Formations of an [8π + 4π] Cycloadduct *via* an Electron-transfer Mechanism and a *meta*-Cycloadduct by Irradiations of Tropone and 9,10-Dicyanoanthracene

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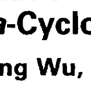
In the photoreaction with 9,10-dicyanoanthracene, tropone **1** behaved as an electron donor to give an [8π + 4π] adduct **10** *via* an electron-transfer mechanism in a mixed solution of MeCN–CH$_2$Cl$_2$ (1 : 1); other products characterized were an unprecedented *meta*-cycloadduct **7**, a *trans* [2π + 4π] **6**, and a [4π + 4π]–[2π + 4π] adducts **8**.

The solvent-dependent photoreactions of cyclohepta-2,4,6-trien-1-one (tropone, **1**) have been known to give dimers, which are a [6π + 6π] dimer **2**,[1] a [6π + 4π] dimer **3**, a [4π + 2π] dimer **4** and a [6π + 2π] dimer **5**.[2–5] Also, vapour phase photolysis of **1** afforded only benzene and carbon monooxide.[6] In the presence of olefins, the excited **1** underwent [8π + 2π] photocycloadditions.[7,8] Here we show the photoreaction of **1** with an electron-accepting sensitizer, 9,10-dicyanoanthracene (DCA), to give an [8π + 4π] adduct *via* an electron-transfer mechanism, a *trans* [2π + 4π] and a [4π + 4π]–[2π + 4π] adducts as well as an unprecedented *meta*-cycloadduct.

Irradiation of **1** and DCA (**1**:DCA = 1:1.2) in benzene (a 400 W high-pressure mercury lamp) through an aqueous 0.7 mol dm^{-3} NaNO$_2$ layer (thickness: 0.6 cm) to cut off the light shorter than 400 nm in wavelength gave three products (**6**–**8**); two (**6** and **7**) of them were 1 : 1 adducts and **8** was a 1 : 2 adduct between **1** and DCA. The stereochemistry of **6** was deduced to be *trans* from the magnitude of the coupling constant (*J* 10.3 Hz) between the two methine protons. Thermal isomerization of **6** in refluxing AcOEt gave a [1,5]hydrogen-shifted isomer **9** (Scheme 1). No further isomerization occurred by prolonged heating under the conditions. This is consistent with the fact that the most stable dihydro derivative of **1** is cyclohepta-3,5-dien-1-one.[9]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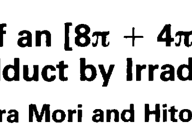
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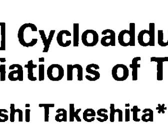
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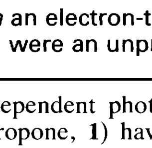
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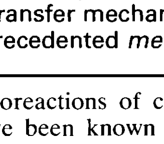
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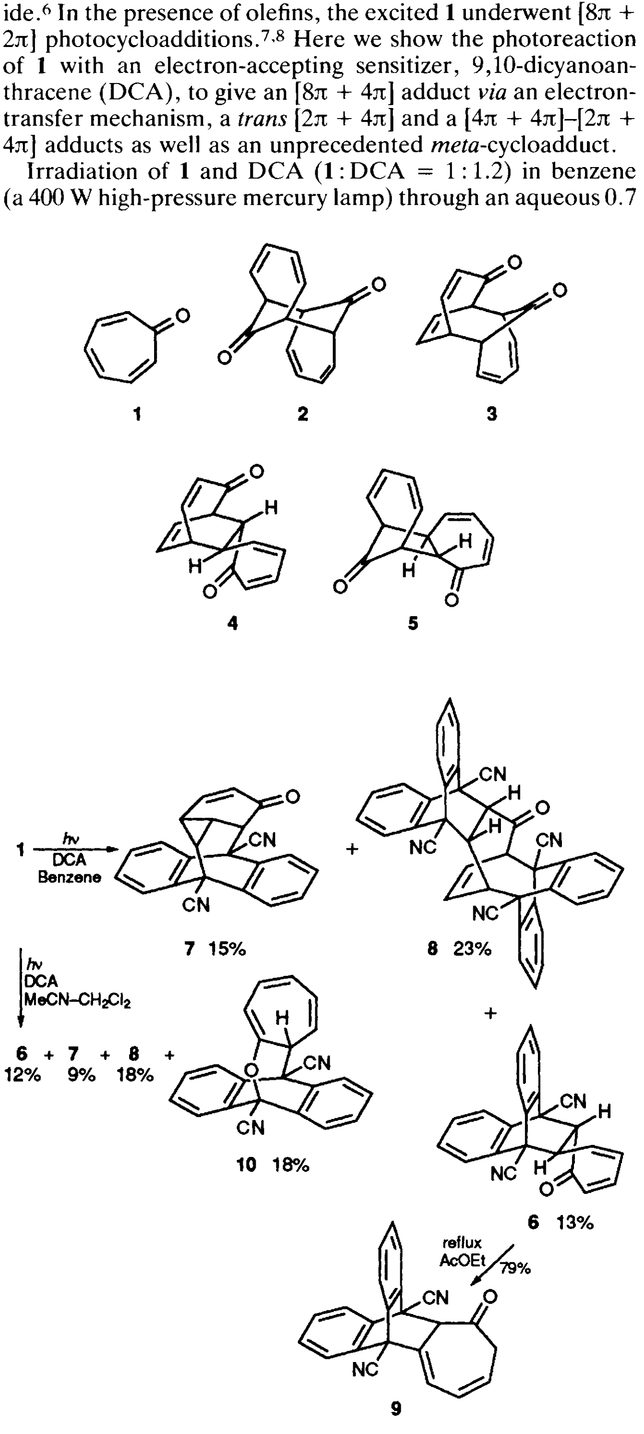


