

Novel Peralkylcyclotetrasilanes of the Type $(R^1R^2Si)_2(R^3R^4Si)_2$

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Novel peralkylcyclotetrasilanes of the type $(R^1R^2Si)_2(R^3R^4Si)_2$ ($R^1 = R^2 = Bu^tCH_2$, $R^3 = R^4 = Pri$; $R^1 = R^2 = Bu^tCH_2$, $R^3 = Bu^t$, $R^4 = Me$) were obtained by co-condensation of two 1,2-dichlorotetra-alkyldisilanes with Li; the structure of the tetraisopropyltetraepentylcyclotetrasilane (**1**), determined by X-ray crystallography, is folded with a large dihedral angle.

Although there is considerable current interest in the chemistry of small-membered cyclopolysilanes, the structures of cyclotetrasilanes so far obtained are limited to rings such as $(R_2Si)_4$ and $(R^1R^2Si)_4$.¹ We have found that cyclotetrasilanes of the type $(R^1R^2Si)_2(R^3R^4Si)_2$, (**1**) and (**4**), can be readily prepared by the co-condensation of the 1,2-dichlorotetra-alkyldisilanes $ClR^1R^2SiSiR^1R^2Cl$ and $ClR^3R^4SiSiR^3R^4Cl$ with lithium (Scheme 1).

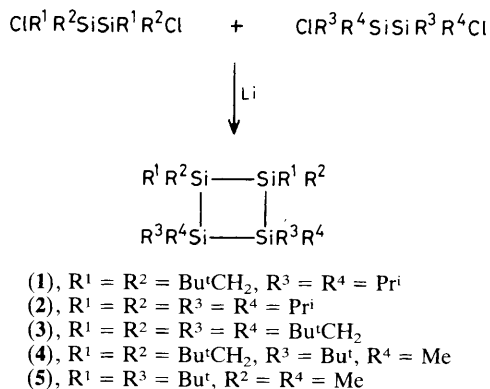
Typically, a mixture of 1,2-dichlorotetraepentylidisilane (6 mmol) and 1,2-dichlorotetraisopropylidisilane (12 mmol) was allowed to react with lithium (30% dispersion, 1.26 g, 55 mg atom) in tetrahydrofuran (THF) at room temperature under argon. The reaction reached completion in 6 h to give 1,1,2,2-tetraisopropyltetraepentylcyclotetrasilane (**1**) as well as octaisopropylcyclotetrasilane (**2**)² and octaneo-

pentylcyclotetrasilane (**3**)[†] [(**1**):(**2**):(**3**) = 26:57:17, 70% combined yield] as shown by g.l.c. analysis. Compound (**1**) was isolated by fractional recrystallization from benzene (18% yield).

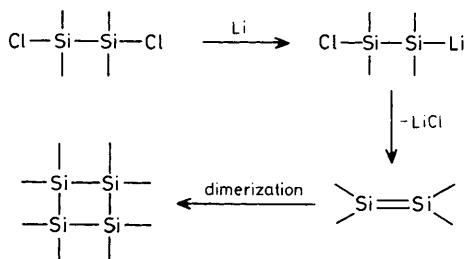
The structure of compound (**1**) (m.p. 310.0–327.8 °C)[‡] was unequivocally established by its physical properties {satisfactory elemental analyses; ¹H n.m.r. (CDCl₃, SiMe₄) δ 1.06 (s, 36H, CMe₃) and 1.29–1.45 (m, 36H, CH₂, CH, and

[†] Satisfactory spectral and analytical data were obtained for all new compounds.

[‡] The cyclotetrasilane melted over a broad temperature range and appeared to undergo phase transitions at temperatures well below the melting point.



Scheme 1



Scheme 2

CMe_2); ^{13}C n.m.r. (CS_2 , SiMe_4) δ 15.78 (d, CHMe_2), 22.72 (q, CHMe_2), 30.09 (t, CH_2), 30.55 (s, CMe_3), and 32.87 (q, CMe_3); ^{29}Si n.m.r. (CS_2 , SiMe_4) δ -3.81 (SiPr_2) and -27.58 p.p.m. [$\text{Si}(\text{CH}_2\text{Bu}^t)_2$], indicating two different silicon atoms in the cyclotetrasilane framework; electron impact mass spectrum (70 eV) m/z 568 (M^+ , 100%), 340 [$(\text{X}_2\text{Si}=\text{SiX}_2)^+$ ($\text{X} = \text{Bu}^t\text{CH}_2$), 20%], 284 [$(\text{X}_2\text{Si}=\text{SiY}_2)^+$ ($\text{Y} = \text{Pr}^i$), 20%], and 228 [$(\text{Y}_2\text{Si}=\text{SiY}_2)^+$ 10%]. As expected, the u.v. spectrum of (1) in cyclohexane (λ_{max} 286 nm) is characteristic of the cyclotetrasilane system and similar to spectra of (2) and (3) (Figure 1). The disposition of the four silicon atoms (Figure 2) was shown by an X-ray crystal structure determination. \S The molecule assumes a folded structure with a large dihedral angle of 39.39°. The original arrangement of the adjacent two silicon atoms in the starting disilanes is retained in the cyclotetrasilane molecule and this fact could possibly be regarded as an indication of the disilene dimerization mechanism

