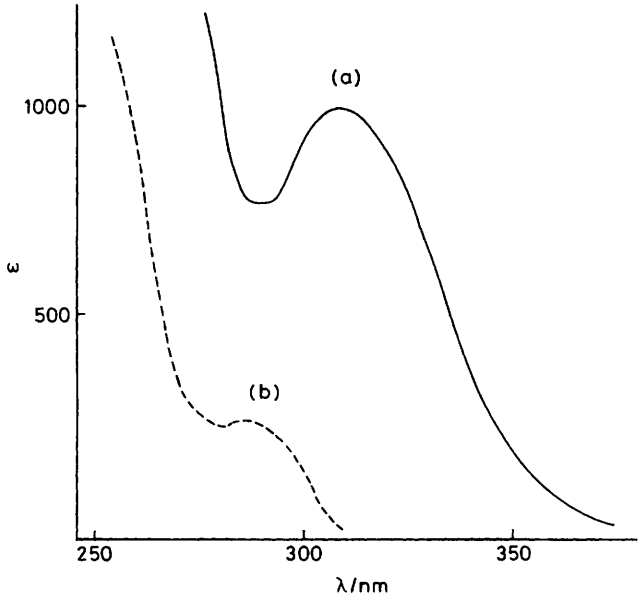


Figure 1. U.v. spectra of (a) the perisopropylbicyclohexasilane (**1**) and (b) the perisopropylcyclotetrasilane (**4**) (ref. 4).

lines, δ 15.07(4C) and 22.87(4C).[4] The ^1H n.m.r. spectrum (C_6D_6, Me_4Si) shows only the $CHMe_2$ and CH_3 signals at δ 1.36—1.80 expected for (**1**). The lowest transition-energy absorption of (**1**) in the u.v. region occurs at 310 nm (ε 970). Figure 1 shows the u.v. spectrum of (**1**) together with that of the monocycle (**4**) ($\lambda_{max.}$ 290 nm, ε 200), showing that the bicyclo Si_6 framework acts as a much more intense chromophore. The bathochromic shift observed for (**1**) relative to (**4**) and the marked increase in intensity of the absorption band for (**1**) are perhaps due to the larger ring strain on the Si–Si bonds in this molecule.[5]

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‡ Also formed were octaisopropylcyclotetrasilane (1%),[4] $Pr^i{}_{12}Si_8$ (2%) which could be tentatively assigned the dodecaisopropyloctasilatricyclo[4.2.0.0^{2,5}]octane structure (field desorption mass spectrum, parent clusters, *m/z* 740—744; u.v. $\lambda_{max.}$ 315 nm), and oligomers of higher molecular weights (~80%).

§ The observed stability suggests that the central Si–Si bond of the bicyclo[2.2.0]hexasilane (**1**) is much more stable against the attacking reagents than that of 1,3-t-butyl-2,2,4,4-tetrakis(2,6-diethylphenyl)-tetrasilabicyclo[1.1.0]butane, which is rapidly oxidised in air and is subject to hydration.[1] Recently, Dabisch and Schoeller have suggested in a theoretical study that bicyclo[2.2.0]hexasilane possesses a strong central bond.[5c]

¶ ^{29}Si n.m.r. spectra of bicyclic peralkylpolysilanes have previously been reported for tetradecamethyloctasilabicyclo[2.2.2]octane and octadecamethyldecasilabicyclo[4.4.0]decane.[6]

‖ Inspection of molecular models indicates that compound (**1**) favourably assumes a folded structure with a *cis* orientation of the isopropyl groups on the ring junction silicon atoms, as in analogous carbon bicyclohexanes.[7] The observed chemical shifts for the methyne carbons tend to support this conformation. An *X*-ray analysis of the molecular structure is underway.

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