The Photolysis of a Cyclopolysilane System containing a Heteroatom, Hexaneopentyltrisilaoxetane; Evidence for the Formation of a Tetraneopentyldisilaoxirane

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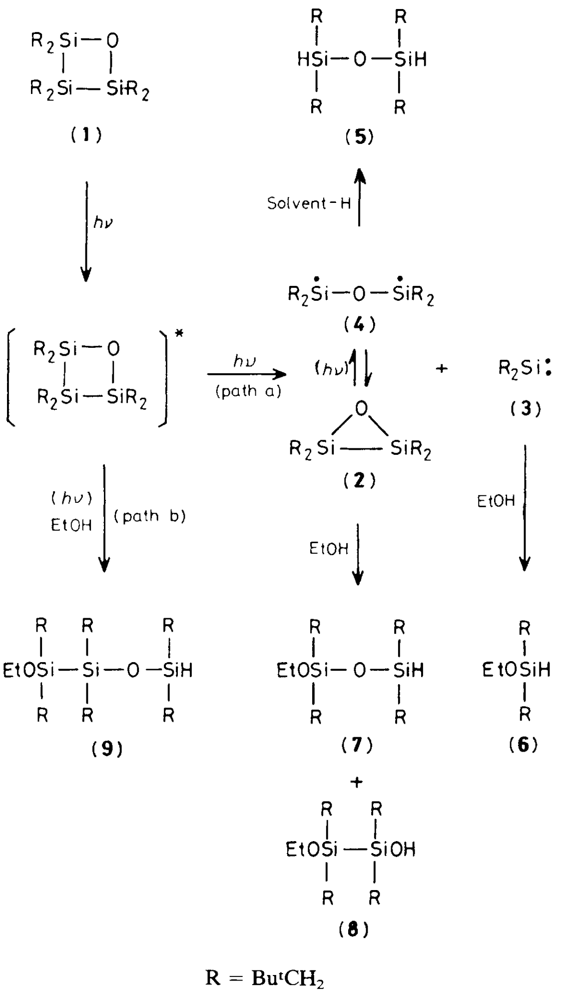
Hexaneopentyltrisilaoxetane (**1**) was synthesised and characterised; irradiation of (**1**) ($\lambda_{max.}$ 250 nm) in a hydrocarbon solvent afforded tetraneopentyldisilaoxirane (**2**) ($\lambda_{max.}$ 300 nm) with extrusion of dineopentylsilanediyl (**3**).

Recently, we reported the photolysis of the first peralkylcyclotrisilane, $[(\mathrm{Bu^tCH_2})_2\mathrm{Si}]_3$ [$\lambda_{max.}$ 310 nm(sh)], which afforded the first peralkyldisilene, $(\mathrm{Bu^tCH_2})_2\mathrm{Si{=}Si(CH_2Bu^t)_2}$ ($\lambda_{max.}$ 400 nm).[1] Subsequently we also found that peralkylcyclotetrasilanes, $[\mathrm{R^1R^2Si}]_4$, undergo photolysis to give successively cyclotrisilanes, $[\mathrm{R^1R^2Si}]_3$, and disilenes, $\mathrm{R^1R^2Si{=}SiR^1R^2}$, with extrusion of silanediyls, $:\mathrm{SiR^1R^2}$.[2] Following our interest in the photochemical behaviour of small-membered cyclopolysilanes, we now report on the photolysis of a cyclopolysilane containing a heteroatom hexaneopentyltrisilaoxetane,† $[(\mathrm{Bu^tCH_2})_2\mathrm{Si}]_3\mathrm{O}$ (**1**), which gave a new type of ring system, the first peralkyldisilaoxirane‡ $[(\mathrm{Bu^tCH_2})_2\mathrm{Si}]_2\mathrm{O}$ (**2**).

