The Photolysis of Octaisopropylcyclotetrasilane; Evidence for the Formation of Hexaisopropylcyclotrisilane and Tetraisopropyldisilene

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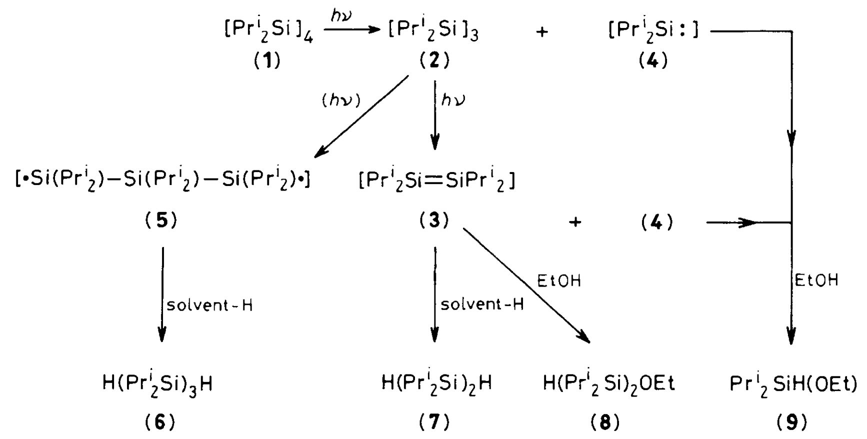
Irradiation of octaisopropylcyclotetrasilane (**1**) in a hydrocarbon solvent successively afforded hexaisopropylcyclotrisilane $[\mathrm{Pr^i{}_2Si}]_3$ (**2**) (λ_{max} 320 nm) and tetraisopropyldisilene $[\mathrm{Pr^i{}_2Si{=}SiPr^i{}_2}]$ (**3**) (λ_{max} 400 nm) with extrusion of di-isopropylsilanediyl (**4**).

We recently described the first synthesis of a peralkylcyclotrisilane, hexaneopentylcyclotrisilane $[(\mathrm{Bu^tCH_2})_2\mathrm{Si}]_3$, which gave on photolysis the first peralkyldisilene, tetraneopentyldisilene $(\mathrm{Bu^tCH_2})_2\mathrm{Si{=}Si}(\mathrm{CH_2Bu^t})_2$.[1] The spectrophotometric properties of these compounds are of interest: both the $\mathrm{Si_3}$ and Si=Si frameworks behave as chromophores *per se*, showing their longest wavelength absorption maxima at 310 and 400 nm, respectively. In close connection with these findings, Helmer and West[2] have shown that prolonged photolysis of $[\mathrm{Bu^tMeSi}]_4$ results in the formation of a linear trisilane, $[\mathrm{H(Bu^tMeSi)_3H}]$, which may arise from photolytic extrusion of t-butylmethylsilanediyl $[\mathrm{Bu^tMeSi{:}}]$ to form a cyclotrisilane, $[\mathrm{Bu^tMeSi}]_3$, followed by ring opening and abstraction of hydrogen from the solvent. Although the formation of the cyclotrisilane as well as the corresponding disilene probably occurred, u.v. absorptions were not recorded for these intriguing systems. In view of our continuing interest in small-ring peralkylcyclopolysilanes,[1,3] we photolysed a stable cyclotetrasilane, octaisopropylcyclotetrasilane $[\mathrm{Pr^i{}_2Si}]_4$ (**1**), and found that ring contraction[2,4] occurred to yield hexaisopropylcyclotrisilane $[\mathrm{Pr^i{}_2Si}]_3$ (**2**) which was in turn converted into tetraisopropyldisilene $[\mathrm{Pr^i{}_2Si{=}SiPr^i{}_2}]$ (**3**) with successive extrusion of di-isopropylsilanediyl $[\mathrm{Pr^i{}_2Si{:}}]$ (**4**).

Thus, upon irradiation (254 nm) at room temperature for 1 h, a cyclohexane solution (3 ml) of (**1**) (15.6 mg) in an evacuated u.v. cell (sealed) showed a new intense absorption band at 320 nm, the intensity of which rapidly increased and attained the highest value after 4—5 h. This band then began



Scheme 1. Absorption bands in the lowest energy transitions, λ_{max} (2) 320, (3) 400 nm (*cf.* 310 and 400 nm for the net Si_3 and Si=Si frameworks, respectively; ref. 1).

to diminish and instead a new weak band at 400 nm appeared after 7 h of irradiation. The colourless solution became yellow and the new band became more intense. On further irradiation (13 h), both bands completely disappeared and the solution became colourless again, showing an absorption band in a shorter wavelength region (275 nm).

In a separate experiment, the absorption bands at 320 and 400 nm gradually dissipated on ceasing irradiation and were observed again on reirradiation. Introduction of air into the coloured solution resulted in the instant disappearance of these bands. Thus it is fairly certain that the band at 320 nm can be ascribed to hexaisopropylcyclotrisilane $[\mathrm{Pr^i_2Si}]_3$ (**2**), since it has been shown that a similarly peralkylated cyclotrisilane, hexaneopentylcyclotrisilane, exhibits an absorption band at 310 nm.[1] Likewise, the observed band at 400 nm can be attributed to tetraisopropyldisilene $[\mathrm{Pr^i_2Si{=}SiPr^i_2}]$ (**3**), since the π–π^* transition in Si=Si bonding has been shown to appear near 400 nm.[1,5a]

To obtain further insight into the photochemical processes actually occurring, a product study was carried out. Thus, photolysis of (**1**) (101.7 mg) in cyclohexane (6 ml) for 64 h afforded hexaisopropyltrisilane (**6**) (28%) and tetraisopropyldisilane (**7**) (19%).† The dihydrotrisilane (**6**) is likely to arise from the cyclotrisilane (**2**) which undergoes ring opening to form the intermediate trisilane diradical (**5**) which in turn abstracts hydrogen from the solvent.[2] The dihydrodisilane (**7**) is explained by the intermediacy of the disilene (**3**) abstracting hydrogen.[1,2,5]

A trapping experiment with ethanol was performed. Irradiation (40 h) of (**1**) (200.5 mg) in ethanol–cyclohexane (1 : 3; 8 ml) gave rise to $\mathrm{H(Pr^i_2Si)_2OEt}$ (**8**) (68%) and $\mathrm{Pr^i_2SiH(OEt)}$ (**9**) (33%).†‡ It is well known that disilene and silanediyl species can be trapped efficiently by ethanol[1,5] (Scheme 1).

In summary, photolysis of peralkylcyclotetrasilanes provides a convenient method for producing peralkylated cyclotrisilanes and disilenes which are still relatively uncommon.

Received, 26th September 1983; Com. 1272

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† The products were isolated by preparative g.l.c. and fully characterised in the usual manner (i.r., n.m.r., and g.c.–mass spectra, as well as elemental analysis).

‡ Other products such as $\mathrm{Pr^i_2Si(OEt)_2}$, $\mathrm{H(Pr^i_2Si)_2H}$, $\mathrm{H(Pr^i_2Si)_2OH}$, $\mathrm{HO(Pr^i_2Si)_2OEt}$, $\mathrm{EtO(Pr^i_2Si)_2OEt}$, $\mathrm{H(Pr^i_2Si)_3OH}$, *etc.* were also detected by g.c.–mass spectroscopy.