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Photooxygenation of Aryldisilanes via Photoinduced Electron Transfer

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Photoreactions of polysilanes entailing electron transfer have received considerable attention in recent years.[1–6] Previous studies on the photosilylation of alkenes,[1] cyano aromatics,[2] and acridinium salts[3] with disilanes have indicated that a key intermediate in this photoreaction is a radical cation of the disilane and that the Si–Si bond of the radical cation is cleaved to give a silyl radical and a silicenium ion. The reactive species thus generated can be trapped by carbon tetrachloride[4] or an alcohol.[5] However, little is known about the chemical behavior of intermediates generated in the photooxygenation of disilanes via electron transfer,[6] although the oxygenation of cyclic polysilanes is known to give siloxanes.[7] We now report on the characteristics of the photooxygenation of aryldisilanes via photoinduced electron transfer. The present study shows that radical cations of aryldisilanes also produce silyl radicals and silicenium ions that are trapped by molecular dioxygen and water, respectively, to give disiloxanes as ultimate products.

Irradiation of an acetonitrile solution containing 1-(4-methoxyphenyl)-1,1,2,2,2-pentamethyldisilane (**1a**, 1 mmol) and 9,10-dicyanoanthracene (DCA) (0.05 mmol) with a high-pressure mercury lamp through an aqueous NH_3–$CuSO_4$ filter solution (>400 nm) under a stream of oxygen for 3 h gave 1,3-bis(4-methoxyphenyl)-1,1,3,3-tetramethyldisiloxane (**2a**) as the sole isolable product in 82% yield (Scheme 1). Similar photoreaction of 1-(4-methylphenyl)-1,1,2,2,2-pentamethyldisilane (**1b**) and 1-phenyl-1,1,2,2,2-pentamethyldisilane (**1c**) with oxygen afforded the corresponding 1,3-diaryldisiloxanes **2b** and **2c** in 64 and 85% yields, respectively. However, the photooxygenation of 1-benzyl-1,1,2,2,2-pentamethyldisilane (**1d**) gave benzaldehyde (**3**) and 1,2-diphenylethane (**4**) in 27 and 11% yields, respectively, and no disiloxane derivatives were formed. The results are summarized in Table 1.

Scheme 1

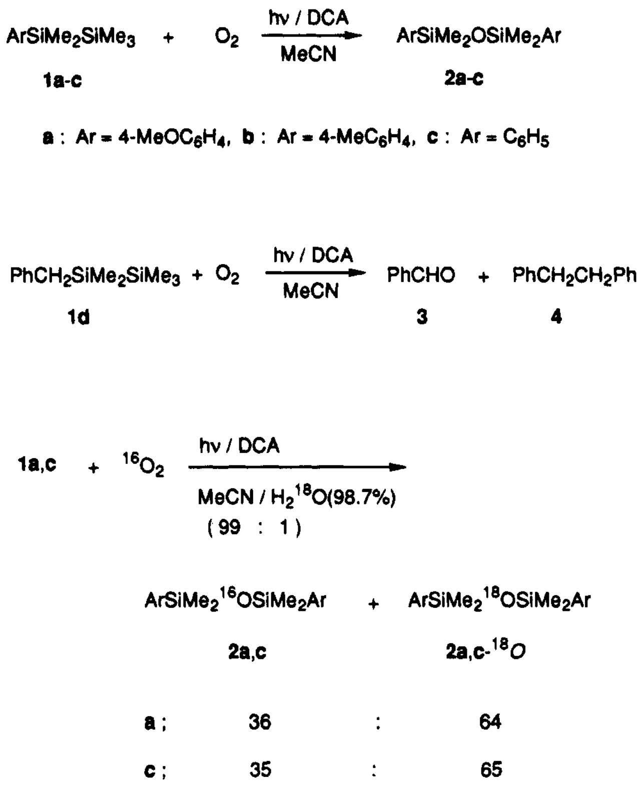

Table 1. DCA-Sensitized Photooxygenation of Aryldisilanes in Acetonitrile[a]

compd	$E^{ox}_{(1/2)}$[b] (V)	k_q[c] × 10^{-10} (M^{-1} s^{-1})	ΔG[d] (kJ mol^{-1})	irradn time (h)	product(s) (%)		
					2	3	4
1a	0.82	1.22	−77.2	3	82	–	–
1b	0.93	0.73	−66.6	5	64	–	–
1c	1.05	0.70	−55.0	6	85	–	–
1d	1.05	0.62	−55.0	3	–	27	11

[a] [1] = 0.05 M. [DCA] = 5 × 10^{-4} M. Conversion was >95%. [b] Oxidation potentials vs $Ag/AgClO_4$ in MeCN. [c] Rate constants for the fluorescence quenching of DCA in aerated MeCN: [DCA] = 1 × 10^{-4} M; τ(DCA, air) = 16.1 ns. [d] Calculated free energy changes for the one-electron transfer process from disilanes to $^1DCA^*$ in MeCN. See ref 11. Reduction potential of DCA = −1.33 V vs $Ag/AgClO_4$ in MeCN.

