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Photooxygenation of Arylmethylsilanes via Photoinduced Electron-Transfer

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The 9,10-dicyanoanthracene (DCA)-sensitized photooxygenation of arylmethylsilanes in acetonitrile and benzene gave aromatic aldehydes and aromatic carboxylic acids in a site-selective manner. This photoreaction involves exciplex and radical ions as reactive intermediates, depending on the solvents.

Photoreactions of organosilicon compounds via electron transfer have received considerable attention in recent years, and the photoallylation and some other related photoreactions by use of these compounds have been reported.1-4) These reactions usually occur in polar solvents via the cleavage of C-Si bond. We now report a photooxygenation5-6) of arylmethylsilanes. This reaction occurs both in polar and nonpolar solvents.

Irradiation of an acetonitrile or a benzene solution containing 1-naphthylmethyltrimethylsilane (**1a**, 0.5 mmol) and DCA (0.02 mmol) with a high-pressure mercury lamp through an aqueous NH_3-$CuSO_4$ filter solution (>400 nm) under oxygen atmosphere gave 1-naphthalenecarboaldehyde (**2a**) and 1-naphthalenecarboxylic acid (**3a**). The photooxygenation of 2-naphthylmethyltrimethylsilane (**1b**) and 4-trimethylsilylmethylbiphenyl (**1c**) gave the corresponding aromatic aldehydes and carboxylic acids. In these reactions, the oxidation of aromatic rings did not occur. These results are in sharp contrast with the photooxygenation of 1- and 2-methylnaphthalenes7a) and 4-methylbiphenyl7b) in the presence of DCA, in which the aromatic rings are competitively oxidized as well as the alkyl groups.

When benzyltrimethylsilane (**1d**, 1.5 mmol) and DCA (0.25 mmol) were irradiated in acetonitrile under oxygen, both of **1d** and DCA disappeared to give benzaldehyde (**2d**), benzoic acid (**3d**), cis- and trans-9-benzyl-9,10-dicyano-9,10-dihydroanthracenes (**4**,**5**),4a) and 10-benzyl-10-cyano-

(9,10H)anthracenone (**6**).[1b] The photoreaction in benzene under similar conditions resulted in the recovery of the starting materials. However, the addition of Bu_4NClO_4 to this reaction system caused the cleavage of C-Si bond to give **2d**, **3d**, **4**, **5**, and **6**. The results are summarized in Table 1.