The starting trisilaoxetane, (**1**), was obtained readily in 88% yield, according to 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.¶ The *X*-ray crystal analysis of (**1**) showed the $\mathrm{Si_3O}$ ring to assume a planar structure in contrast with the folded structures of the cyclotetrasilanes reported previously,[3] and the bond angles of the four-membered ring indicate that the strain in the molecule is remarkable (Figure 1).‖ Nevertheless, compound (**1**) was found to be stable to oxygen, moisture, and heat below its melting point. The u.v. spectrum of (**1**) exhibited an intense absorption maximum at 250 nm (log ε 4.04) due to the cyclic $\mathrm{Si_3O}$ system, which compares with the maximum for the related silicon ring catenates such as $[(\mathrm{Bu^tCH_2})_2\mathrm{Si}]_3$ [310 nm(sh)][1] and $[\mathrm{R^1R^2Si}]_4$ (*ca.* 290 nm).[3,4] Therefore, it is of special interest to compare the photochemical behaviour of hexaneopentyltrisilaoxetane (**1**), with that of the related cyclopolysilane catenates.



Scheme 1. Possible pathways to products from (**1**).

$$\mathrm{Cl[(Bu^tCH_2)_2Si]_3Cl} \xrightarrow[(\mathrm{OH^-})]{\mathrm{H_2O}} (\mathbf{1}) \qquad (1)$$

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† Quite recently, two other peralkyltrisilaoxetanes were reported by other workers (ref. 5).

‡ A diaryldialkyldisilaoxirane, $[\mathrm{mes(Bu^t)Si}]_2\mathrm{O}$ (mes = $\mathrm{C_6H_2Me_3}$-2,4,6), has been prepared by West *et al.* from the corresponding diaryldialkyldisilene: see ref. 6.

§ Extensive study on four-membered cyclic compounds containing three silicon atoms and one heteroatom is currently in progress.

¶ Colourless crystals, m.p. 151—153 °C (sealed capillary). U.v. $\lambda_{max.}$ 250 nm (ε 11 400 $\mathrm{dm^3\ mol^{-1}\ cm^{-1}}$) (cyclohexane). ^{1}H N.m.r. ($\mathrm{C_6D_6}$, $\mathrm{Me_4Si}$) δ 0.97 (s, 18H, $\mathrm{Si^3CH_2C}Me_3$), 1.03 (s, 36H, $\mathrm{Si^2CH_2C}Me_3$), 1.22 (s, 4H, $\mathrm{Si^3C}H_2$), and 1.28 (s, 8H, $\mathrm{Si^2C}H_2$). ^{13}C N.m.r. ($\mathrm{CDCl_3}$, $\mathrm{Me_4Si}$) δ (tentative) 34.010 (q, $\mathrm{Si^3CH_2C}Me_3$), 33.735 (q, $\mathrm{Si^2CH_2C}Me_3$), 29.040 (t, $\mathrm{Si^3CH_2}$), 36.449 (t, $\mathrm{Si^2CH_2}$), 31.814 (s, $\mathrm{Si^3CH_2CMe_3}$), and 31.479 (s, $\mathrm{Si^2CH_2CMe_3}$). ^{29}Si N.m.r. ($\mathrm{CDCl_3}$, $\mathrm{Me_4Si}$) δ −22.10 ($\mathrm{Si^3}$) and 29.41 p.p.m. ($\mathrm{Si^2}$). I.r. (KBr) 2950s, 2900sh, 2860s, 1475sh, 1460s, 1400sh, 1385m, 1360m, 1250m, 1225s, 1152m, 1105m, 1005m, 930w, 910w, 846s (SiOSi), 780sh, and 755s $\mathrm{cm^{-1}}$. Isotopic pattern coefficients of molecular ions by electron impact (30 eV), obs. (calc.) (*M*) 100 (100), (*M* + 1) 50 (50), (*M* + 2) 22 (22), and (*M* + 3) 6 (5). Satisfactory elemental (C, H) analyses were obtained.