The effect of solvent on the photooxygenations was remarkable. The addition of a small amount of water to the reaction systems (CH_3CN:H_2O = 97.5:2.5) had no influence on the progress of the photoreactions, and the same products were obtained. However, when the photooxygenation of **1a** was carried out in benzene in the presence of DCA, only a trace amount of **2a** was formed and most of **1a** was recovered. In the absence of DCA, **1a** was completely recovered from both acetonitrile and benzene reaction mixtures.[8] Furthermore, the photoreaction of **1a** in the presence of DCA in CH_3CN and CH_3CN:H_2O (97.5:2.5) under an argon atmosphere gave a complex mixture. The photooxygenation of **1a** in dichloromethane in the presence of Rose Bengal (a singlet oxygen-generating sensitizer) resulted in a quantitative recovery of the starting material.

Irradiation of **1a** (0.04 mmol) and DCA (5 × 10^{-3} mmol) in CH_3CN:$H_2{}^{18}O$ (99:1, [$H_2{}^{18}O$] = 0.5 M) under oxygen for 0.75 h gave **2a** and 1,3-bis(4-methoxyphenyl)-1,1,3,3-

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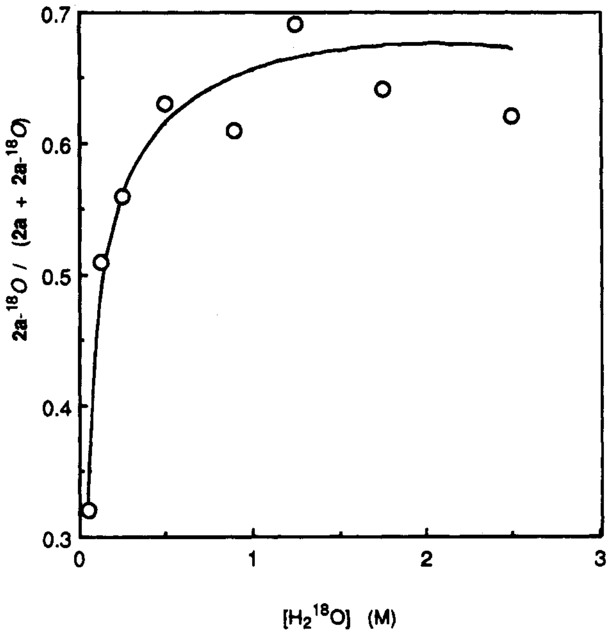


Figure 1. Plots of **2a**-^{18}O/(**2a** + **2a**-^{18}O) vs [H_2O], the product ratios for **2a** and **2a**-^{18}O in the DCA-sensitized photooxygenation of **1a** in acetonitrile containing various concentrations of $H_2{}^{18}O$. Key: (○) **2a**-^{18}O/(**2a** + **2a**-^{18}O).

