

Sensitised (Electron-transfer) Photochemical Reactions of Cyclopolysilanes, (R¹R²Si)_n (n = 3 or 4), in a Polar, Nucleophilic Solvent; Electron Donating Nature of Cyclopolysilanes (n = 3—7)†

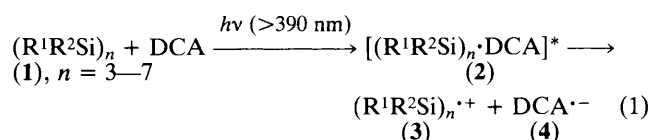
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Irradiation (>390 nm) of cyclopolysilanes, (R¹R²Si)_n (n = 3 or 4), in a mixed solvent (EtOH–MeCN–cyclo-C₆H₁₂), with 9,10-dicyanoanthracene as sensitiser, gave the corresponding α-ethoxy-ω-hydropolysilanes resulting from ring-opening addition of ethanol to the polysilanes; a mechanism involving facile electron transfer from the polysilanes is proposed.

Much attention has been focused on small-ring peralkylcyclopolysilanes because of their unusual properties. Recently, we reported on the oxidation potentials [0.4–1.5 V vs. standard calomel electrode (S.C.E.)] measured by cyclic voltammetry in MeCN for a series of peralkylcyclopolysilanes, (R¹R²Si)_n (n = 3–7),¹ which are markedly lower than those for the corresponding carbon analogues and decrease with decreasing ring size, indicating their facile electron donating nature. Also, we pointed out that the oxidation potentials parallel the ring-strain energies which in turn parallel the relative reactivities of ring-opening reactions with iodine.² From the anodic oxidation diagrams, it was suggested that the cyclopolysilanes initially undergo one-electron transfer reactions leading to the formation of an acyclic α,β-radical cation *via* the intimate molecular cation radical, (R¹R²Si)_n^{•+}. In connection with these findings,³ we report here a new general photoreaction of these polysilanes; cyclopolysilanes react with alcohols to give the corresponding ring-opening adducts *via* photosensitised [9,10-dicyanoanthracene (DCA)]⁴ electron transfer in which the polysilane behaves as an electron donor [reaction (1)].

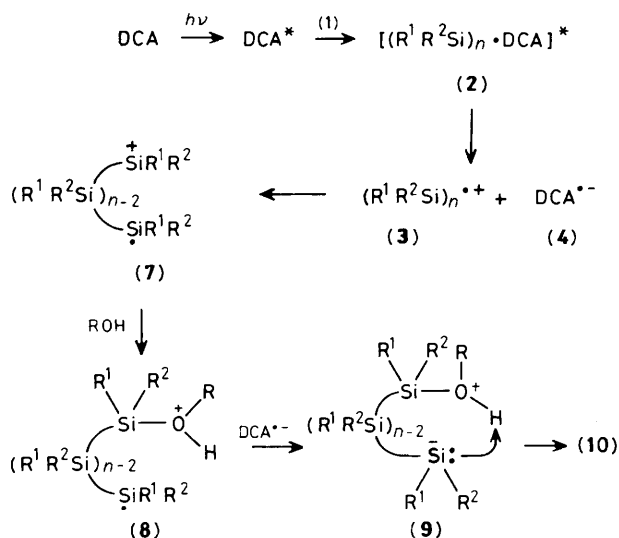


First, in order to investigate electron transfer in the present system, a small amount of a solution containing (1a) (1.5 × 10⁻² mmol) and DCA (5 × 10⁻³ mmol) in a mixed solvent (EtOH–MeCN–cyclo-C₆H₁₂, 5:4:6, v/v) (4 ml) was sealed in an evacuated e.s.r. tube which was placed in the cavity of an e.s.r. spectrometer. Upon irradiation (>390 nm, halogen lamp) at room temperature (*ca.* 25 °C), an intense e.s.r. signal with hyperfine structure appeared immediately. ‡ On ceasing the irradiation, this signal persisted, with a slow decrease in intensity, but the strong signal reappeared upon reirradiation. This signal was due to 9,10-dicyanoanthracene anion radical (DCA)^{•-} (4).⁵ Similar e.s.r. experiments using the other cyclopolysilanes gave similar results, as expected. The intensity of the signal observed upon irradiation was greatest for R¹R² = (Bu^tCH₂)₂, and decreased in the following order: [(Bu^tCH₂)₂Si]₃ > (PrⁱSi)₄ > (PrⁿSi)₅ > (Me₂Si)₆ > (PrⁿSi)₇.

