The Preparation and Properties of the Peralkylcyclotrisilane, Hexaneopentylcyclotrisilane, and the Peralkyldisilene, Tetraneopentyldisilene

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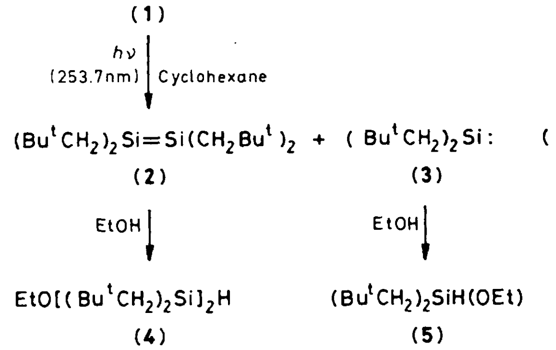
The reaction of $(\mathrm{Bu^tCH_2})_2\mathrm{SiCl_2}$ with Li in tetrahydrofuran gave the peralkylcyclotrisilane, hexaneopentylcyclotrisilane $[(\mathrm{Bu^tCH_2})_2\mathrm{Si}]_3$ (**1**), which showed a u.v. absorption maximum λ_{max} at 310 nm; irradiation of (**1**) in a hydrocarbon solvent afforded the peralkyldisilene, tetraneopentyldisilene $(\mathrm{Bu^tCH_2})_2\mathrm{Si{=}Si}(\mathrm{CH_2Bu^t})_2$, which was shown to be a coloured compound (λ_{max} 400 nm) owing to the presence of the Si=Si bond framework which acts as a chromophore.

The chemistry of cyclotrisilanes and disilenes is an intriguing subject of current interest because of their unusual structures and properties. Since the first isolation of a stable disilene tetramesityldisilene (by West *et al.*),[1] a different synthesis of this compound by Boudjouk *et al.*[2] and the synthesis of closely related compounds *via* hexa-arylcyclotrisilane (which is the first example of a cyclotrisilane) by Masamune *et al.*,[3] have been reported. The disilenes and cyclotrisilanes synthesised so far have aryl substituents on silicon and are not always convenient for assessing the electronic properties of the cyclotrisilane and silicon–silicon double bond frameworks, because of the perturbation caused by the aryl substituent. Our continuing interest in peralkylcyclosilanes,[4] leads us to report the first synthesis of the peralkylcyclotrisilane, hexaneopentylcyclotrisilane (**1**), which affords on photolysis the first peralkyldisilene, tetraneopentyldisilene, and we also describe some of their properties.

A solution of dineopentyldichlorosilane (10 mmol) in tetrahydrofuran (THF) was treated with lithium (22 mg atom) at 0 °C for 9 h and worked up to give a solid which afforded, on recrystallization from EtOH–n-$\mathrm{C_5H_{12}}$, an analytically pure

$$(\mathrm{Bu^tCH_2})_2\mathrm{SiCl_2} \xrightarrow[\text{THF}]{\text{Li}} \underset{(\mathbf{1})}{[(\mathrm{Bu^tCH_2})_2\mathrm{Si}]_3} \tag{1}$$

sample of hexaneopentylcyclotrisilane (**1**) (0.24 g, 14%; m.p. 224—239 °C†) (equation 1). The assigned structure of (**1**) is fully supported by n.m.r., i.r., and mass spectral data as well as elemental analysis.‡ Compound (**1**) was found to be stable to oxygen, moisture, and heat, below its melting point. The u.v. spectrum of (**1**) showed an absorption maximum at 310 nm (log ε 2.52) due to the cyclic $\mathrm{Si_3}$ system, compared to the maxima for larger peralkylcyclosilanes§ such as $\mathrm{Pr^i_8Si_4}$[4]



(2)

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† In a sealed capillary; the cyclotrisilane melted over a broad temperature range and appeared to undergo phase transitions at temperatures well below the melting point, in a manner similar to the $[\mathrm{Me_2Si}]_n$ oligomers as shown by West *et al.* (see refs. 5d and 6).