Scheme 1

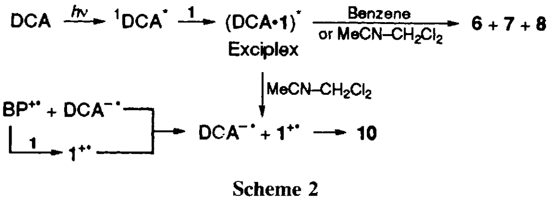
The ^{1}H NMR spectrum of **7** showed three methine protons at δ 1.48 (1H, dddd, *J* 10.6, 9.5, 8.8, 0.7 Hz), 1.76 (1H, dddd, *J* 9.5, 8.8, 4.0, 0.7 Hz), and 1.99 (1H, t, *J* 9.5 Hz) to indicate a presence of a cyclopropane ring. The ^{13}C NMR spectrum also revealed three cyclopropyl carbon signals at δ 14.5, 18.4 and 32.0. Consequently, **7** is a *meta*-cycloadduct of **1**. This is the first example of the *meta* cycloaddition of **1**.

The third product **8** showed four methine proton signals at δ 1.70 (1H, d, *J* 9.5 Hz), 2.72 (1H, dd, *J* 9.5, 2.2 Hz), 3.92 (1H, br d, *J* 9.5 Hz), and 4.28 (1H, ddm, *J* 10.3, 2.2 Hz) and two olefinic proton signals at 4.60 (1H, ddd, *J* 10.3, 9.5, 0.7 Hz) and 4.93 (1H, td, *J* 10.3, 1.1 Hz) as well as sixteen aromatic protons in the ^{1}H NMR spectrum. Therefore, **8** was deduced to be a [2π + 4π]–[2π + 4π] cycloadduct. The stereochemistry of the [2π + 4π] junction was determined to be *cis* by the NOE experiment of the two methine protons.

When **1** and DCA (**1**:DCA = 1:1.2) were irradiated for 10 h in a mixture of MeCN–CH$_2$Cl$_2$ (1 : 1), an [8π + 4π] adduct **10** was obtained together with the three adducts **6**–**8**. The ^{1}H NMR spectrum of **10** revealed five consecutive olefinic protons at δ 5.55 (1H, dd, *J* 10.2, 0.5 Hz), 6.42 (1H, ddm, *J* 10.2, 6.0 Hz), 6.64 (1H, ddm, *J* 11.0, 6.8 Hz), 6.69 (1H, ddm, *J* 11.0, 6.0 Hz), and 6.95 (1H, d, *J* 6.8 Hz) and a methine proton singlet at δ 1.75, showing it to be an [8π + 4π] adduct.

Since the light shorter than 400 nm in wavelength is cut off, only DCA can absorb the light. The fluorescence of DCA in MeCN was efficiently quenched (k_q = 9.37 × 10^9 dm^3 mol^{-1} s^{-1}) by **1** [oxidation potential of **1** ($E^{ox}_{1/2}$) = 1.95 V, reduction potential of DCA = −1.05 V].† According to the Weller's equation,[10] the electron-transfer process from **1** to ^{1}DCA* is estimated to be endothermic (ΔG_{ET} = 1.2 kcal mol^{-1}). However, the coupling reaction between DCA$^{-\bullet}$ and **1**$^{+\bullet}$ to **10** could make the electron-transfer process shifted to generate DCA$^{-\bullet}$ and **1**$^{+\bullet}$ (Scheme 2).

In the presence of a co-sensitizer, biphenyl (BP), in MeCN–CH$_2$Cl$_2$ (1 : 1), only **10** was obtained in 31% yield after 2 h irradiation. By adding BP, the yield of **10** increased from 18 to 31% and the product distribution changed dramatically from that without BP. BP is oxidized more easily ($E^{ox}_{1/2}$ = 1.70 V)† than **1**, and it is known that BP generates DCA$^{-\bullet}$ and BP$^{+\bullet}$



Scheme 2

from $^1DCA^*$.[11] A reversible electron transfer from **1** to $BP^{+\bullet}$ could generate $\mathbf{1}^{+\bullet}$ to give **10** although it is endothermic.[12]

In nonpolar benzene, where the fluorescence of DCA was also efficiently quenched ($k_q = 6.46 \times 10^9$ dm^3 mol^{-1} s^{-1}) by **1**, no **10** was formed. Thus, the significant solvent polarity effect on the product distribution also supported that **10** was formed *via* the electron-transfer mechanism.

In the photoreaction of **1** and DCA, the adducts (**6–8**) were formed from the cycloadditions *via* an exciplex intermediate and in MeCN–CH_2Cl_2, the electron-transfer process to give the [8π + 4π] adduct **10** competed with the formations of **6–8**.

This is the first example of the photoinduced electron-transfer reaction and the formation of a *meta*-cycloadduct of **1**.

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Footnote

† Oxidation and reduction potentials were obtained in MeCN solution with $LiClO_4$ by means of cyclic voltammetry in a standard three-electrode cell with platinum working and counter electrodes and Ag/AgCl reference electrode (ferrocene: 0.27 V) under N_2 with scan rate 100 mV s^{-1}.

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