

## Photooxygenation of Cyanoanthracenes via Their Radical Anions

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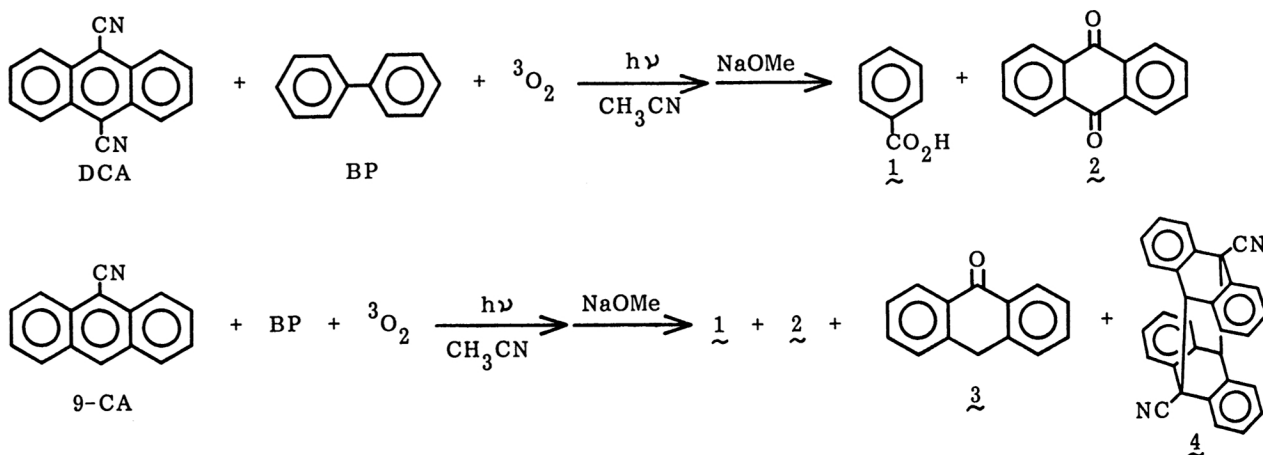
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The photoreactions of 9,10-dicyanoanthracene and 9-cyanoanthracene in the presence of biphenyl in acetonitrile under oxygen atmosphere gave anthraquinone and 9(10H)anthracenone, respectively, via the reaction of the radical anions of cyanoanthracenes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

The photooxygenation of organic compounds via their radical cations has been extensively investigated in the last several years.<sup>1-4)</sup> However, little is known about the photooxygenation of electron deficient organic compounds via their radical anions.<sup>5)</sup> 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<sup>3</sup>) 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  $\text{CuSO}_4\text{-NH}_3$  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.<sup>6)</sup> When concentration of 9-CA ( $0.025 \text{ mol dm}^{-3}$ ) was low, the oxidation of 9-CA occurred to give a mixture of 2 and 3 in preference to the dimerization of 9-CA.<sup>7)</sup> 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  $\text{Mg}(\text{ClO}_4)_2$  ( $0.02 \text{ mol dm}^{-3}$ ) to the reaction system in acetonitrile suppressed the formation of 2, but the formation of 1 was accelerated as reported previously.<sup>4)</sup> DCA was not oxidized by singlet oxygen  $^1\text{O}_2$ ; indeed, the methylene blue- or rose bengal-sensitized photoreactions of DCA in a stream of molecular dioxygen  $^3\text{O}_2$  in

Table 1. The Photooxygenation of Cyanoanthracenes

Cyano-anthracene <sup>a)</sup>	Additive <sup>b)</sup>	Solvent	Atmosphere	Reaction time / h	Product(s) / % <sup>c)</sup>			
					<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
DCA	BP	$\text{CH}_3\text{CN}$	$\text{O}_2$	11	80	58	0	-
DCA	BP $\text{Mg}(\text{ClO}_4)_2$	$\text{CH}_3\text{CN}$	$\text{O}_2$	6	76	tr <sup>d)</sup>	0	-
DCA	BP	$\text{C}_6\text{H}_6$	$\text{O}_2$	10	0	0	0	-
DCA	MB	$\text{CH}_2\text{Cl}_2$	$\text{O}_2$	10	-	0	0	-
DCA	RB	$\text{CH}_2\text{Cl}_2$	$\text{O}_2$	10	-	0	0	-
DCA	$\text{KO}_2$ <sup>e)</sup>	$\text{CH}_3\text{CN}$	Ar	60	-	58	0	-
9-CA <sup>f)</sup>	BP	$\text{CH}_3\text{CN}$	$\text{O}_2$	4	52	31	tr <sup>d)</sup>	tr <sup>d)</sup>
9-CA <sup>f)</sup>	BP	$\text{C}_6\text{H}_6$	$\text{O}_2$	2	0	0	0	90
9-CA <sup>g)</sup>	BP	$\text{CH}_3\text{CN}$	$\text{O}_2$	2	tr <sup>d)</sup>	tr <sup>d)</sup>	0	98
9-CA <sup>f)</sup>	MB	$\text{CH}_2\text{Cl}_2$	$\text{O}_2$	10	-	0	0	-

