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Unusual Effects of Acetate Ion on Photosensitized Oxygenation of Naphthalene Derivatives via Electron Transfer

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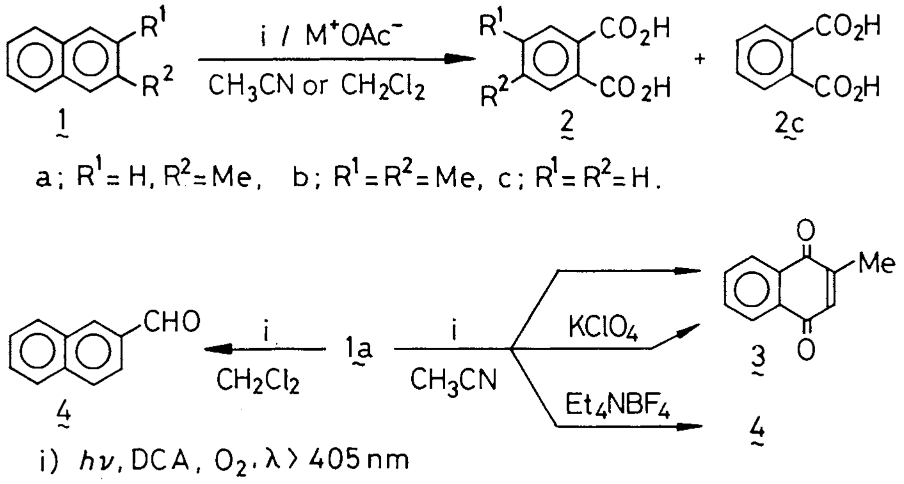
The oxygenation of 2-methylnaphthalene photosensitized by 9,10-dicyanoanthracene in an O_2-saturated acetonitrile gave phthalic acid and 4-methylphthalic acid in the presence of Et_4NOAc or KOAc/18-crown-6, but different products in the presence of Et_4NBF_4 and $KClO_4$ and without a salt. The photosensitized ring oxygenation also occurred with naphthalene and 2,3-dimethylnaphthalene.

The great interest in photochemical electron transfer reactions has been paid to control the outcome of these processes.1) The addition of salts is often effective to the controlling of photoreactions proceeding through exciplexs and ion radicals, since charge separation and chemical reactivities of ion radicals may be affected by interactions with salt ions as well as by a salt-induced increase of solvent polarity.2) Consequently, such salt effects can generally bring about remarkable changes in reaction efficiencies but usually no alteration of reaction courses.3) We have found that the oxygenation of naphthalene derivatives (**1**) photosensitized by 9,10-dicyanoanthracene (DCA) in the presence of acetate salts gives phthalic acid products in contrast with that in the presence of other salts or without the use of a salt.

An O_2-saturated acetonitrile solution (40 cm^3) containing **1a-c** (4 mmol), DCA (0.04 mmol), and a salt (4 mmol) was irradiated under an oxygen atmosphere by a high-pressure mercury arc using an aqueous $CuSO_4$-NH_3 filter solution. The results are shown in Scheme 1 and Table 1. The photooxygenation of 2-methylnaphthalene (**1a**) gave 4-methylphtalic acid (**2a**) and phthalic acid (**2c**) in the presence of tetraethylammonium acetate (Et_4NOAc) or KOAc/18-crown-6 but only 2-methyl-1,4-naphthoquinone (**3**) in the absence of the salt.

Similarly, the photooxygeantion of 2,3-dimethylnaphthalene (**1b**) and naphthalene (**1c**) in the presence of Et_4NOAc gave the corresponding phthalic acids. When KSCN/18-crown-6 ether was used, **2a** and **2c** were formed in 14% and 10% yields, respectively. By contrast, Et_4NBF_4 and $KClO_4$ were not effective to the formation of **2** at all; the photooxygenation of **1a** did not give **2** but **3** in the case of $KClO_4$ or 2-naphthaldehyde (**4**) in the case of Et_4NBF_4 at low conversion of **1a** (< 15%), though further irradiation resulted



Scheme 1.

Table 1. DCA-sensitized Photooxygenation of Arenes in the Presence of Salts[a)]

