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PHOTOOXYGENATION OF 1,2-DIARYLCYCLOPROPANES: FORMATION OF 3,5-DIARYL-1,2-DIOXOLANES VIA PHOTOINDUCED ELECTRON TRANSFER

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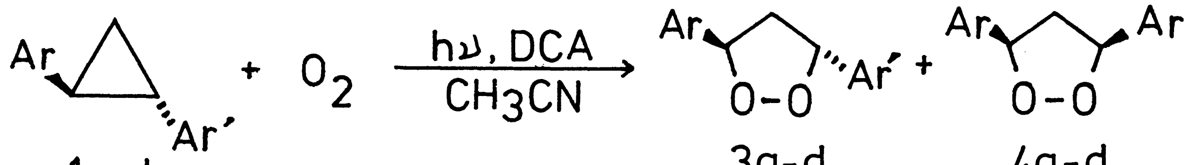
The photooxygenation of electron-rich 1,2-diarylcyclopropanes such as 1,2-bis(4-methoxyphenyl)cyclopropane and 1-(4-methoxyphenyl)-2-phenylcyclopropane in the presence of 9,10-dicyanoanthracene(DCA) as a sensitizer in acetonitrile affords trans- and cis-3,5-diaryl-1,2-dioxolanes in high yields. This photooxygenation is initiated by the electron transfer from 1,2-diarylcyclopropanes to the excited singlet DCA, involving the cation radical of cyclopropanes as a key intermediate.

Recently, much attention has been focussed on the photooxygenation of electron-rich molecules via electron transfer from synthetic and mechanistic viewpoints.[1-5] However, little is known about the photooxygenation of carbon-carbon single bond.[5,6] We now report a novel type of photooxygenation of 1,2-diarylcyclopropanes(CP) using 9,10-dicyanoanthracene(DCA) as a sensitizer to give 3,5-diaryl-1,2-dioxolanes.

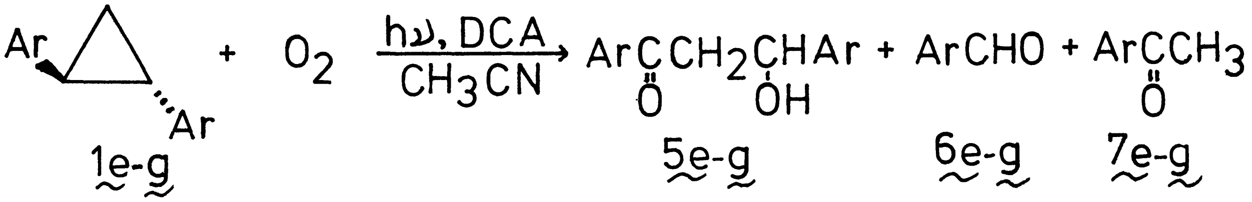
Irradiation of an oxygen-saturated dry acetonitrile solution of trans-1,2-bis(4-methoxyphenyl)cyclopropane(1a) (0.2 mmol) in the presence of DCA(0.008 mmol) with a 300 W high-pressure mercury arc for 5 h gave trans- and cis-3,5-bis(4-methoxyphenyl)-1,2-dioxolanes(3a and 4a) in a 95% yield.[7,8] The product ratio of 3a to 4a remained constant(3a/4a = 23/77) up to 95% conversion. These products were isolated by repeated recrystallizations from n-hexane. The structures were assigned from their elemental analyses and spectral properties, and also by the following chemical transformations. Chromatography of a mixture of 3a and 4a on silica gel gave 1,3-bis(4-methoxyphenyl)-3-keto-1-propanol(5a), 4-methoxybenzaldehyde(6a), and 4-methoxyacetophenone(7a). Treatment of a mixture of 3a and 4a with $NaBH_4$ gave 1,3-bis(4-methoxyphenyl)propane-1,3-diol(8a) as a mixture of the meso and dl isomers in good yields (≥ 80%).