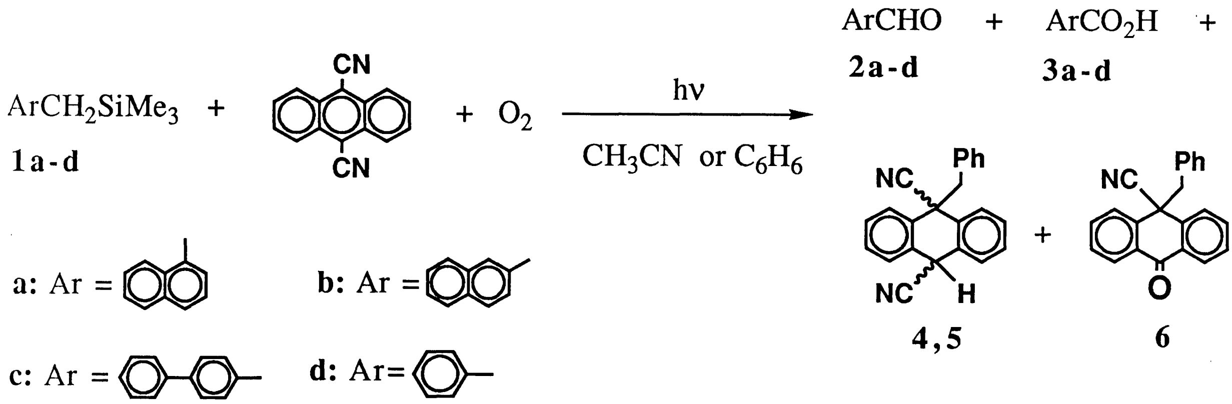


Table 1. DCA-Sensitized Photooxygenation of Arylmethylsilanes

Compd	Solvent	$E^{ox}_{1/2}$ a) V	ΔG b) kJ mol^{-1}	k_q c) x 10^{-9} $dm^3mol^{-1}s^{-1}$	Irradn time/h	Conv %	Products (yields d)/%)
1a	CH_3CN	0.96	-81.6	14.1	1.5	95	**2a**(13), **3a**(29)
1a	C_6H_6			7.5	24	83	**2a**(31), **3a**(20)
1a	C_6H_{12}				120	<5	**2a**(trace)
1b	CH_3CN	0.96	-81.6	13.8	1.5	95	**2b**(33), **3b**(34)
1b	C_6H_6			7.8	24	70	**2b**(16), **3b**(15)
1c	CH_3CN	1.0	-77.8	11.8	0.3	>98	**2c**(66), **3c**(7)
1c	C_6H_6			5.1	20	95	**2c**(35), **3c**(24)
1d	CH_3CN	1.22	-56.5	7.5	12	90	**2d**(9), **3d**(35), **4**+**5**(4), **6**(7)
1d	C_6H_6			0.005	120	<5	**2d**(trace)
1d	C_6H_6 e)			0.014	77	85	**2d**(10), **3d**(47) **4**+**5**(3), **6**(7)

a) Oxidation potentials vs. $Ag/AgClO_4$ in CH_3CN. b) Calculated values in CH_3CN; see Ref. 8. c) Rate constants for fluorescence quenching of DCA in aerated solutions; [DCA] = 1 x 10^{-4} mol dm^{-3}, τ(air)= 16.1 ns (CH_3CN), τ(air) = 15.2 ns (C_6H_6). d) Yields are based on arylmethylsilanes used. e) [Bu_4NClO_4] = 5 x 10^{-3} mol dm^{-3}.

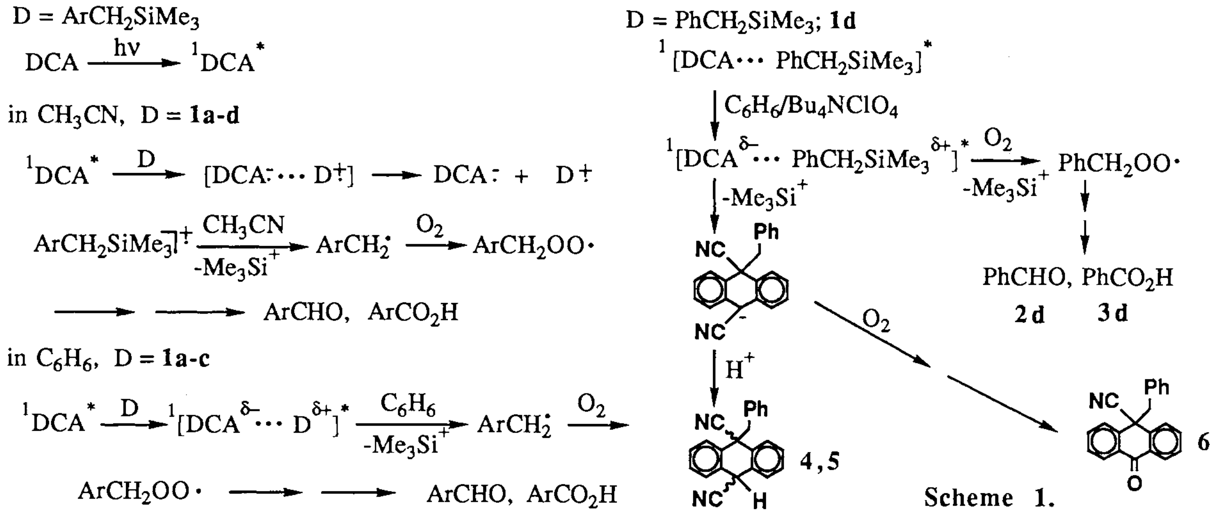
Table 2. Exciplex Quenching by Bu_4NClO_4 in Benzene

