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Photooxygenation of Cyanoanthracenes via Their Radical Anions

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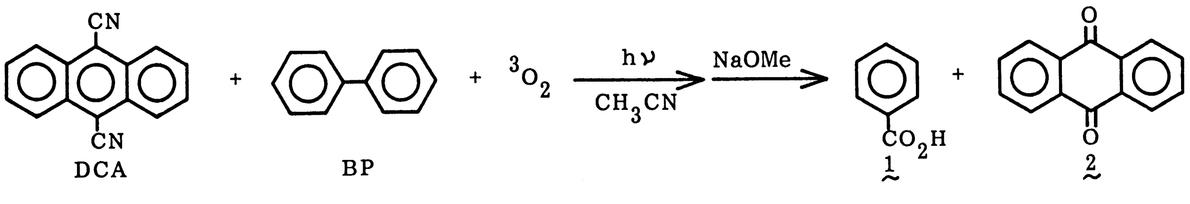
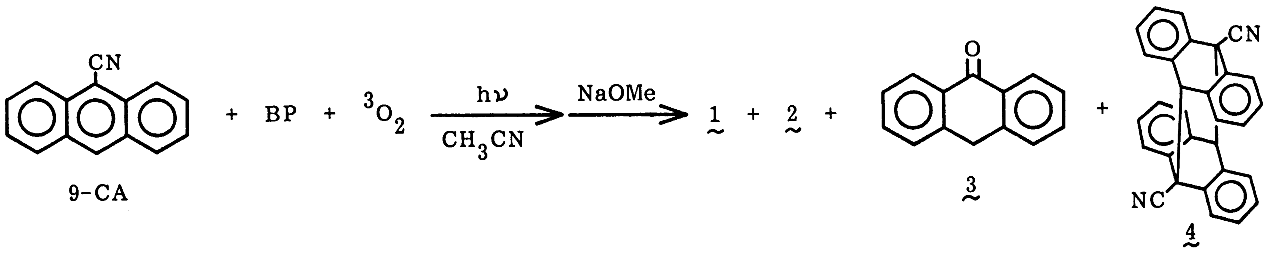
The photoreactions of 9,10-dicyanoanthracene and 9-cyanoanthracene in the presence of biphenyl in acetonitrile under oxygen atmosphere gave anthraquinone and 9(10H)anthracenone, respectively, via the reaction of the radical anions of cyanoanthracenes with molecular dioxygen.

The photooxygenation of organic compounds via their radical cations has been extensively investigated in the last several years.[1-4] However, little is known about the photooxygenation of electron deficient organic compounds via their radical anions.[5] We now report a novel photooxygenation of 9,10-dicyanoanthracene (DCA) and 9-cyanoanthracene (9-CA) in the presence of biphenyl (BP).

An acetonitrile solution (20 cm^3) containing DCA (0.48 mmol) and BP (0.5 mmol) was irradiated under oxygen bubbling with a 300 W high-pressure mercury lamp





through an aqueous $CuSO_4$-NH_3 filter solution ($\geq$400 nm) for 11 h. During this period, the yellow color of DCA disappeared. The reaction mixture was treated with NaOMe, and then the products were isolated by column chromatography on silica gel, giving benzoic acid (**1**) and anthraquinone (**2**) in 80 and 58% yields, respectively.

The photoreaction of 9-CA afforded four products; **1**, **2**, 9(10H)anthracenone (**3**) and a ($4\pi + 4\pi$) cyclodimer (**4**) of 9-CA.6) When concentration of 9-CA (0.025 mol dm^{-3}) was low, the oxidation of 9-CA occurred to give a mixture of **2** and **3** in preference to the dimerization of 9-CA.7) With 1,4-dicyanonaphthalene (DCN), **1** was obtained as a sole isolable product, but the product derived from DCN could not be isolated. However, no photoreaction occurred for 1,4-dicyanobenzene (DCB) with a quantitative recovery of the starting materials.

