

Formation of Ozonides *via* 9,10-Dicyanoanthracene-sensitized Photo-oxidation of Epoxides¹

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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% NaNO₂ solution ($\lambda > 400$ nm) in the presence of DCA (10^{-4} mol) under an O₂ 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

[†] Physical and spectral data for (**2**). (**2b**): m.p. 73.9–74.5 °C, ¹H-n.m.r. (CDCl₃) 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).

oxide in stoichiometric yield, provide support for (**2**) being an ozonide.⁴

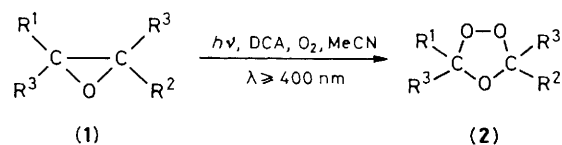
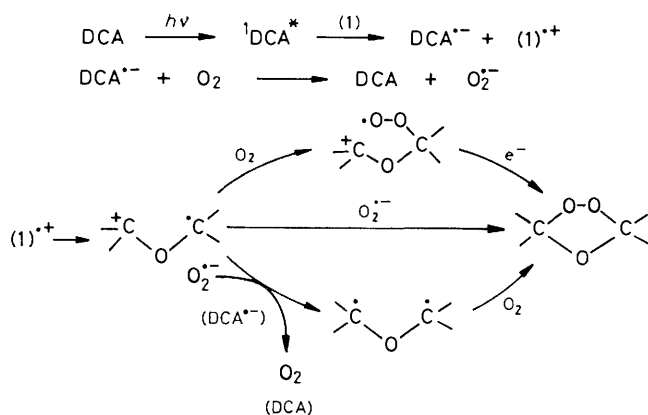


Table 1.

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 = <i>p</i> -MeOC ₆ H ₄ , R ³ = H	3	100
c ; R ¹ = R ² = Ph, R ³ = Me	23	—
d ; R ¹ = R ² = <i>p</i> -MeOC ₆ H ₄ , R ³ = Et	1	88
e ; R ¹ = <i>p</i> -MeOC ₆ H ₄ , R ² = <i>p</i> -MeC ₆ H 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.



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 $\text{Ru}(\text{bpy})_3^{2+}$. The DCA fluorescence is quenched and linear Stern-Volmer plots are obtained for **(1b)** ($k_q = 2.00 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$), **(1d)** ($k_q = 1.64 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) and **(1e)** ($k_q = 1.71 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$), 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 ($1.00 \times 10^{-3} \text{ mol}$) or 1,2,4-trimethoxybenzene ($1.13 \times 10^{-3} \text{ mol}$), 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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References

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