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

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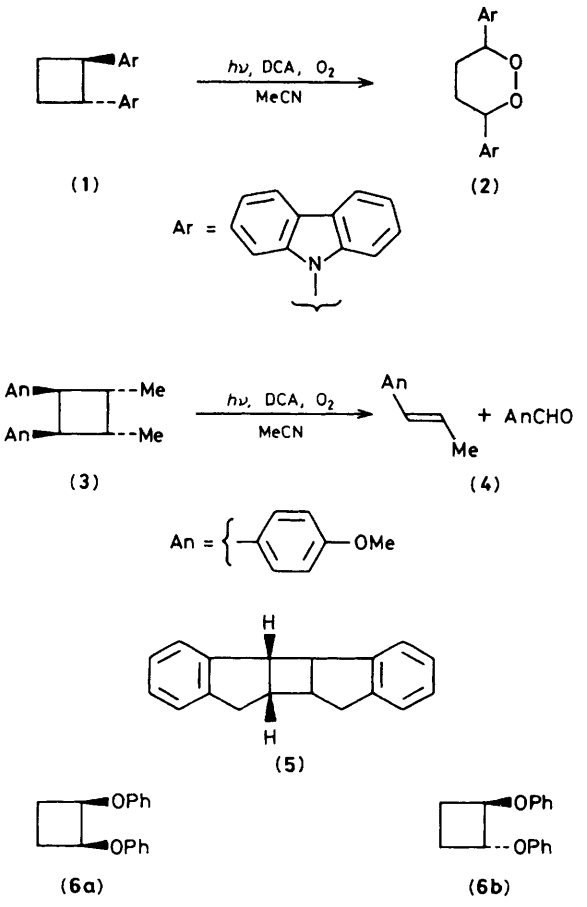
9,10-Dicyanoanthracene-sensitized photo-oxygenation of *trans*-1,2-di(carbazol-9-yl)cyclobutane in acetonitrile efficiently affords 3,6-di(carbazol-9-yl)-1,2-dioxan.

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

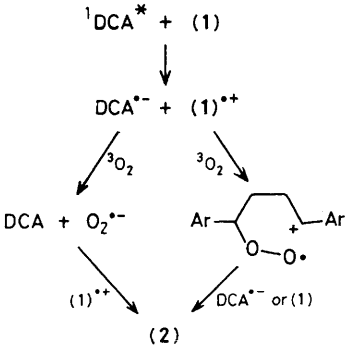


of carbon–carbon single bonds.[3] We now report the photo-oxygenation of a cyclobutane ring *via* electron-transfer to give a 1,2-dioxan.

Irradiation of an oxygen-saturated acetonitrile solution (100 ml) of *trans*-1,2-di(carbazol-9-yl)cyclobutane (**1**) (836 mg, 0.02 mol/dm^3) containing 9,10-dicyanoanthracene (DCA) (1×10^{-4} mol/dm^3) as an electron-acceptor through an aqueous $CuSO_4$–NH_3 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 O_2 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 $NaBH_4$ 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 ($k_q\tau$ 442 mol^{-1} dm^3) and benzene ($k_q\tau$ 327 mol^{-1} dm^3), although (**1**) was unreactive towards DCA-sensitized photo-oxygenation in benzene. No exciplex emission 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/dm^3) and triethylamine (0.005 mol/dm^3), 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 (^{1}DCA*) (Scheme 1).[1,3,4]



Scheme 1

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 $^1O_2$ sensitizers such as Rose Bengal and Ru(bpy)$^{2+}$ (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 ^{1}MB*.[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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† Compound (**2**): m.p. 183–184 °C (decomp.); i.r. ν_{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; ^{1}H n.m.r. δ($CDCl_3$) 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**).