‡ ^{1}H N.m.r. ($\mathrm{CDCl_3}$, $\mathrm{Me_4Si}$) δ 0.93 (s, 12H, $\mathrm{CH_2}$; temperature dependent) and 1.07 (s, 54H, CMe); the $\mathrm{CH_2}$ proton signal exhibited two pairs of AX-type signals at −40 °C: δ $\mathrm{H_A}$ 0.44 and $\mathrm{H_X}$ 1.44; J_{AX} *ca.* 14—15 Hz (ref. 7). ^{13}C N.m.r. ($\mathrm{CDCl_3}$, $\mathrm{Me_4Si}$) δ (p.p.m.) 29.63 (t, $\mathrm{CH_2}$), 31.68 (s, quaternary C), and 33.48 (q, $\mathrm{CH_3}$). ^{29}Si N.m.r. ($\mathrm{C_6D_6}$, $\mathrm{Me_4Si}$) δ (p.p.m.) −81.68. I.r. (KBr) ν ($\mathrm{cm^{-1}}$) 2950s, 2900s, 2860s, 1461s, 1381s, 1360s, 1222s, 1152m, 1106s, 1010s, 960w, 932w, 908w, 768s, 708m, and 696m. T.l.c. (silica gel, light petroleum) R_f 0.98. Mass spectrum (20 eV) m/z 510 (M^+, 32%), 439 [$(M - \mathrm{C_5H_{11}})^+$, 5], 340 [$(M - \mathrm{C_{10}H_{22}Si})^+$, 15], 269 [$(M - \mathrm{C_{15}H_{33}Si})^+$, 8], 170 [$(\mathrm{C_{10}H_{22}Si})^+$, 2], 99 [$(\mathrm{C_5H_{11}Si})^+$, 26], 73 [$(\mathrm{Me_3Si})^+$, 100]. An *X*-ray crystal analysis is underway.

§ The absorption maxima for peralkylcyclosilanes depend primarily on their ring sizes, rather than the substituents on silicon.

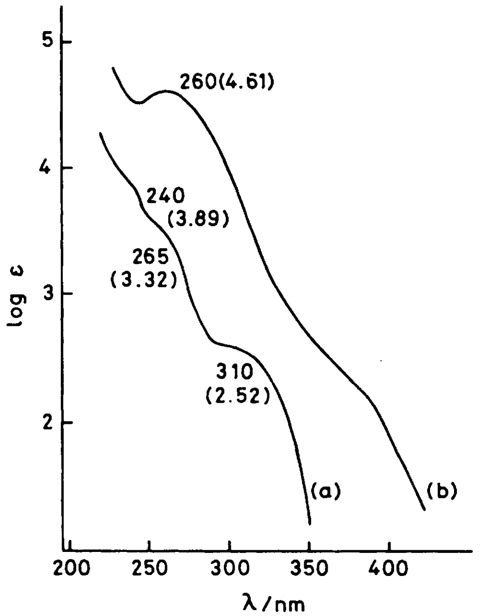

Figure 1. U.v. spectra of (a) hexaneopentylcyclotrisilane (**1**) and (b) hexakis(2,6-dimethylphenyl)cyclotrisilane (ref. 3).

(290sh), $Bu^{n}_{10}Si_5$[4] (260), $Me_{12}Si_6$ (253),[8] and $Me_{14}Si_7$ (242 nm).[8] The u.v. spectrum of (**1**) has considerably different absorption maxima and coefficients to those of hexakis(2,6-dimethylphenyl)cyclotrisilane (Figure 1), and this spectral difference apparently reflects the difference in electronic structure between the peralkyl and peraryl systems.

Upon irradiation (253.7 nm) at room temperature, a cyclohexane (1 ml) solution of (**1**) (5 mg) in an evacuated u.v. cell (sealed) became yellow (λ_{max} 400 nm). This absorption band gradually dissipated on ceasing irradiation and was observed again on reirradiation. Introduction of air into the coloured solution resulted in the instant disappearance of the colour. It has been shown[1–3] that the tetra-aryldisilenes have an intense yellow colour (λ_{max} 420 nm) and react rapidly with oxygen. These phenomena strongly suggest that photolysis of the peralkylcyclotrisilane (**1**) produced the peralkyldisilene, $(Bu^tCH_2)_2Si{=}Si(CH_2Bu^t)_2$ (**2**),¶ which is fairly stable under the conditions used.

An experiment to trap the disilene with ethanol was attempted.[1–3] Thus, irradiation (5 h) of (**1**) (15 mg) in an ethanol–cyclohexane mixture (1 : 3, 4 ml) gave, on evaporation of the solvent, the main products which were identified as 1,1,2,2-tetraneopentyl-1-ethoxydisilane (**4**) and dineopentylethoxysilane (**5**), by a g.c.–mass spectral technique and by comparison with authentic samples using g.l.c. The formation of (**4**) is in keeping with the observations by West *et al.*[1] and Boudjouk *et al.*[2] that tetramesityldisilene forms an adduct with methanol. The formation of (**5**) can be reasonably interpreted in terms of the intermediacy of the silanediyl radical, dineopentylsilanediyl (**3**), since alcohols such as methanol and ethanol are generally recognized to be good reagents for trapping silanediyl radicals.

