Exciplex Formation and Electron-transfer in the Photoreaction of 9,10-Dicyanoanthracene and Methyl 1,2-Diphenylcyclopropene-3-carboxylate

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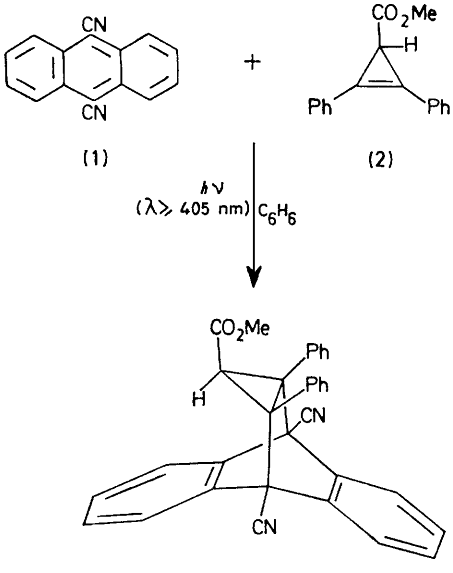
Summary The title compounds form an emitting exciplex in benzene, which leads to the cycloadduct (**3**), whereas in polar solvents the isomeric adduct (**4**) and the dimer of the olefin are formed *via* an electron-transfer reaction which partially leads to triplet formation; the efficiency of the dimerization *via* the latter process is strongly enhanced in the presence of tetracyanobenzene.

THE role of exciplexes and electron-transfer reactions in organic photochemistry is currently attracting considerable interest. This report deals with the intermediacy of these processes in the photoreaction of 9,10-dicyanoanthracene (**1**) with methyl 1,2-diphenylcyclopropene-3-carboxylate (**2**) in nonpolar and polar solvents.



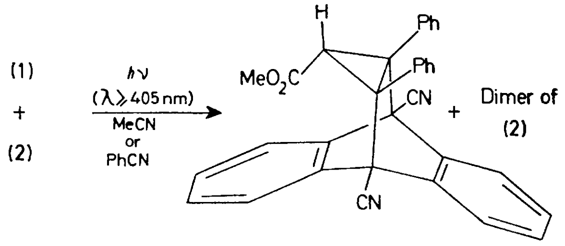
(3)

In benzene the fluorescence of (**1**) is quenched by (**2**) at a rate† of $2{\cdot}6 \times 10^9$ l mol^{-1} s^{-1} and an emitting exciplex is formed (λ_{max} 510 nm). The excitation spectrum for this structureless band is identical with that for the residual fluorescence of (**1**).

Irradiation ($\lambda \geqslant 405$ nm) of these reactants {[(**2**)] = 0·05M} in benzene led to the formation of the adduct (**3**)‡ (Φ *ca.* 0·002), besides traces of the dimer[1] of (**2**).

In acetonitrile the fluorescence of (**1**) is quenched by (**2**) at an approximately diffusion-controlled rate ($1.5_5 \times 10^{10}$ l mol^{-1} s^{-1}).† Irradiation in acetonitrile or benzonitrile led to the isomeric adduct (**4**) and the dimer of (**2**). The structure‡ of the sterically unfavourable compound (**4**) was confirmed by *X*-ray crystallographic analysis.

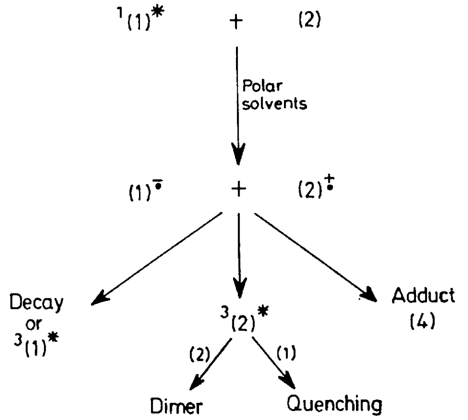
Whereas the quantum yield for the formation of (**4**) (Φ *ca.* 0·002) is relatively insensitive to the concentration of the reactants, that of the dimerization of (**2**) varies almost linearly with [(**2**)] and [(**1**)]$^{-1}$. These data are best explained in terms of the mechanism outlined in Scheme 1.



(4)

In agreement with the proposed electron-transfer reaction, compounds having low oxidation potentials, such as 1,4-dimethoxynaphthalene, substantially quench both adduct and dimer formation even at very low concentrations relative to that of (**2**), insufficient to react with ^{1}(**1**)* to any significant percentage.