The photooxygenation of DCA and BP did not occur in benzene. The addition of $Mg(ClO_4)_2$ (0.02 mol dm^{-3}) to the reaction system in acetonitrile suppressed the formation of **2**, but the formation of **1** was accelerated as reported previously.4) DCA was not oxidized by singlet oxygen $^1O_2$; indeed, the methylene blue- or rose bengal-sensitized photoreactions of DCA in a stream of molecular dioxygen $^3O_2$ in

Table 1. The Photooxygenation of Cyanoanthracenes

Cyano-anthracene a)	Additive b)	Solvent	Atmosphere	Reaction time / h	Product(s) / % c)			
					1	**2**	**3**	**4**
DCA	BP	CH_3CN	O_2	11	80	58	0	-
DCA	BP $Mg(ClO_4)_2$	CH_3CN	O_2	6	76	tr d)	0	-
DCA	BP	C_6H_6	O_2	10	0	0	0	-
DCA	MB	CH_2Cl_2	O_2	10	-	0	0	-
DCA	RB	CH_2Cl_2	O_2	10	-	0	0	-
DCA	KO_2 e)	CH_3CN	Ar	60	-	58	0	-
9-CA f)	BP	CH_3CN	O_2	4	52	31	tr d)	tr d)
9-CA f)	BP	C_6H_6	O_2	2	0	0	0	90
9-CA g)	BP	CH_3CN	O_2	2	tr d)	tr d)	0	98
9-CA f)	MB	CH_2Cl_2	O_2	10	-	0	0	-

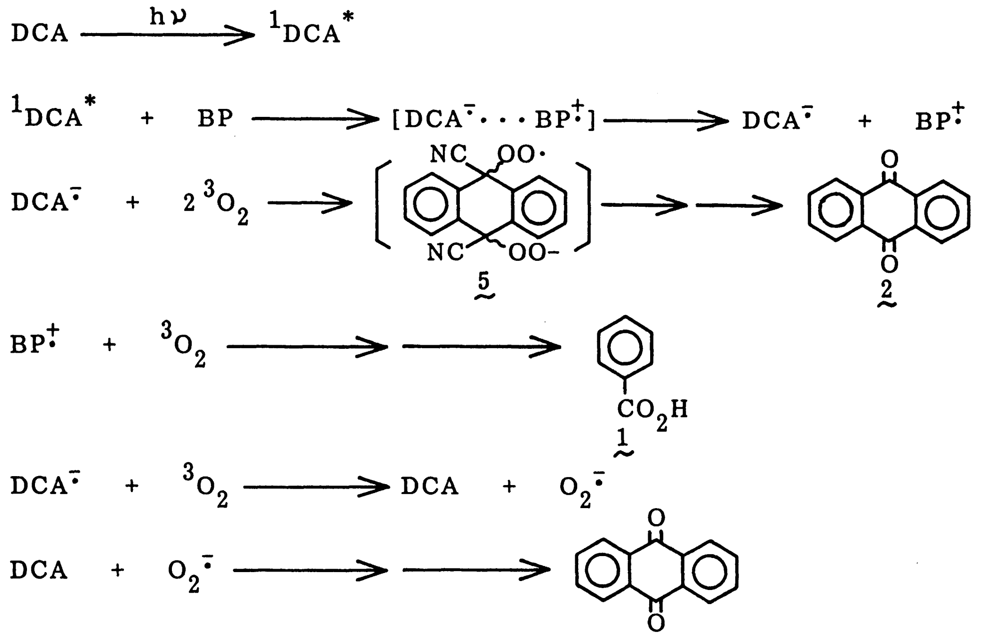
a) [DCA] = 5.0×10^{-4} mol dm^{-3}. b) MB; Methylene Blue, RB; Rose Bengal, [MB] = [RB] = 2.5×10^{-4} mol dm^{-3}, [BP] = 0.03 mol dm^{-3}, [$Mg(ClO_4)_2$] = 0.015 mol dm^{-3}. c) Isolated yields. d) Trace. e) The reaction of DCA (0.25 mmol) with KO_2 (1.75 mmol) in CH_3CN (15 ml) was carried out in the dark at ambient temperature. f) [9-CA] = 1.8×10^{-3} mol dm^{-3}. g) [9-CA] = 2.5×10^{-2} mol dm^{-3}

dichloromethane resulted in a complete recovery of DCA. The results were summarized in Table 1.