Compd	λ_{max}[a)] nm	τ[b)] ns	k'_q[c)] x 10^{-9} $dm^3mol^{-1}s^{-1}$
1a	550	27.4	2.41
1b	529	32.8	1.36
1c	535	16.4	2.85

a) The maximum of wavelength of exciplex emission. b) The life-time of exciplexes. c) The rate constants for quenching of the exciplex emission by Bu_4NClO_4.

Fluorescence of DCA in acetonitrile was efficiently quenched by arylmethylsilanes. Free energy changes (ΔG) estimated by the Rehm-Weller equation for one-electron transfer process from arylmethylsilanes to $^1DCA^*$ were negative (Table 1).[8)] The k_q values in benzene were smaller than those in acetonitrile. For **1a-c**, weak emissions due to exciplex formation with DCA were observed in a longer wavelength region than the emission of $^1DCA^*$ in benzene. The exciplex emissions were quenched by Bu_4NClO_4 (Table 2). [9)]

A proposed mechanism for the photooxygenation is as shown in Scheme 1. In acetonitrile, the radical cations of arylmethylsilanes (D) and the radical anion of DCA are produced by a one-electron transfer from D to $^1DCA^*$. The C-Si bond of $D^{\cdot+}$ is cleaved by the aid of a nucleophilic attack of acetonitrile on trimethylsilyl group, giving arylmethyl radicals and trimethylsilyl cation.[4)] Arylmethyl radicals then react with O_2 to give aldehydes and carboxylic acids. In benzene, emissive exciplexes between $^1DCA^*$ and **1a-c** are formed and they are quenched by Bu_4NClO_4 in a nearly diffusion controlled rate. These exciplexes seem to have a strong charge-transfer character even in the absence of Bu_4NClO_4 because of lower oxidation potentials of **1a-c**. In these cases, the C-Si bond may be cleaved through interaction of trimethylsilyl group with benzene; in this case benzene probably acts as a π-donor toward $D^{\cdot+}$.[2b)] This hypothesis was partly supported by the fact that no photooxygenation of **1a** occurred in cyclohexane under similar conditions.



$D = ArCH_2SiMe_3$

$$DCA \xrightarrow{h\nu} {}^1DCA^*$$

in CH_3CN, D = **1a-d**

$$^1DCA^* \xrightarrow{D} [DCA^{\cdot-}\cdots D^{\cdot+}] \longrightarrow DCA^{\cdot-} + D^{\cdot+}$$

$$ArCH_2SiMe_3]^{\cdot+} \xrightarrow[-Me_3Si^+]{CH_3CN} ArCH_2^{\cdot} \xrightarrow{O_2} ArCH_2OO\cdot \longrightarrow \longrightarrow ArCHO,\ ArCO_2H$$

in C_6H_6, D = **1a-c**

$$^1DCA^* \xrightarrow{D} {}^1[DCA^{\delta-}\cdots D^{\delta+}]^* \xrightarrow[-Me_3Si^+]{C_6H_6} ArCH_2^{\cdot} \xrightarrow{O_2} ArCH_2OO\cdot \longrightarrow \longrightarrow ArCHO,\ ArCO_2H$$

Scheme 1.

In the case of **1d**, the addition of Bu_4NClO_4 facilitated the ionic dissociation of the exciplex between $^1DCA^*$ and **1d** in benzene. The quenching rate of fluorescence of $^1DCA^*$ with **1d** in the presence of Bu_4NClO_4 was three times faster than that in the absence of Bu_4NClO_4. The benzyl radical generated by the cleavage of the C-Si bond reacts with O_2 and $DCA^{\cdot-}$ to give **2d**, **3d**, **4**, **5**, and **6**.

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