‖ *Crystal data* for (**1**): $\mathrm{C_{30}H_{66}Si_3O}$, *M* 527.118, dimensions 0.3 mm × 0.3 mm × 0.1 mm, monoclinic, $a = 11.250(2)$, $b = 16.015(1)$, $c = 11.715(4)$ Å, $\beta = 119.28(2)°$, $U = 1841.3(9)$ Å^3, space group $P2_1$, $Z = 2$, $D_c = 0.950\ \mathrm{g\ cm^{-3}}$, $\mu(\mathrm{Mo}\text{-}K_\alpha) = 1.47\ \mathrm{cm^{-1}}$. Data were collected on a Rigaku-Denki Model AFC-4 diffractometer with Mo-K_α *X*-radiation (monochromated with a graphite filter) using θ—2θ scans. The structure was solved by direct methods and all non-hydrogen atoms were refined anisotropically to $R = 0.07$ for 2282 observed reflections (numbers used for the calculations) ($|F_o| > 3\sigma\,|(F_o)|$, $3 \leqslant 2\theta \leqslant 55°$). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Thus, upon irradiation (254 nm) at room temperature for 13 min, a cyclohexane solution (4 ml) of (**1**) (16.7 mg) in an evacuated u.v. cell (sealed) showed a new intense absorption band at 300 nm, the intensity of which remained unchanged even after standing for one week in the dark. However, introduction of air into the solution resulted in the instant disappearance of the band. In a separate experiment, the newly developed absorption band at 300 nm decreased with increasing irradiation time and disappeared completely after 90 min. At the end of the irradiation, an absorption band at a shorter wavelength ($\lambda_{max.}$ 225 nm) was observed, which was not affected by air. Thus, the band at 300 nm can be reasonably ascribed to tetraneopentyldisilaoxirane, $[(Bu^tCH_2)_2Si]_2O$ (**2**), which is reminiscent of an absorption band at 310 nm[1] for the homocatenation analogue, hexaneopentylcyclotrisilane $[(Bu^tCH_2)_2Si]_3$.

To obtain further insight into the photochemical processes in this system, a product study was carried out. Thus, photolysis of (**1**) (6.0 mg) in cyclohexane (4 ml) for 90 min afforded tetraneopentyldihydrodisiloxane, $H(Bu^tCH_2)_2SiOSi(CH_2Bu^t)_2H$ (**5**)** (40% yield), together with small amounts of higher molecular weight by-products. The dihydrodisiloxane (**5**) is likely to arise from the disilaoxirane (**2**) which undergoes ring opening to form the intermediate disiloxane diradical (**4**) which in turn abstracts hydrogens from the solvent. It is also reasonable that the formation of (**2**) from (**1**) was accompanied by the generation of silanediyl (**3**) in a similar manner to that of cyclotetrasilanes as shown previously.[3]

A trapping experiment of the reactive intermediates, (**2**) and (**3**), with ethanol was then performed. Irradiation (90 min) of (**1**) (54 mg) in ethanol–cyclohexane (1 : 3, 4 ml) gave rise to (**5**) (15%), $(Bu^tCH_2)_2SiH(OEt)$ (**6**) (85%), $H(Bu^tCH_2)_2SiOSi(CH_2Bu^t)_2OEt$ (**7**) (38%), and $HO[(Bu^tCH_2)_2Si]_2OEt$ (**8**) (22%) (conversion yields are given, based on the reacted oxetane (**1**), Scheme 1, path a), and $H(Bu^tCH_2)_2SiO[Si(CH_2Bu^t)_2]_2OEt$ (**9**) in 70% yield based on the used oxetane (**1**) (Scheme 1, path b); thus, a 30% conversion of (**1**) into the intermediate (**2**) [or (**3**)] along path a was attained.

These observations suggest that the peralkyltrisilaoxetane (**1**) photochemically decomposed into (**2**) and silanediyl (**3**); (**2**) then gave (**5**), (**7**), and (**8**), and (**3**) gave (**6**) (Scheme 1). Compound (**9**) could be formed from the reaction between (**1**) and EtOH. The reaction pathway depicted is analogous to that of the photolysis of cyclotetrasilanes.[2] Thus, it was found that compound (**1**) did not cleave to form a disilene (Si=Si) and silanone (Si=O).

Finally, it should be emphasised that the disilaoxirane system is also a chromophore *per se*, and that the photolysis of hexaneopentyltrisilaoxetane (Si_3O) (**1**) leading to tetraneopentyldisilaoxirane (Si_2O) (**2**) provides a new aspect in the chemistry of three- and four-membered peralkylcyclopolysilane systems containing a heteroatom of type Si_nX (n = 2,3; X = O, N, *etc.*).