The fluorescence of DCA, 9-CA, and DCN in acetonitrile was efficiently quenched by BP at nearly diffusion controlled rates.4) From the Rehm-Weller equation,8) ΔG values for the one-electron transfer from BP to the excited singlet cyanoaromatic compounds were estimated to be negative.

From these results, we propose the mechanism as represented in Scheme 1 for the photooxygenation of DCA and 9-CA in the presence of BP. The first step is a one-electron transfer from BP to the excited singlet DCA to give the radical cation $BP^{+\cdot}$, and the radical anion $DCA^{-\cdot}$. The second step is the attack of $^3O_2$ on $DCA^{-\cdot}$ to afford the peroxy intermediate 5 that decomposes to 2 under basic conditions. At the same time, $BP^{+\cdot}$ is oxidized by $^3O_2$ to give 1.4) The photooxygenation of 9-CA in the presence of BP would proceed via the similar pathways. These processes may compete with the generation of $O_2^{-\cdot}$ which can be formed by a one-electron transfer from $DCA^{-\cdot}$ or 9-$CA^{-\cdot}$ to $^3O_2$. This electron-transfer process is exothermic by 0.7 kcal mol^{-1} for DCA and by 12.2 kcal mol^{-1} for 9-CA.1b) It is, therefore, reasonable to suppose that the one-electron transfer from $O_2^{-\cdot}$ to DCA occurs slowly and that from $O_2^{-\cdot}$ to 9-CA does not occur under the reaction conditions.

Treatment of DCA and 9-CA with a large excess of KO_2 in the presence of 18-crown-6 in acetonitrile under argon atmosphere for 60 h in the dark afforded



Scheme 1.

2. Therefore, the possibility of a direct nucleophilic attack of $O_2^{\bar{\bullet}}$ on cyanoanthracenes to produce **2** cannot be ruled out even in the photoreaction. However, for the present photooxygenation of DCA and 9-CA the mechanism as shown in Scheme 1 is more profitable because the photoreaction is much faster than the dark reaction with KO_2.

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References

1) a) J. Eriksen, C. S. Foote, and T. L. Parker, J. Am. Chem. Soc., 99, 6455 (1977); b) L. T. Spada and C. S. Foote, ibid., 102, 391 (1980); c) J. Eriksen and C. S. Foote, ibid., 102, 6083 (1980).

2) I. Saito, K. Tamoto, and T. Matsuura, Tetrahedron Lett., 1979, 2889; W. Ando, T. Nagashima, K. Saito, and S. Kohmoto, J. Chem. Soc., Chem. Commun., 1979, 154; A. P. Schaap, S. Siddiqui, G. Prasad, E. Palomino, and M. Sandison, Tetrahedron, 41, 2229 (1985); T. Miyashi, M. Kamata, and T. Mukai, J. Am. Chem. Soc., 109, 2780 (1987) and references cited therein.

3) K. Mizuno, N. Kamiyama, and Y. Otsuji, Chem. Lett., 1983, 477; K. Mizuno, K. Murakami, N. Kamiyama, and Y. Otsuji, J. Chem. Soc., Chem. Commun., 1983, 462; K. Mizuno, N. Ichinose, and Y. Otsuji, Chem. Lett., 1985, 455; K. Mizuno, N. Kamiyama, N. Ichinose, and Y. Otsuji, Tetrahedron, 41, 2207 (1985); K. Mizuno, N. Ichinose, and Y. Otsuji, "The Role of Oxygen in Chemistry and Biochemistry," ed by W. Ando and Y. Moro-oka, Elsevier, Tokyo (1988), p.79.

4) K. Mizuno, N. Ichinose, T. Tamai, and Y. Otsuji, Tetrahedron Lett., 26, 5823 (1985).

5) R. Akaba, H. Sakuragi, and K. Tokumaru, Chem. Lett., 1984, 1677.

6) K. Mizuno, C. Pac, and H. Sakurai, J. Chem. Soc., Perkin Trans. 1, 1974, 2360.

7) **3** was gradually oxidized to anthraquinone **2** under the reaction condition.

8) D. Rehm and A. Weller, Isr. J. Chem., 8, 259(1970).

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