The triplet formation from the recombination of radical ion pairs is well documented.[2] Support for the intermediacy of such a process in the reaction mentioned above was obtained from the fact that the dimer formation decreases with increasing concentrations of (**1**). The triplet energy of (**2**), as determined from the kinetics of reversible energy transfer to low-lying triplet sensitizers,[3] is *ca.* 55 kcal mol^{-1}. The triplet energy of (**1**) is expected to be lower than or similar to that of anthracene, *i.e.*, *ca.* 40 kcal mol^{-1}, hence the efficient quenching of ^{3}(**2**)* by (**1**).



SCHEME 1.

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† The slope of the plot of $(\Phi_0/\Phi)_{fl}$ *vs.* [(**2**)] is 32 and 235 l mol^{-1} in degassed benzene and acetonitrile, respectively. The lifetime of ^{1}(**1**)* in these solvents was determined previously by Ware *et al.* as 12·4 and 15·2 ns, respectively (W. R. Ware, J. D. Holms, and D. R. Arnold, *J. Amer. Chem. Soc.*, 1974, **96**, 7861). The reaction constant in benzene will be larger if the exciplex formation is reversible.

‡ The n.m.r. spectra (270 MHz) of (**3**) and of (**4**) show two different AA′ BB′ systems for the aromatic protons of the anthracene group. The *X*-ray analysis of (**4**) was performed by Molecular Structure Corporation, College Station, Texas.

An interesting observation was made when the radical anion $(\mathbf{1})^{\dot{-}}$ was intercepted with 1,2,4,5-tetracyanobenzene (**5**). Addition of (**5**) to the reaction mixture quenched, as expected, the formation of (**4**) but led to over an order of magnitude increase in the quantum yield of dimerization of (**2**).§ These results can be best explained in terms of a secondary electron-transfer reaction leading to $(\mathbf{5})^{\dot{-}}$ which would react with $(\mathbf{2})^{\dot{+}}$ to give, at least partially, $^{3}(\mathbf{2})^{*}$, as shown in Scheme 2.

$$(\mathbf{1})^{\dot{-}} + (\mathbf{5}) \rightleftharpoons (\mathbf{1}) + (\mathbf{5})^{\dot{-}}$$

$$(\mathbf{5})^{\dot{-}} + (\mathbf{2})^{\dot{+}} \longrightarrow {}^{3}(\mathbf{2})^{*} \xrightarrow{(\mathbf{2})} \text{Dimer}$$

Scheme 2.

The effect of $(\mathbf{5})^{\dot{-}}$ in increasing Φ_{dimer} is rationalized in terms of one or both of the following points. (a) The reaction of $(\mathbf{1})^{\dot{-}}$ and $(\mathbf{2})^{\dot{+}}$ can lead to much less $^{3}(\mathbf{2})^{*}$, owing to competing formation of $^{3}(\mathbf{1})^{*}$, as compared with the corresponding reaction of the radical anion of (**5**). (b) In the absence of (**5**), $^{3}(\mathbf{2})^{*}$ is formed in the vicinity or active sphere of (**1**), which can lead directly to nondiffusion-controlled 'static quenching',[4] whereas in the presence of (**5**), only the diffusion-controlled dynamic quenching by (**1**) is competing with the dimerization.

An attractive rationalization for the formation of the sterically hindered adduct (**4**) would be that $(\mathbf{2})^{\dot{+}}$ undergoes enolization. The driving force for such a process is the high stability of the resulting cyclic two-electron radical cation. This would lead to an adduct in the enol form, which upon ketonization would be protonated from the least hindered side thus forcing the methoxycarbonyl group to the *endo*-position. This is supported by the formation of *ca.* 80% [^{2}H$_{1}$]-(**4**) on carrying out the reaction in the presence of 10% Bu^{t}OD.

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§ Reversible reduction potentials in acetonitrile *vs.* SCE of −0·87 and −0·64 V were measured for (**1**) and (**5**), respectively. The electron transfer from $(\mathbf{1})^{\dot{-}}$ to (**5**) is, therefore, exothermic and proceeds probably at a diffusion-controlled rate. As a consequence the quantum yield for the dimerization of (**2**) is the same (*ca.* 0·03) at $[(\mathbf{5})] = 0{\cdot}003$ and $0{\cdot}03$ mol l^{-1}. Compound (**5**) quenches the fluorescence of (**1**) and forms a charge-transfer complex with (**2**), but under the chosen reaction conditions the interference from these processes is negligible.

[1] C. D. DeBoer, D. H. Wadsworth, and W. C. Perkins, *J. Amer. Chem. Soc.*, 1973, **95**, 861.
[2] K. H. Grellmann, A. R. Watkins, and A. Weller, *J. Phys. Chem.*, 1972, **76**, 469; H. Schomburg, H. Staerk, and A. Weller, *Chem. Phys. Letters*, 1973, **21**, 433.
[3] S. Farid and K. A. Brown, unpublished results.
[4] See J. B. Birks, 'Photophysics of Aromatic Molecules,' Wiley–Interscience, London, 1970.