

9,10-Dicyanoanthracene-sensitized Photo-oxygenation of *trans*-1,2-Di-(carbazol-9-yl)cyclobutane *via* Electron-transfer

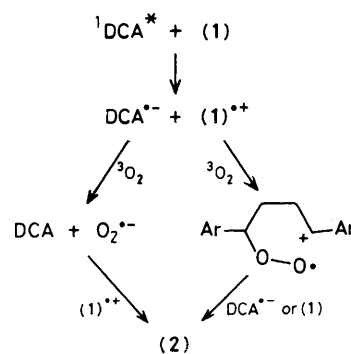
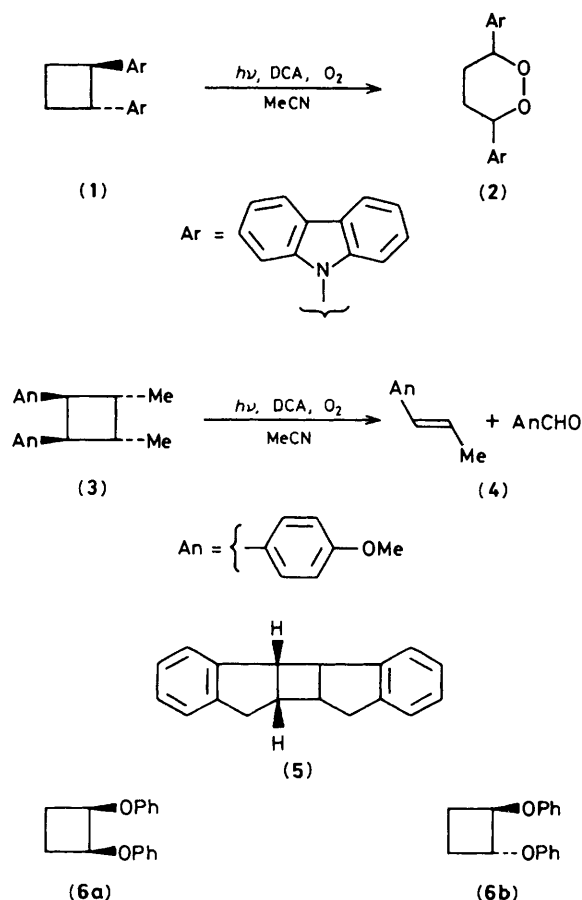
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9,10-Dicyanoanthracene-sensitized photo-oxygenation of *trans*-1,2-di(carbazol-9-yl)cyclobutane in acetonitrile efficiently affords 3,6-di(carbazol-9-yl)-1,2-dioxan.

The photo-oxygenation of organic substrates *via* electron-transfer is of current interest.¹⁻³ However, the substrates so

far studied are restricted mostly to electron-rich unsaturated compounds and little is known about the photo-oxygenation



Scheme 1

sion was observed in both acetonitrile and benzene. The DCA-sensitized photo-oxygenation of (1) in acetonitrile was completely quenched by addition of 1,4-diazabicyclo[2.2.2]octane (DABCO) (0.005 mol/dm³) and triethylamine (0.005 mol/dm³), which have low oxidation potentials. These results suggest that the DCA-sensitized photo-oxygenation of (1) proceeds *via* an electron-transfer from (1) to the excited singlet DCA (¹DCA*) (Scheme 1).^{1,3,4}

The Methylene Blue (MB)-sensitized photo-oxygenation of (1) in acetonitrile also afforded (2) at a slow rate compared with the DCA-sensitized photo-oxygenation. Interestingly, other ¹O₂ sensitizers such as Rose Bengal and Ru(bpy)₃²⁺ (bpy = 2,2'-bipyridine) were ineffective for the photo-oxygenation of (1). Foote *et al.* have reported that the MB-sensitized photo-oxidation of electron-rich organic compounds occurs *via* an electron-transfer from the substrates to ¹MB*.² The MB-sensitized photoreaction of (1) probably occurs *via* a similar mechanism.

The reactivity of other cyclobutane compounds was also examined. Irradiation of an oxygen-saturated acetonitrile solution of (3) in the presence of DCA efficiently gave the cycloreversion product (4) along with a small amount of 4-methoxybenzaldehyde, an oxygenated product of (4).^{5,6} However, (5) and (6a,b) were less reactive under these conditions.†

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of carbon-carbon single bonds.³ We now report the photo-oxygenation of a cyclobutane ring *via* electron-transfer to give a 1,2-dioxan.

Irradiation of an oxygen-saturated acetonitrile solution (100 ml) of *trans*-1,2-di(carbazol-9-yl)cyclobutane (1) (836 mg, 0.02 mol/dm³) containing 9,10-dicyanoanthracene (DCA) (1 × 10⁻⁴ mol/dm³) as an electron-acceptor through an aqueous CuSO₄-NH₃ filter solution (405 nm) for 20 min afforded 3,6-di(carbazol-9-yl)-1,2-dioxan (2) in 60–70% isolated yield after chromatography on silica gel. The photoreaction did not proceed in the absence of DCA and/or O₂ with a quantitative recovery of (1).

The structure of (2) was established from analytical and spectral data† and also by chemical conversion, although the stereochemistry of the two carbazol-9-yl substituents remained equivocal. Upon photolysis in benzene through a Pyrex filter or thermolysis at 200 °C, (2) gave carbazole and carbazole-9-carbaldehyde in a 1 : 1 ratio in good yields. The reaction of (2) with NaBH₄ in MeOH gave carbazole in 80–90% yield. These chemical properties of (2) are consistent with its assigned structure.

The fluorescence of DCA was efficiently quenched by (1) in both acetonitrile (*k_qτ* 442 mol⁻¹ dm³) and benzene (*k_qτ* 327 mol⁻¹ dm³), although (1) was unreactive towards DCA-sensitized photo-oxygenation in benzene. No exciplex emis-

† Compound (2): m.p. 183–184 °C (decomp.); i.r. *v*_{max} (KBr) 1580, 1440, 1300, 1220, 1150, 1120, 920, 740, and 710 cm⁻¹; mass spectrum *m/z* 418 (*M*⁺, very weak), 251, 195, and 166; ¹H n.m.r. δ(CDCl₃) 2.21 (br. d, *J* 9 Hz, 2H), 3.21 (br. t, 2H), 6.69 (br. d, *J* 11 Hz, 2H), and 7.2–8.1 (m, 16H).

‡ Prolonged irradiation of (5) and (6) afforded a complex mixture containing oxygenated products of (5) and (6).