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Formation of Ozonides *via* 9,10-Dicyanoanthracene-sensitized Photo-oxidation of Epoxides[1]

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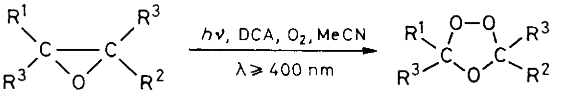
9,10-Dicyanoanthracene-sensitized photo-oxidation of electron-rich epoxides in acetonitrile affords the corresponding ozonides.

Photosensitized electron transfer oxidation is of current interest and a variety of organic compounds have been oxidized *via* electron transfer mechanisms.[2,3] We now report the 9,10-dicyanoanthracene(DCA)-sensitized photo-oxidation of epoxides.

trans-4,4′-Dimethoxystilbene oxide (**1b**) (10^{-2} mol) was irradiated in acetonitrile through an aqueous 75% $NaNO_2$ solution ($\lambda > 400$ nm) in the presence of DCA (10^{-4} mol) under an O_2 stream to afford an ozonide, (**2b**), quantitatively. Ozonides were also obtained in excellent yields from the other electron-rich epoxides such as (**1d**) and (**1e**), while (**1a**), (**1c**), and (**1f**) were unreactive towards the photo-oxidation (see Table 1).

The physical and spectroscopic data,† and also the fact that reduction of the product with triphenylphosphine gives the corresponding carbonyl compounds and triphenylphosphine oxide in stoicheiometric yield, provide support for (**2**) being an ozonide.[4]



(**1**) (**2**)

Table 1.

Substrate (**1**)	Irrad. time/h	% Yield[a] of ozonides (**2**)
a; $R^1 = R^2 = Ph, R^3 = H$	18	—
b; $R^1 = R^2 = p\text{-}MeOC_6H_4, R^3 = H$	3	100
c; $R^1 = R^2 = Ph, R^3 = Me$	23	—
d; $R^1 = R^2 = p\text{-}MeOC_6H_4, R^3 = Et$	1	88
e; $R^1 = p\text{-}MeOC_6H_4, R^2 = p\text{-}MeC_6H_4, R^3 = H$	2	90
f; $R^1 = R^2 = R^3 = Ph$	24	—

[a] Based on the initial concentration of (**1**). Where no yield is given, (**1**) does not react and is recovered quantitatively.

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† Physical and spectral data for (**2**). (**2b**): m.p. 73.9—74.5 °C, ^1H-n.m.r. ($CDCl_3$) δ, 3.73 (s, 6H), 6.13 (s, 2H), 6.83 (d, 4H), and 7.37 (d, 4H); (**2d**): m.p. 78.8—79.1 °C, ^1H-n.m.r., 0.67 (d, 6H), 1.67 (m, 4H), 3.53 (s, 6H), 6.37 (d, 4H), and 6.87 (d, 4H); (**2e**): m.p. 66.2—66.6 °C, ^1H-n.m.r., 2.30 (s, 3H), 3.70 (s, 3H), 6.13 (s, 1H), 6.18 (s, 1H), and 6.67—7.50 (m, 8H).

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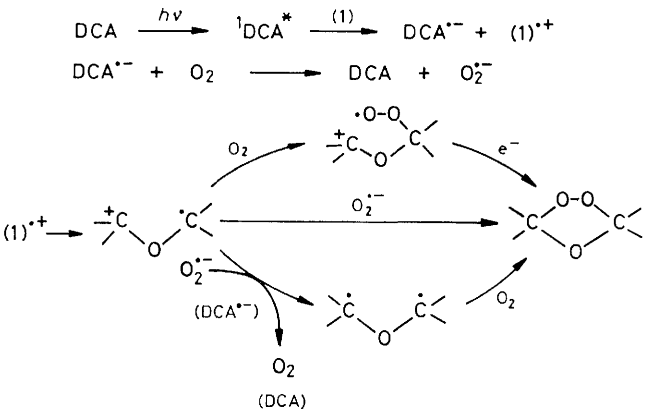

Scheme 1

The reaction does not seem to involve singlet oxygen, since (**1**) is stable under the photo-oxygenation conditions in the presence of singlet oxygen sensitizers such as Rose Bengal, Methylene Blue, and $Ru(bpy)_3^{2+}$. The DCA fluorescence is quenched and linear Stern–Volmer plots are obtained for (**1b**) ($k_q = 2.00 \times 10^{10}$ dm^3 mol^{-1} s^{-1}), (**1d**) ($k_q = 1.64 \times 10^{10}$ dm^3 mol^{-1} s^{-1}) and (**1e**) ($k_q = 1.71 \times 10^{10}$ dm^3 mol^{-1} s^{-1}), but is not quenched by (**1a**), (**1c**), or (**1f**). This shows that only the epoxides that quench the DCA fluorescence are reactive under the reaction conditions. It also confirms that DCA, O_2, and visible light are all necessary for the reaction.

The addition of 1,4-dimethoxybenzene (1.00×10^{-3} mol) or 1,2,4-trimethoxybenzene (1.13×10^{-3} mol), each of which has a lower oxidation potential and is unreactive to DCA-sensitized photo-oxygenation in MeCN/O_2,[2] quenches the reaction, indicating that DCA-sensitized photo-oxidation of (**1**) proceeds *via* an electron transfer mechanism. A plausible reaction mechanism is shown in Scheme 1.

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