a)  $[\text{DCA}] = 5.0 \times 10^{-4} \text{ mol dm}^{-3}$ . b) MB; Methylene Blue, RB; Rose Bengal,  $[\text{MB}] = [\text{RB}] = 2.5 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[\text{BP}] = 0.03 \text{ mol dm}^{-3}$ ,  $[\text{Mg}(\text{ClO}_4)_2] = 0.015 \text{ mol dm}^{-3}$ .

c) Isolated yields. d) Trace. e) The reaction of DCA (0.25 mmol) with  $\text{KO}_2$  (1.75 mmol) in  $\text{CH}_3\text{CN}$  (15 ml) was carried out in the dark at ambient temperature.

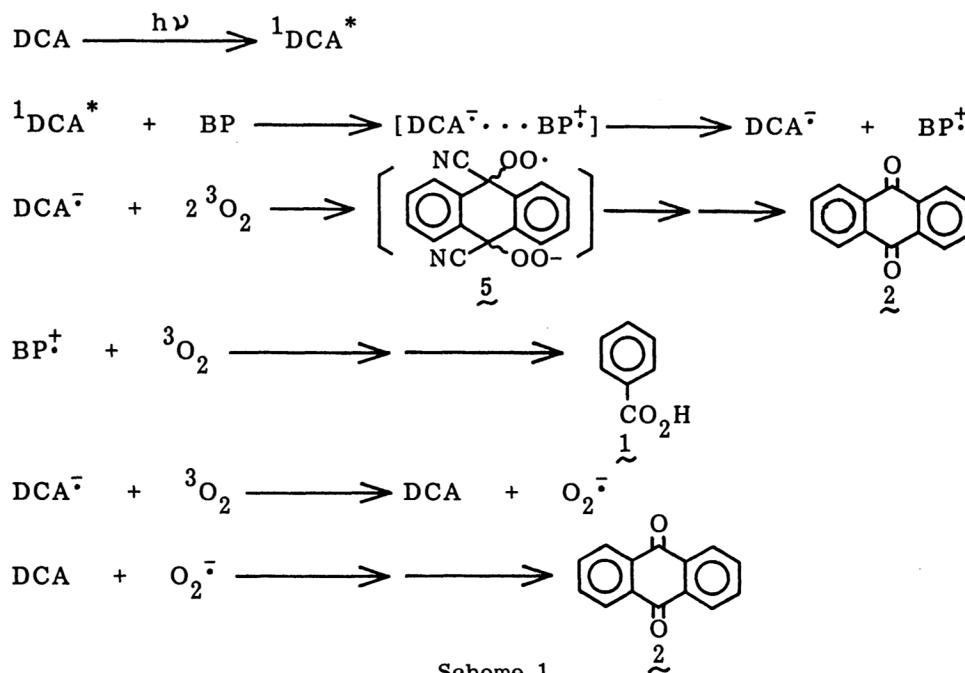
f)  $[\text{9-CA}] = 1.8 \times 10^{-3} \text{ mol dm}^{-3}$ . g)  $[\text{9-CA}] = 2.5 \times 10^{-2} \text{ mol dm}^{-3}$ .

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.<sup>4)</sup> From the Rehm-Weller equation,<sup>8)</sup>  $\Delta G$  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.<sup>4)</sup> 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<sup>-1</sup> for DCA and by 12.2 kcal mol<sup>-1</sup> for 9-CA.<sup>1b)</sup> 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  $O_2^{\cdot -}$  on cyano-anthracenes 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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