\S Crystal data: $\text{C}_{32}\text{H}_{72}\text{Si}_4$, $M = 569.275$, monoclinic, space group Cc , $a = 10.017(9)$, $b = 19.639(8)$, $c = 20.129(2)$ Å, $\beta = 106.744(5)^\circ$, $U = 3791.8(5)$ Å 3 , $Z = 4$, $D_c = 0.9973$ g cm $^{-3}$, $F(000) = 320$. Intensity data ($2\theta_{\text{max}}$ 55.0°) were recorded on a Rigaku-Denki four-circle diffractometer (AFC-4) using graphite monochromated Mo- K_α radiation and the ω - θ scan technique. 3633 unique reflections with $|F| > 3\sigma(|F_o|)$ were observed. The structure was solved by direct methods using Multan 78. \S Si(3) was fixed. The hydrogen atoms were placed at calculated positions assuming a C-H bond length of 1.10 Å and a tetrahedral arrangement around carbon; terminal hydrogen atoms were assumed to be in *gauche* positions. Refinement by block-diagonal least-squares using the UNICS III program 6 with anisotropic thermal parameters for non-hydrogen atoms and isotropic parameters for the hydrogen atoms led to $R = 0.051$ ($R_w = 0.052$).

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

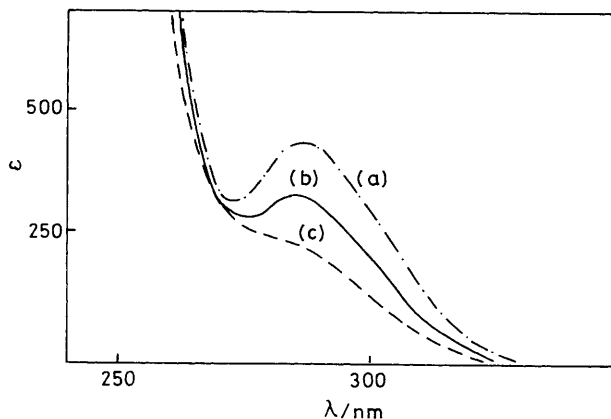


Figure 1. U.v. spectra for peralkylcyclotetrasilanes: (a), (3); (b), (1); (c), (2).

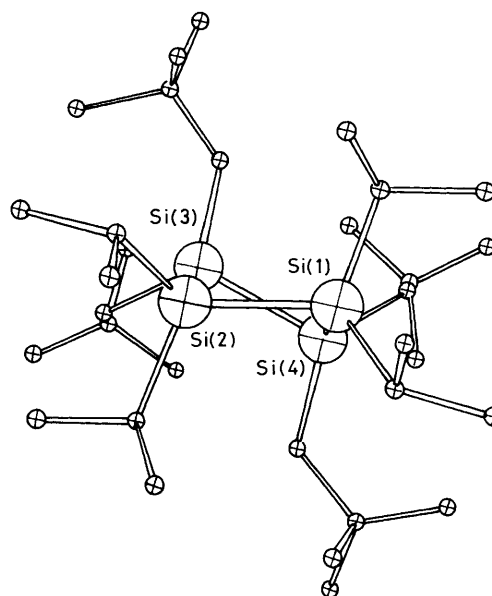


Figure 2. Molecular structure of cyclotetrasilane (1) with all hydrogen atoms omitted for clarity. Bond lengths (Å) and bond angles (°): Si(1)-Si(2) 2.375(3), Si(2)-Si(3) 2.397(3), Si(3)-Si(4) 2.416(2), Si(4)-Si(1) 2.417(3); Si(4)-Si(1)-Si(2) 86.7(1), Si(1)-Si(2)-Si(3) 87.6(1), Si(2)-Si(3)-Si(4) 86.2(1), Si(3)-Si(4)-Si(1) 86.2(1).

ism operating in cyclotetrasilane-forming reactions from 1,2-dichlorodisilanes with lithium which has been suggested previously (Scheme 2). $^3\parallel$

A similar reaction of a 1:1 mixture of 1,2-dichlorotetraneopentylididilane and 1,2-dichloro-1,2-di-*t*-butyldimethyldisilane with lithium gave compound (4), † as

\parallel A disilene trapping experiment was conducted as follows. A mixture of 1,2-dichlorotetraneopentylididilane (0.54 mmol), lithium (30% dispersion, 0.011 g, 1.5 mg atom), and THF (6 ml) was stirred at room temperature under argon until the dichlorodisilane was almost completely consumed (3 h). A solution of anthracene (0.13 mmol) in THF (3 ml) was then added to the resulting reddish yellow solution. After 5 min, the reddish yellow colour faded. The resulting solution was found by g.l.c. to contain 11,11,12,12-tetraneopentyl-11,12-disila-9,10-dihydro-9,10-ethanoanthracene (0.06 mmol, 11%) as well as (3) (49%) and 1,2-dihydro-1,2-tetraneopentylididilane (10%). However, other mechanistic possibilities involving disilanyl anions cannot be excluded

well as (3) and (5)⁴ [(4):(3):(5) = 69:1:30, 67% combined yield].

These results open a synthetic pathway to novel peralkylcyclotetrasilanes with unprecedented stereochemical environments.

We thank Professor N. Kamigata, Tokyo Metropolitan University, for spectra.

Received, 14th May 1985; Com. 660

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