1a-d 3a-d , 4a-d

a; Ar=Ar′=4-$MeOC_6H_4$
b; Ar=Ph, Ar′=4-$MeOC_6H_4$
c; Ar=Ph, Ar′=4-$Me_2NC_6H_4$
d; Ar=Ar′=3,4-$(MeO)_2C_6H_3$

When cis-1,2-bis(4-methoxyphenyl)cyclopropane(2a) was irradiated under similar conditions, the rapid isomerization of 2a to 1a occurred at the initial stage.$^{9)}$ Further irradiation of the reaction mixture yielded 3a and 4a in a ratio identical with that in the photoreaction of 1a. The photoreaction of other trans-1,2-diarylcyclopropanes(1b-d), bearing electron-donating substituents, which have lower oxidation potentials(Table 1), gave the corresponding 1,2-dioxolanes 3b-d and 4b-d in excellent yields. However, the photoreaction of the cyclopropanes 1e-g, which have higher oxidation potentials than 1a-d, under similar conditions afforded a variety of oxidized products such as 5e-g, 6e-g, and 7e-g after prolonged irradiation. In these cases, it is conceivable that the corresponding 3,5-diaryl-1,2-dioxolanes are produced at slow rates, but they decompose rapidly to the corresponding ketoalcohols, aldehydes, and ketones. The results are summarized in Table 1.



e; Ar=Ph, f; Ar=4-MeC_6H_4, g; Ar=4-ClC_6H_4

The fluorescence of DCA in acetonitrile was efficiently quenched by 1a-g in nearly diffusion-controlled rates(Table 1). The free energy changes(ΔG) for the electron-transfer process from these quenchers to the excited singlet DCA(^{1}DCA*) were estimated to be negative(Table 1).$^{10)}$ The photooxygenation of 1a in acetonitrile was also sensitized by 9-cyanoanthracene and 1,4-dicyanonaphthalene.

The reactivity of CP strongly depended on the solvent polarity: (1) The relative rate for the formation of 3a and 4a decreased with decreasing solvent polarity; $CH_3CN > C_2H_5CN > n\text{-}C_3H_7CN$. (2) No product was obtained in benzene and methylene chloride. Moreover, the formation of 3a and 4a in the presence of DCA in acetonitrile was completely quenched by addition of 1,4-diazabicyclo[2.2.2]octane(DABCO, 0.005 mol/dm^3) or triethylamine(TEA, 0.005 mol/dm^3), whose oxidation potentials are low(Table 1).

A proposed mechanism for the photooxygenation of CP is shown in Eqs. (1)-(7). The photochemically generated cation radicals CP$^{+\cdot}$ are attacked by either $O_2^{-\cdot}$ or $^3O_2$, giving directly 3 and 4 or the intermediate X. In the latter case, the electron transfer from DCA$^{-\cdot}$ or the electron-rich CP(1a-d) to X affords the 1,2-dioxolanes. This mechanism was supported by the following facts: (1) In the isomerization of 1 via their cation radicals, the C-C bonds of CP$^{+\cdot}$ have been demonstrated to be broken.$^{9,11)}$ (2) Foote and his coworkers have shown that $O_2^{-\cdot}$ can be formed by the electron transfer from DCA$^{-\cdot}$ to $^3O_2$(Eq. (3)).$^{1)}$ (3) The reaction of 1a(5 mmol) with $^3O_2$ in the presence of a catalytic amount(0.5 mmol) of $Ph_3C^+BF_4^-$ in acetonitrile in the dark afforded 3a and 4a in 60-70% yield. This reaction was accompanied by the isomerization of 1a to 2a. However, similar treatment of 1e, which has lower oxidation potential than 1a, resulted in an almost quantitative recovery of the substrate. These results strongly suggest that the corresponding CP$^{+\cdot}$ which is formed by the electron transfer from 1a

Table 1. Photooxygenation of 1,2-Diarylcyclopropanes[a)]

CP	$E_{1/2}^{ox}$[b)] /V	ΔG[c)] /kJ mol^{-1}	k_q[d)] x 10^{10} /dm^{3}mol^{-1}s^{-1}	Irrad. time/h	Total[e)] yield/%	Product ratio[e)]/%				
						3	4	5	6	7
1a	0.55	-102.8	1.60	5	95	23	77	0	0	0
1b	0.75	-83.6	1.49	4.5	95	22	78	0	0	0
1c	0.25	-131.7	2.23	4.5	95[f)]	30	70	0	0	0
1d	0.55	-102.8	1.68	4.5	85[f)]	24	76	0	0	0
1e	1.14	-46.8	1.23	32	19	0	0	48	35	17
1f	0.90	-69.0	1.36	32	21	0	0	44	40	16
1g	1.05	-53.5	1.25	32	17	0	0	52	29	19
(DABCO)[g)]	0.31	-125.8	2.45							
(TEA)[g)]	0.48	-109.5	2.01							

