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($2\sigma + 4\pi$) PHOTOCYCLOADDITION OF 1,2-DIARYLCYCLOPROPANES TO 9,10-DICYANOANTHRACENE VIA GEMINATE RADICAL ION PAIR

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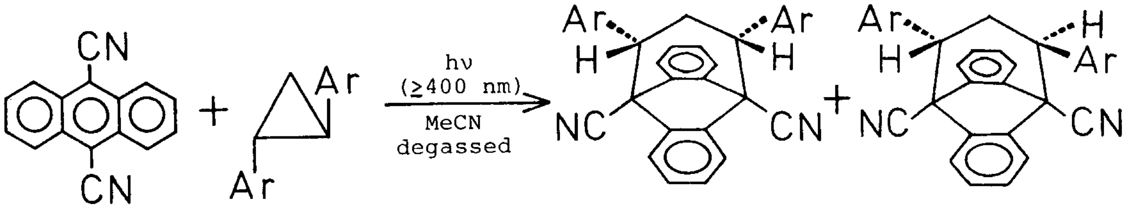
Abstract Irradiation of a degassed acetonitrile solution containing 9,10-dicyanoanthracene (DCA) and 1,2-diarylcyclopropanes gave ($2\sigma + 4\pi$) photocycloadducts in good yields. The geminate radical ion pairs between DCA and the cyclopropanes are involved as key intermediates in this photoreaction.

Photocycloaddition of unsaturated compounds to anthracene ring has been widely investigated from the mechanistic and synthetic viewpoints in recent years.1) We now report a novel ($2\sigma + 4\pi$) photocycloaddition of 1,2-diarylcyclopropanes to 9,10-dicyanoanthracene (DCA) via electron transfer.

Irradiation of a degassed acetonitrile solution containing DCA (0.5 mmol) and trans-1,2-bis(4-methoxyphenyl)cyclopropane (1a, 0.5 mmol) with a 500 W high-pressure mercury arc through an aqueous $CuSO_4$-NH_3 filter solution (≥400 nm light) for 10-15 h gave the ($2\sigma + 4\pi$) cycloadducts 3a and 4a in 85% yield. The photoreaction was carried out with vigorous stirring until the yellow color of DCA disappeared. Similarly the photoreaction of DCA with the cis-isomer 2a and cyclopropanes 1b-d and their cis-isomers 2b-d in degassed acetonitrile solutions gave the corresponding ($2\sigma + 4\pi$) cycloadducts 3a-d and 4a-d in good yields.2) The products were isolated by column chromatography on silica gel, and their structures were assigned from the analytical and spectral properties. The cis-diaryl configuration of 3a-d was assigned on the basis of their 270 MHz ^{1}H NMR spectral analyses.

The photocycloadduct 3a was not produced in degassed benzene solution, although the fluorescence of DCA was efficiently quenched by 1a and 2a in



DCA 1a-d 3a-d 4a-d

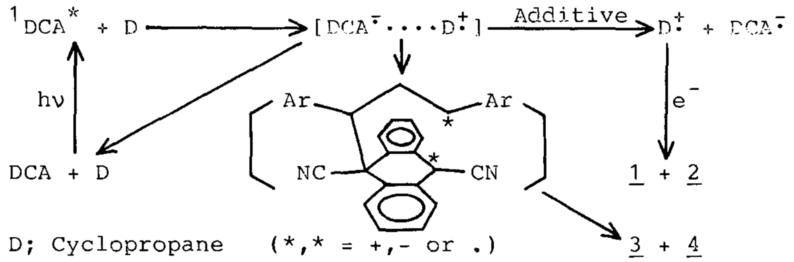
	Total yield/%
a; Ar = 4-$MeOC_6H_4$	85
b; Ar = 4-MeC_6H_4	58
c; Ar = C_6H_5	90
d; Ar = 4-ClC_6H_4	87

acetonitrile and also in benzene at nearly diffusion controlled rates.

The quantum yield for the formation of 3a and 4a in degassed acetonitrile was low (Φ=0.004), but significant. The addition of a small amount of phenanthrene (0.001 mol dm^{-3}), $Mg(ClO_4)_2$ (0.001 mol dm^{-3}), or triethylamine (0.001 mol dm^{-3}) completely quenched the formation of 3a and 4a. In aerated acetonitrile, only the geometrical photoisomerization from 1a to 2a or from 2a to 1a occurred, but 3a and 4a were not produced even by prolonged irradiation. The quantum yield for the photoisomerization from 2a to 1a was remarkably enhanced by the addition of phenanthrene, $Mg(ClO_4)_2$, or air.³⁾

These results can be explained by the mechanism as shown in Scheme 1. The photocycloaddition proceeds via the geminate radical ion pair produced by the photoinduced electron-transfer from cyclopropanes (D) to the excited singlet DCA. In degassed acetonitrile, the major decay process of the geminate radical ion pair is the back-electron transfer from $\mathrm{DCA}^{-\cdot}$ to $\mathrm{D}^{+\cdot}$ in cage. The photocycloaddition between $\mathrm{DCA}^{-\cdot}$ and $\mathrm{D}^{+\cdot}$ occurs in the cage in a small probability. The addition of additives facilitates the dissociation of the radical ion pair to give free radical ions. The free radical cation $\mathrm{D}^{+\cdot}$ undergoes the cis-trans photoisomerization in a chain process.

It is noteworthy here that the reaction of two closely related reactive intermediates, geminate radical ion pair and free radical ions, can be differentiated from each other by the addition of appropriate additives.⁴⁾



Scheme 1

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2) The cycloadducts 3 and 4 were obtained almost in the same ratio (3 : 4 = 80 ± 5 : 20 ∓ 5) from both the photoreactions of DCA with 1 and its isomer 2. This result suggests that the photoreactions proceed via biradical or dipolar intermediate which could be produced by coupling of geminate radical ion pair.
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