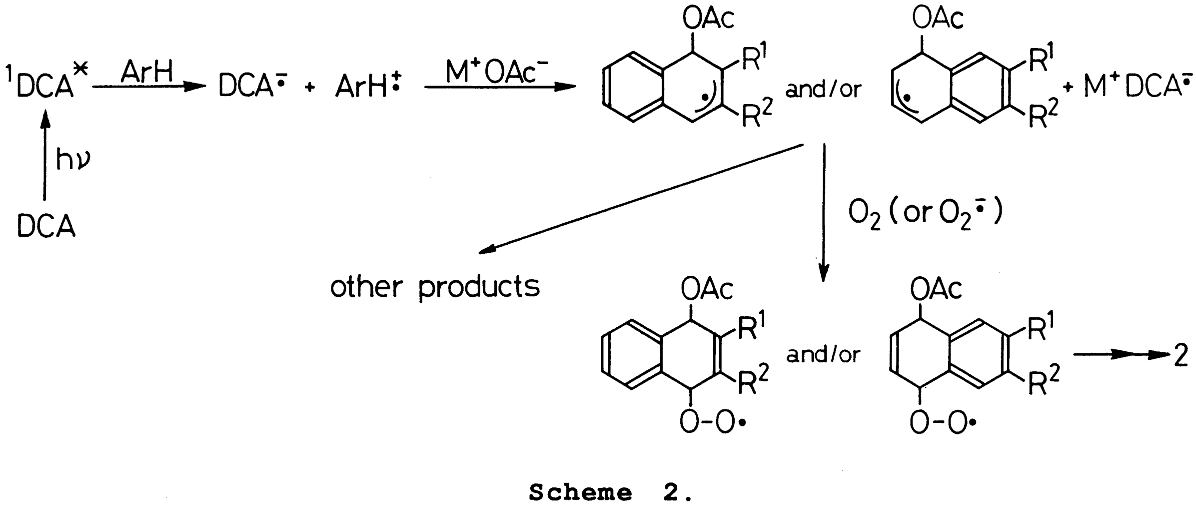
Run No.	ArH	Salt	Irradn. Time / h	Oxidation Products (Yield / %)[b)]		Conversion of **1** / %
1	**1a**	Et_4NOAc	7	**2a** (21)	**2c** (14)	74
2	**1a**	Et_4NOAc	1	**2a** (10)	**2c** (7)	15
3	**1a**	KOAc/ 18-crown-6	6	**2a** (27)	**2c** (17)	63
4	**1a**	$KClO_4$	0.5[c)]	**3** (12)		11
5	**1a**	Et_4NBF_4	1[c)]	**4** (37)		15
6	**1a**	none	0.3[c)]	**3** (26)		7
7	**1b**	Et_4NOAc	9	**2b** (39)	**2c** (22)	94
8	**1c**	Et_4NOAc	7	**2c** (50)		67
9[d)]	**1a**	Et_4NOAc	41	**2a** (17)	**2c** (12)	68
10[d)]	**1a**	none	50	**4** (44)		78

a) For an acetonitrile solution. b) HPLC yields based on consumed **1**. c) Further irradiation for >1h brought about the consumption of the **3** and **4** without the formation of other definite products. d) For a dichloromethane solution.

in the consumption of **3** and **4** without the accumulation of **2** and any other definite products. Moreover, the photooxygenation of **1a** in dichloromethane gave again **2a** and **2c** in the presence of Et_4NOAc, but **4** in the absence of a salt.[4)]

The DCA-sensitized photooxygenation of some arenes are suggested to proceed via the arene cation radicals ($ArH^{+\cdot}$) generated by an electron transfer from the arenes to the excited singlet-state of DCA.[5,6)] It was confirmed that the fluorescence of DCA is efficiently quenched by **1a-c** in acetonitrile and also in dichloromethane. The unusual effects of M^+OAc^- on the specific oxygenation of the aromatic rings can be explained assuming that AcO^- undergoes the nucleophilic addition to $ArH^{+\cdot}$ followed by a reaction or reactions of the adduct radical (·ArH-OAc) with O_2 and/or related oxygen species to give **2a-c** as the final products, though mechanistic details for the follow-up processes are still unknown (Scheme 2). The nucleophilic addition of AcO^- to $ArH^{+\cdot}$ seems to be supported by the observation that irradiation of DCA, **1a**, and Et_4NOAc under deaerated conditions resulted in the consumption of **1a** though no definite products could be isolated. Presumably, the adduct radical would undergo unreclaimed complex reactions in the absence of O_2 but would be trapped by O_2 and/or related oxygen species. This mechanistic speculation was born out of our previous works on the efficient addition of such nucleophiles as CN^-,[7)] BH_4^-,[8)] and RNH_2[9)] to photogenerated $ArH^{+\cdot}$.[10,11)] In accord with this mechanism, the lack of the phthalic acid formation in the presence of Et_4NBF_4 or $KClO_4$ can be easily explained in terms of the negligible or very weak nucleophilicity of BF_4^- and ClO_4^-.

It is of synthetic significance to note that the selective oxidative cleavage of the aromatic rings by the DCA-sensitized photooxygenation of **1a-c** in the presence of M^+OAc^- is in a sharp contrast with usual photooxidations



Scheme 2.

of alkylated arenes that generally result in oxidation of the alkyl substituents.[12] The present investigation reveals that the reaction courses of photooxygenation reactions of arenes via electron transfer can be controlled by the use of M^+OAc^- or other non-nucleophilic salts as well as by the choice of solvents. Also, it is found that the photosensitized oxygenation of p-methyl or p-methoxystilbenes by DCA or 9-cyanoanthracene gave effectively benzaldehydes in the presence of M^+OAc^- but gave mainly oxiranes in the absence of salts.

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