From the above observations, it is likely that the cyclotrisilane (**1**) photochemically decomposed into (**2**) and (**3**), which were then trapped by ethanol to yield (**4**) and (**5**), respectively. Reaction (2) is analogous to the ring contraction accompanied by silanediyl extrusion encountered in other, larger, cyclosilanes.[5]

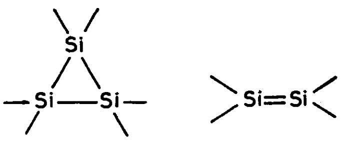

Figure 2

The u.v. absorption maximum exhibited by (**2**) is attributable to the Si=Si framework and *ca.* 20 nm shorter than those for the peraryldisilenes.[1–3] The observed 20 nm difference in the u.v. wavelength is presumably due to the absence of aryl perturbation in the tetra-alkyldisilene, but the difference is not very large and might imply that the conjugation of the silicon–silicon double bond with aryl groups is less effective than those of the corresponding all-carbon systems. Further, it should be emphasized that both of the systems shown in Figure 2 are chromophores *per se* and surprisingly the peralkyldisilene (**2**) was found to be a coloured compound. Thus the preparation of peralkylcyclotrisilanes and peralkyldisilenes has been useful in the study of the physical properties of compounds containing the cyclic Si_3 or the Si=Si framework.

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References

1 R. West, M. J. Fink, and J. Michl, *Science*, 1981, **214**, 1343; M. J. Fink, D. J. DeYoung, and R. West, *J. Am. Chem. Soc.*, 1983, **105**, 1070.

2 P. Boudjouk, B.-H. Han, and K. R. Anderson, *J. Am. Chem. Soc.*, 1982, **104**, 4992.

3 S. Masamune, Y. Hanzawa, S. Murakami, T. Bally, and J. F. Blount, *J. Am. Chem. Soc.*, 1982, **104**, 1150.

4 H. Watanabe, T. Muraoka, M. Kageyama, and Y. Nagai, *J. Organomet. Chem.*, 1981, **216**, C45; H. Watanabe, T. Muraoka, Y. Kohara, and Y. Nagai, *Chem. Lett.*, 1980, 735.

5 (a) M. Ishikawa and M. Kumada, *Chem. Commun.*, 1970, 612; 1971, 507; (b) M. Ishikawa and M. Kumada, *J. Organomet. Chem.*, 1972, **42**, 325; (c) M. Laguerre, J. Dunogues, and R. Calas, *Chem. Commun.*, 1970, 272; (d) C. W. Carlson, K. Matsumura, and R. West, *Organometallics*, 1982, **1**, 1458.

6 D. W. Larsen, B. A. Stolz, F. E. Stary, and R. West, *J. Chem. Soc., Chem. Commun.*, 1978, 1093.

7 D. T. Dix, G. Fraenkel, H. A. Karnes, and M. S. Newman, *Tetrahedron Lett.*, 1966, 517.

8 B. G. Ramsey, 'Electronic Transitions in Organometalloids,' Academic Press, New York, 1969; E. Carberry, R. West, and G. E. Glass, *J. Am. Chem. Soc.*, 1969, **91**, 5446; L. F. Brough and R. West, *ibid.*, 1981, **103**, 3049.

9 P. P. Gaspar, 'Reactive Intermediates,' vol. 1, eds. M. Jones and R. S. Moss, John Wiley, New York, 1978, ch. 7; D. N. Roark and G. J. D. Peddle, *J. Am. Chem. Soc.*, 1972, **94**, 5837; T. J. Barton and J. A. Kilgour, *ibid.*, 1976, **98**, 7746; Y. Nakadaira, T. Kobayashi, T. Otsuka, and H. Sakurai, *ibid.*, 1979, **101**, 486; C.-S. Chen, B. H. Cohen, and P. P. Gaspar, *J. Organomet. Chem.*, 1980, **195**, C1; J. D. Rich, T. J. Drahnak, R. West, and J. Michl, *ibid.*, 1981, **212**, C1; Y. Nakadaira, T. Otsuka, and H. Sakurai, *Tetrahedron Lett.*, 1981, 2417; Y.-S. Chen and P. P. Gaspar, *Organometallics*, 1982, **1**, 1410.

¶ Disilene species have been postulated as reaction intermediates; see ref. 9.