The Persilylcyclotrisilane $[(Et_3Si)_2Si]_3$

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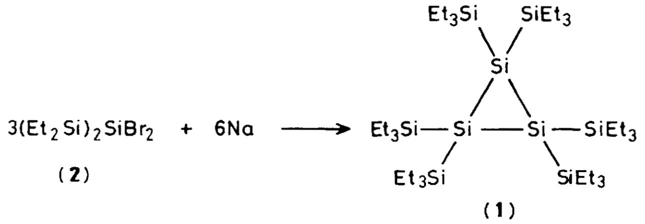
The novel persilylcyclotrisilane, hexakis(triethylsilyl)cyclotrisilane (**1**), was obtained by the reaction of 2,2-dibromohexaethyltrisilane with sodium; compound (**1**) was very photolabile under u.v. irradiation.

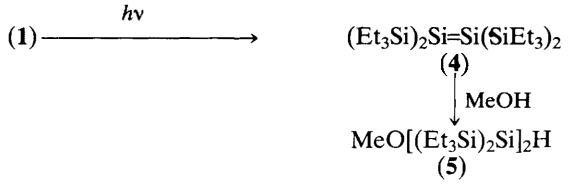
There is intense current interest in the chemistry of cyclotrisilanes because of their unique properties arising from high ring strain. However, the structures of cyclotrisilanes so far prepared are limited to peralkyl,[1] peraryl,[2] and alkyl–aryl[3] derivatives. We describe herein the first synthesis of a persilylcyclotrisilane, hexakis(triethylsilyl)cyclotrisilane (**1**), featuring the persilyl Si_3 framework, which acts as an intense u.v. chromophore.

The persilylcyclotrisilane (**1**) could be obtained in reasonable yield by the reductive trimerization of 2,2-



Scheme 1

$[(Bu^tCH_2)_2Si]_3$
(3)



$$(1) \xrightarrow{h\nu} (Et_3Si)_2Si{=}Si(SiEt_3)_2 \; (4) \xrightarrow{MeOH} MeO[(Et_3Si)_2Si]_2H \; (5)$$

Scheme 2

dibromohexaethyltrisilane (**2**)† with sodium (Scheme 1). Thus, a mixture of (**2**) (3.76 mmol), sodium (8.70 mmol), and toluene (27 ml) was refluxed for 10 h under nitrogen with stirring. Work up gave a semi-solid which was recrystallized from acetone to give colourless needles of (**1**)‡ (0.10 g, 11% yield), m.p. 270—275 °C (decomp.).

Compound (**1**) was found to be stable to oxygen and moisture, indicating that the triethylsilyl substituents can serve as effective steric blockades against external attack. In its u.v. spectrum the lowest energy transition occurs at 335 nm with an extinction coefficient of 1300. Figure 1 shows the u.v. spectrum of (**1**) together with that of a peralkylcyclotrisilane, $[(Bu^tCH_2)_2Si]_3$ (**3**) ($\lambda_{max.}$ 310 nm, ε 390), compound (**3**) having afforded the first opportunity for assessing the electronic properties of the peralkyl Si_3 framework;[1a] it is clear that the persilyl Si_3 framework of (**1**) acts as a much more intense chromophore. We feel that the bathochromic shift observed for (**1**) relative to (**3**) and the marked increase in intensity of the absorption band for (**1**) may be attributable to the electronic perturbation of the Si_3 ring by the complete silyl substitution as well as the large steric congestion caused by the substituents.

As a consequence, (**1**) should be more photoactive under u.v. irradiation than the peralkyl derivative (**3**). In fact, (**1**) (3.5 mg in 4 ml of cyclohexane) was completely decomposed upon irradiation for 1 h at room temperature in an evacuated u.v. cell with a 30 W low-pressure mercury lamp, while the complete photolysis of (**3**) required several hours of irradiation under similar conditions. Upon irradiation, the solution of (**1**) developed an intense yellow colour ($\lambda_{max.}$ 430 nm) which survived for at least 2 hours but disappeared instantly upon introduction of air, as previously observed for (**3**).[1a] These findings suggest that the photolysis of (**1**) produced the disilene $(Et_3Si)_2Si{=}Si(SiEt_3)_2$ (**4**), the first example of a persilyl derivative of disilene which is marginally stable in solution. Further evidence for the formation of the disilene was obtained in the photolysis of (**1**) (21 mg) in methanol–cyclohexane (2 : 1; 30 ml) which gave the methoxy tetrasilane (**5**)§ (26% yield) (Scheme 2).

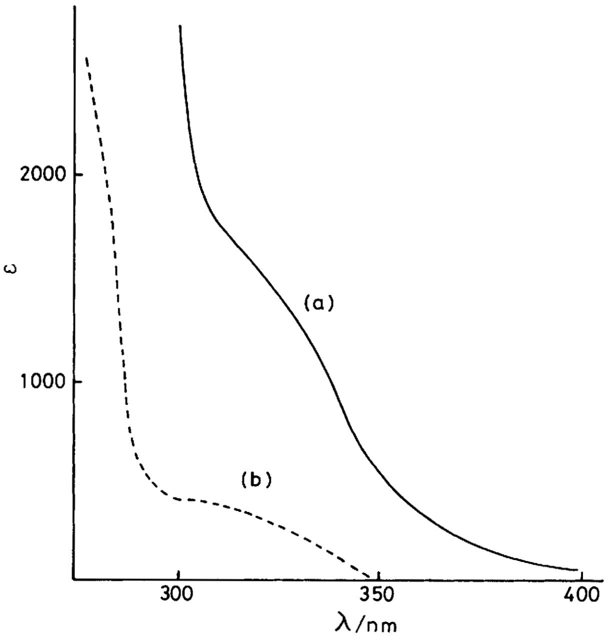


Figure 1. U.v. spectra of (a) the persilylcyclotrisilane (**1**) and (b) the peralkylcyclotrisilane (**3**) (ref. 1a).

The present work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture.

Received, 12th August 1986; Com. 1154

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[†] The dibromotrisilane (**2**)§ (b.p. 143—145 °C at 1 mmHg) can be readily prepared by the reaction of Ph_2SiCl_2 with Et_3SiCl in the presence of magnesium in hexamethylphosphoric triamide–tetrahydrofuran, which gave $(Et_3Si)_2SiPh_2$§ in 86% yield, followed by reaction of the latter with $HBr–AlBr_3$ in benzene, which gave (**2**) in 80% yield.

[‡] Compound (**1**) exhibited physical properties fully consistent with the cyclotrimeric structure: field desorption mass spectrum, parent clusters, *m/z* (rel. inten.) 774 (100), 775 (88), 776 (68), 777 (34), and 778 (21); electron impact (70 eV), *m/z* 774.4968, calc. for $C_{36}H_{90}Si_9$ 774.4966; ^1H n.m.r. (C_6D_6, $SiMe_4$) δ 0.90—1.30 (m, Et); ^{29}Si n.m.r. (C_6D_6, $SiMe_4$) δ 6.10 (Et_3Si) and −174.38 p.p.m. $[(Et_3Si)_2\textit{Si}]$.

[§] All new compounds were fully characterized by spectral and elemental analyses.