In contrast, e.s.r. signals of the expected cyclopolysilane cation radicals, (R¹R²Si)_n^{•+} (3), could not be detected, even at 77 K, probably because of their high reactivity (see below).¹

Using tetracyanoethylene (TCNE) as a stronger electron acceptor,⁶ evidence for electron transfer in the dark from cyclopolysilanes was obtained. The electron transfer occurred *via* a charge-transfer (C.T.) complex,[§] in contrast to linear polysilanes the reaction of which required irradiation.^{6b} Thus, solutions containing a cyclopolysilane and TCNE exhibited e.s.r. signals due to the tetracyanoethylene anion radical (TCNE)^{•-} (6)⁷ [reaction (2)], the order of intensity being the same as that observed using DCA as electron acceptor.

Secondly, the reaction of (1a) with EtOH in the presence of DCA shows a new type of photosensitised ring-opening reaction. Thus, irradiation (>390 nm) of a solution of (1a) and DCA at room temperature for 40 min in an evacuated Pyrex tube (sealed), connected with a u.v. monitoring cell, led to a new intense absorption band at 305 nm. The intensity of the band remained unchanged on further irradiation, while the absorption bands due to DCA (350–450 nm region) decreased gradually. Upon irradiation for 3–4 h, the new band



Scheme 1. Possible pathway for formation of ring-opened adducts (10) from cyclopolysilanes (1) and the alcohol ROH *via* photosensitised (DCA) electron transfer.

† Part of this work was presented at the 50th Annual Meeting of the Japan Chemical Society, April 4, 1985 (Tokyo); Abstracts 4K29, p. 538.

‡ In the present system, similar experiments in the absence of one of the substrates or of MeCN did not lead to an e.s.r. signal, however.

§ We found that (1) and TCNE in the mixed solvent readily formed the C.T. complexes which are yellow to orange in colour (C.T. complexes in CH₂Cl₂: ref. 8), and also that no C.T. complex was formed between (1) and DCA in the same solvent.

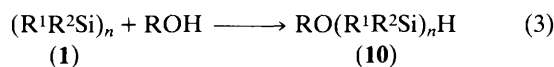
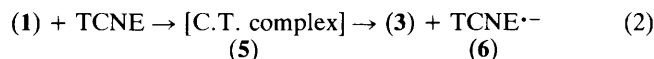
Table 1. Photosensitised reactions of cyclopolysilanes (**1a–d**) with ethanol.^a

Reaction time/h	% Conversion of (1) ^c	Product, % yield ^d
1.5	99	(10a), 47
19	69	(10b), 49
20	64	(10c), 26
16	76	(10d), 56

^a Substrate solution (1.5–3.5 × 10⁻² mmol) in EtOH–MeCN–cyclo-C₆H₁₂ (5:4:6, v/v) (4–6 ml) was irradiated in a sealed, evacuated Pyrex tube (molar ratio Si_n: DCA, 5:1). ^b 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 (high resolution)]. Small amounts of by-products were also formed. ^c Based on (1) used. ^d Conversion yield.

disappeared and the DCA absorption bands became very weak. In separate experiments, the absorption band at 305 nm slowly diminished in the dark during 21 h, but introduction of air led to its instant disappearance. Thus, since the e.s.r. signal of DCA^{•-} was fairly stable, it is likely that the band at 305 nm may be attributed to the radical anion (**4**).⁵

To obtain further insight into the sensitised photochemical processes actually occurring, a product study was carried out. The photoreaction of (**1a**) with ethanol in the presence of DCA gave, in 47% yield (see Table 1), 1-ethoxy-1,1,2,2,3,3-hexaneopentyltrisilane (**10a**), the product arising from ring-opening addition of ethanol to the cyclotrisilane [reaction (3)].



- a;** $n = 3$; $\text{R}^1 = \text{R}^2 = \text{Bu}^t\text{CH}_2$
b; $n = 4$; $\text{R}^1 = \text{R}^2 = \text{Pr}^i$
c; $n = 4$; $\text{R}^1 = \text{Bu}^t$, $\text{R}^2 = \text{Me}$
d; $n = 4$; $\text{R}^1 = \text{R}^2 = \text{Bu}^s$

R = Et; Conditions: DCA, *hν*, in ROH–MeCN–cyclo-C₆H₁₂.

We suggest that, by analogy with the mechanism for photosensitised addition of alcohols to alkenes,⁹ the products arising from ring-opening addition of the alcohol to the cyclopolysilanes (**1**) are formed by a mechanism involving photosensitised electron transfer processes *via* the formation of cation radicals (**3**) and the anion radical (**4**) (Scheme 1). Finally, the present reaction not only provides a convenient method for preparing relatively inaccessible linear α -alkoxy-polsilanes which have a variety of bulky substituents on silicon, but also adds an interesting new aspect to cyclopolysilane photochemistry. Further, the present work clearly demonstrates that the electron donating nature of cyclopolysilanes is a general property.

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