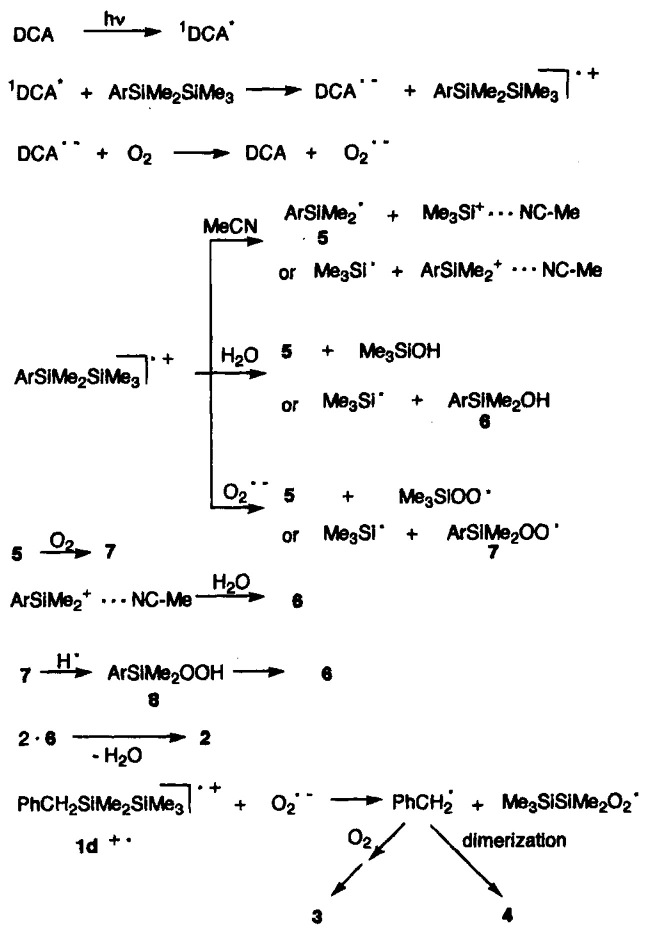
tetramethyldisiloxane-*2*-^{18}O (**2a**-^{18}O) in a 36:64 ratio (Scheme 1). The ratio of **2a**-^{18}O/(**2a** + **2a**-^{18}O) increased with increasing $H_2{}^{18}O$ over a relatively low concentration range (0.05–0.9 M). However, the ratio increased no further with relatively high concentrations (0.9–2.5 M), and the ratio did not exceed 0.7 (Figure 1).[9] The photoreaction of **1c** under similar conditions (CH_3CN: $H_2{}^{18}O$ = 99:1) gave a mixture of **2c** and **2c**-^{18}O in a 35:65 ratio.

The GC–MS analysis of the reaction mixture of the DCA-sensitized photooxygenation of **1a** in acetonitrile showed the formation of 4-(methoxyphenyl)dimethylsilanol **6a**. This indicated that **6a** is formed as a primary product and **2a** is produced concomitant with the disappearance of **6a**, upon concentration of the mixture.[10]

Fluorescence of DCA in acetonitrile was efficiently quenched by all of the disilanes. Free energy changes (ΔG), estimated by the Rehm–Weller equation for a one-electron transfer process from the disilanes to $^1DCA^*$ in acetonitrile, were negative (Table 1).[11]

From these results, we propose the mechanism shown in Scheme 2 for the photooxygenation of aryldisilanes. The first step is a one-electron transfer from the disilane to $^1DCA^*$ to give a pair of radical ions, $ArSiMe_2SiMe_3{}^{\bullet+}$ and $DCA^{\bullet-}$. A secondary electron transfer from $DCA^{\bullet-}$ to molecular dioxygen affords DCA and superoxide ion $O_2{}^{\bullet-}$.[12] The Si–Si bond of $ArSiMe_2SiMe_3{}^{\bullet+}$ is cleaved by the attack of a nucleophile such as CH_3CN,[13] water, and $O_2{}^{\bullet-}$ to give the silyl radical **5**, the silicenium ions $ArSiMe_2{}^+$ and Me_3Si^+, the silanol **6**, and the silylperoxyl radical **7**. It is well-known that the silicenium ions are stabilized by coordination with CH_3CN and that $ArSiMe_2{}^+$ reacts with water to give **6**.[14] The reaction of **5** with molecular dioxygen also gives **7**, and hydrogen abstraction of **7** produces the hydroperoxide **8**. Although **8** was not detected under the reaction conditions, it would be converted into the disiloxane **2** via dehydration from two molecules of **6**.

Scheme 2



In the case of **1d**, the nucleophile-assisted cleavage of the C–Si bond of **1d**$^{\bullet+}$ occurs in preference to the cleavage of the Si–Si bond to give a benzyl radical. This radical reacts with molecular dioxygen to give **3** or dimerizes to give **4**. It may be of interest to note that molecular dioxygen and/or $O_2{}^{\bullet-}$ play an important role in the bond cleavage of **1d**$^{\bullet+}$. The photooxygenation of **1d** in the

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[9] At the relatively low concentration of $H_2{}^{18}O$, $ArSiMe_2SiMe_3{}^{\bullet+}$ will react with $H_2{}^{16}O$ and $H_2{}^{18}O$ competitively. In fact, the ratios **2a**-^{18}O/(**2a** + **2a**-^{18}O) depended on the dryness of acetonitrile. When less freshly distilled acetonitrile (CH_3CN:$H_2{}^{18}O$ = 99:1) was used, the ratio decreased to 0.3–0.4.