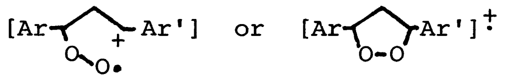
[a)] Oxygen-saturated acetonitrile solutions(8 ml) containing DCA(0.008 mmol) and 1 (0.2 mmol) were irradiated. [b)] Oxidation potentials were obtained by cyclic voltammetry: Pt electrode, tetraethylammonium perchlorate(0.1 mol dm^{-3}) in acetonitrile solution, vs. Ag/Ag$^+$. [c)] Calculated values in acetonitrile; see Ref. 10. [d)] Rate constants for fluorescence quenching of DCA in aerated acetonitrile solutions; [DCA]=1.0 x 10^{-4} mol dm^{-3}. [e)] Total yields based on 1 used and product ratios were determined by the GLC and/or the 100 or 60 MHz ^{1}H NMR spectroscopic analyses of the reaction mixtures. [f)] A mixture of trans- and cis-1,2-dioxolanes were obtained. [g)] Quencher; see Text.

$$^1DCA^* + CP \longrightarrow DCA^{\cdot -} + CP^{\cdot +} \qquad (1)$$

$$DCA^{\cdot -} + CP^{\cdot +} \longrightarrow DCA + CP \qquad (2)$$

$$DCA^{\cdot -} + {}^3O_2 \longrightarrow DCA + O_2^{\cdot -} \qquad (3)$$

$$CP^{\cdot +} + {}^3O_2 \longrightarrow \qquad (4)$$



X Ar=Ar'=aryl

$$CP^{\cdot +} + O_2^{\cdot -} \longrightarrow 3 + 4 \qquad (5)$$

$$X + DCA^{\cdot -} \longrightarrow 3 + 4 + DCA \qquad (6)$$

$$X + CP \longrightarrow 3 + 4 + CP^{\cdot +} \qquad (7)$$

to Ph_3C^+ is involved as an intermediate in the Ph_3C^+ catalyzed oxidation of 1a, and that $CP^{\cdot +}$ can be converted into 3a and 4a in the presence of $^3O_2$ via the pathways of Eqs. (4) and (7).

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7) **3a**: mp 122-124 °C; ^{1}H NMR($CDCl_3$) δ: 2.92(2H, t, J=7.5 Hz, CH_2), 3.79(6H, s, OMe), 5.40(2H, t, J=7.5 Hz, CH), 6.84 and 7.26(8H, AB q, J=9.0 Hz, aromatic); Found: C, 71.01; H, 6.19%. Calcd for $C_{17}H_{18}O_4$: C, 71.31; H, 6.34; O, 22.35%. **4a**: mp 92-94 °C; ^{1}H NMR($CDCl_3$) δ: 2.65(1H, dt, J_{gem}=12.3 Hz, J=7.5 Hz, CH_2), 3.34(1H, dt, J_{gem}= 12.3 Hz, J=7.5 Hz, CH_2), 3.76(6H, s, OMe), 5.37(2H, t, J=7.5 Hz, CH), 6.86 and 7.26 (8H, AB q, J=9.0 Hz, aromatic); Found: C, 71.16; H, 6.35%. Calcd for $C_{17}H_{18}O_4$: C, 71.31; H, 6.34; O, 22.35%. **3b**: mp 84-86 °C. **4b**: mp 48-49.5 °C.

8) Prolonged irradiation gave **5a** and **6a** along with a lot of polymeric materials.

9) Irradiation of a deaerated acetonitrile solution containing DCA and **1a** or **2a** gave a photostationary mixture of **1a** and **2a** in 95 : 5 ratio. This ratio was independent of the stereochemistry of the starting materials.

10) These values were calculated by using the excited singlet energy of DCA(2.89 V) and the reduction potential of DCA(-1.33 V vs. Ag/Ag^+): $\Delta G(\mathrm{kJ/mol})=96.8[E(D/D^+)_V-E(A^-/A)-e_0^2/(\varepsilon a)]-E_{0-0}$: D. Rehm and A. Weller, Israel J. Chem., **8**, 259(1970).

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