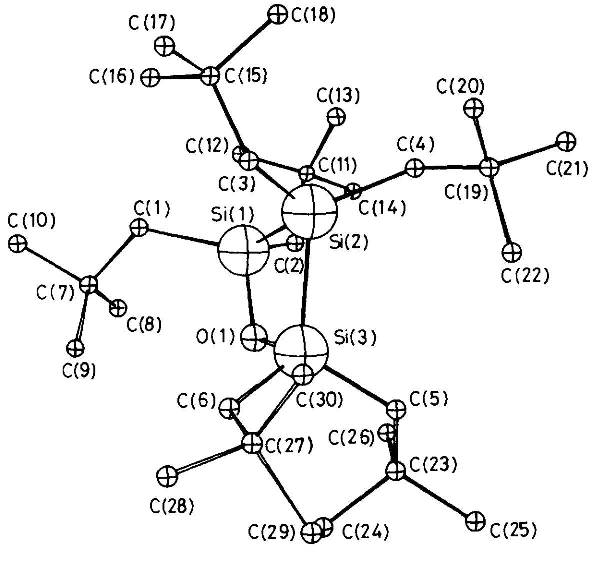

Figure 1. Molecular structure of (**1**). Bond lengths (Å): Si(1)–Si(2) 2.445(5), Si(2)–Si(3) 2.421(5), O(1)–Si(1) 1.645(11), O(1)–Si(3) 1.665(12). Interatomic distance (Å): Si(1)–Si(3) 2.73. Bond angles (°): Si(1)–Si(2)–Si(3) 68.2(2), O(1)–Si(1)–Si(2) 90.1(4), O(1)–Si(3)–Si(2) 90.5(4), Si(1)–O(1)–Si(3) 111.1(5), C(1)–Si(1)–C(2) 115.5(8), C(3)–Si(2)–C(4) 117.3(5), C(5)–Si(3)–C(6) 115.0(7). Dihedral angle (°) between the two planes, Si(1)Si(3)O(1) and Si(1)Si(3)Si(2) 2.8(6) (almost planar structure of the Si_3O ring).

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References

1 H. Watanabe, T. Okawa, M. Kato, and Y. Nagai, *J. Chem. Soc., Chem. Commun.*, 1983, 781.

2 H. Watanabe, Y. Kougo, and Y. Nagai, *J. Chem. Soc., Chem. Commun.*, 1984, 66; H. Watanabe, Y. Kougo, M. Kato, H. Kuwabara, T. Okawa, and Y. Nagai, *Bull. Chem. Soc. Jpn.*, 1984, **57**, 3019.

3 H. Watanabe and Y. Nagai, 'Organosilicon and Bioorganosilicon Chemistry,' ed. H. Sakurai, Ellis Horwood Limited, Chichester, England, 1985, pp. 107—114; H. Watanabe, M. Kato, T. Okawa, Y. Kougo, Y. Nagai, and M. Goto, *Appl. Organomet. Chem.*, 1987, in the press; C. L. Wadsworth, R. West, Y. Nagai, H. Watanabe, H. Matsumoto, and T. Muraoka, *Chem. Lett.*, 1985, 1525.

4 H. Watanabe, T. Muraoka, M. Kageyama, K. Yoshizumi, and Y. Nagai, *Organometallics*, 1984, **3**, 141; H. Matsumoto, M. Minemura, K. Takatsuna, Y. Nagai, and M. Goto, *Chem. Lett.*, 1985, 1005.

5 M. Weidenbruch and A. Schäfer, *J. Organomet. Chem.*, 1984, **269**, 231; S. Masamune, H. Tobita, and S. Murakami, *J. Am. Chem. Soc.*, 1983, **105**, 6524.

6 M. J. Michalczyk, R. West, and J. Michl, *J. Chem. Soc., Chem. Commun.*, 1984, 1525.

** All the final products in the present photolyses were isolated by preparative g.l.c. and fully characterised in the usual manner [i.r., n.m.r., and g.c.–mass spectra (high resolution mass, m.w.)].