[10] The disiloxane and alkoxysilane derived from Me_3Si^+ were not detected even in the presence of 4-methylbenzyl alcohol,[14a] but the GC–MS analysis of the reaction mixture of the photooxygenation of **1a** in acetonitrile showed the formation of a small amount of $ArSiMe_2OSiMe_3$, which is probably produced by the reaction of Me_3SiOH and $ArSiMe_2OH$.

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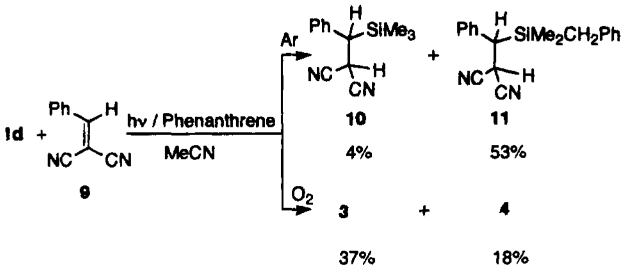
Scheme 3



presence of 1,1-dicyano-2-phenylethene **9** and phenanthrene gave **3** and **4** (Scheme 3). The yields and product ratio of **3** and **4** in this photoreaction were similar to those of the DCA-sensitized photooxygenation. However, when this photoreaction was carried out under an argon atmosphere, the silylation of **9** by **1d** produced the silylated products **10** and **11** via the cleavage of the Si–Si bond.[1c] These results suggest that the attack of $O_2^{\bullet -}$ on the Si atom of $\mathbf{1d}^{\bullet +}$ probably promotes the C–Si bond cleavage of the radical cation.

Experimental Section

General. GC–MS analyses were performed on JEOL JMS-DX303HF connected with a Hewlett-Packard 5890J gas chromatograph equipped with capillary glass column TC-1 (GL Science, 30 m × 0.53 mm, i.d. 1.5 μm). Other general experimental information was described in a previous paper.[15]

Materials. Disilanes were prepared according to the method described in the literature.[16] $H_2{}^{18}O$ (ISOTEC, 98.7 atom %) was purchased and used without further purification. Other organic chemicals were purchased and purified by distillation or recrystallization. Acetonitrile was distilled three times over P_2O_5 and once over anhydrous K_2CO_3 for usual photoreactions and redistilled once over calcium hydride for photoreactions in CH_3CN:$H_2{}^{18}O$.

Typical Procedure for DCA-Sensitized Photooxygenation of Aryldisilanes. A mixture of **1a** (238 mg, 1 mmol) and DCA (11 mg, 0.05 mmol) in anhydrous acetonitrile (20 mL) was irradiated at room temperature with a 500 W high-pressure Hg arc through an aqueous NH_3–$CuSO_4$ filter solution (>400 nm) for 3 h with O_2 bubbling through the reaction mixture. After consumption of **1a**, the solvent was removed under reduced pressure. The residue was chromatographed on silica gel. Elution with hexane:benzene (8:2) gave **2a** (142 mg, 82%). The structure was determined on ^1H- and ^{13}C-NMR, IR, and mass spectral data.[17]

DCA-Sensitized Photooxygenation of Aryldisilanes in Acetonitrile Containing $H_2{}^{18}O$. A mixture of **1a** (10 mg, 0.04 mmol) and DCA (1 mg, 5 × 10^{-3} mmol) in CH_3CN:$H_2{}^{18}O$ (99:1, 1 mL) was irradiated for 0.75 h with O_2 bubbling through. After irradiation, the solvent was removed and the residue was analyzed by GC–MS. The relative intensities in the mass spectrum showed that **2a** and **2a**-^{18}O were formed in a 36:64 ratio.

Phenanthrene -Sensitized Photooxygenation of 1-Benzyl-1,1,2,2,2-pentamethyldisilane. A mixture of **1d** (222 mg, 1 mmol), 1,1-dicyano-2-phenylethene (111 mg, 1 mmol), and phenanthrene (178 mg, 1 mmol) in anhydrous acetonitrile (20 mL) was irradiated at room temperature with a 500 W high-pressure Hg arc through a Pyrex filter (>280 nm) for 1 h with O_2 bubbling through. After irradiation, the solvent was removed and then the analysis of the residue by ^1H-NMR and GC showed the formation of **3** (37%) and **4** (18%).

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