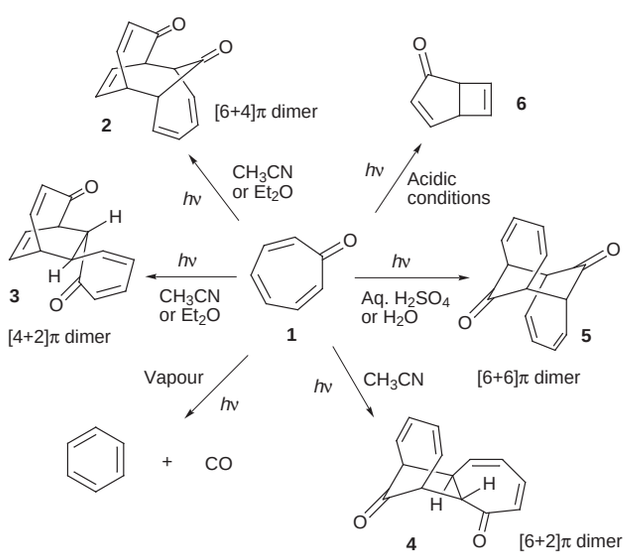
Photocycloaddition reaction of tropone and electron-accepting 9,10-dicyanoanthracene

Akira Mori,* Shu-Ping Wu, Nobuo Kato and Hitoshi Takeshita

Institute of Advanced Material Study, 86 Kyushu University, Kasuga-koen, Kasuga, Fukuoka 816-8580, Japan

The photoreaction of tropone 1 and electron-accepting 9,10-dicyanoanthracene (DCA) gave four products in less polar benzene while in more polar acetonitrile–dichloromethane (1 : 1) solution an [8+4]π adduct was formed together with the above four products. The formation of the [8+4]π adduct was enhanced by biphenyl and quenched by 1,4-dimethoxybenzene. According to Weller's equation, electron transfer from tropone 1 to DCA is estimated to be the endothermic ($\Delta G = +1.2$ kcal mol^{-1}). The following coupling reaction between DCA$^{\cdot -}$ and 1$^{\cdot +}$ to the [8+4]π adduct, however, could make the electron-transfer process shift to generate the radical-ion pair.

About three decades ago, the photochemical reactions of troponoids were a focus of considerable interest. Tropone, cyclohepta-2,4,6-trienone **1** has been dimerized in various polar solvents.[1–5] The reaction modes of tropone **1** were dependent on the reaction media; a [6+4]π dimer **2** and a [4+2]π dimer **3** were produced in diethyl ether[3] and acetonitrile whereas a [6+2]π dimer **4** was formed in CH_3CN.[2–5] The [6+6]π dimer **5** was obtained by irradiation in aq. sulfuric acid in low yield.[1] Under acidic conditions such as CH_3CN–BF_3, tropone **1** gave bicyclo[3.2.0]hepta-3,6-dien-2-one **6**,[6] which is different from the products obtained in CH_3CN.[2–5] The formation of dimer **5** only under aqueous acidic conditions suggested that the π–π* transition of tropone **1** around 310 nm is more stabilized in polar solvents than is the n–π* transition, while the [6+4]π dimer **2** was formed by a stepwise process *via* triplet intermediates.[7] The vapour-phase photolysis of tropone **1** afforded only benzene and carbon monoxide.[8] These reactions are summarized in Scheme 1.



Scheme 1

In 1971, Cantrell reported that the photochemical cycloaddition of tropone **1** to a ten-fold excess of isobutenes gave 2,3-dihydrocyclohepta[*b*]furan derivatives in 35–40% yield.[9] He used a large excess of alkenes to avoid the dimerization of tropone **1**. This disadvantage was overcome by Feldman *et al.* by means of the intramolecular photocyclization of 2-(pent-4-enyl)tropones in acidic media, in which the two reactive moieties are present in the same molecule.[10] In all the photocycloaddition reactions mentioned above, however, tropone **1** was excited directly.

In this work, we investigated the photoreaction of tropone **1** with 9,10-dicyanoanthracene (DCA), which worked as a sensitizer as well as a cycloaddition partner for tropone **1**.[11] DCA has a relatively low reduction potential and a higher excitation energy ($E = 2.89$ eV)[12] and usually it is taken as being an electron accepter in a photoinduced electron-transfer (ET) reaction. Since DCA can be excited at wavelengths longer than 400 nm, then by the proper use of filters the excitation of tropone **1** can be avoided.

On the other hand, it is known that the photocycloaddition of DCA to alkenes gives [4+2]π adducts. In nonpolar benzene, DCA and a strained cyclopropene **7** gave the *exo*-Diels–Alder adduct **8** *via* an exciplex. In polar acetonitrile the *endo*-Diels–Alder adduct **9** was obtained from the radical-ion-pair *via* ET. In the latter case, a dimer **10** of substrate **7** was formed.[13,14] The solvent polarity altered the reaction pathway (see Scheme 2).

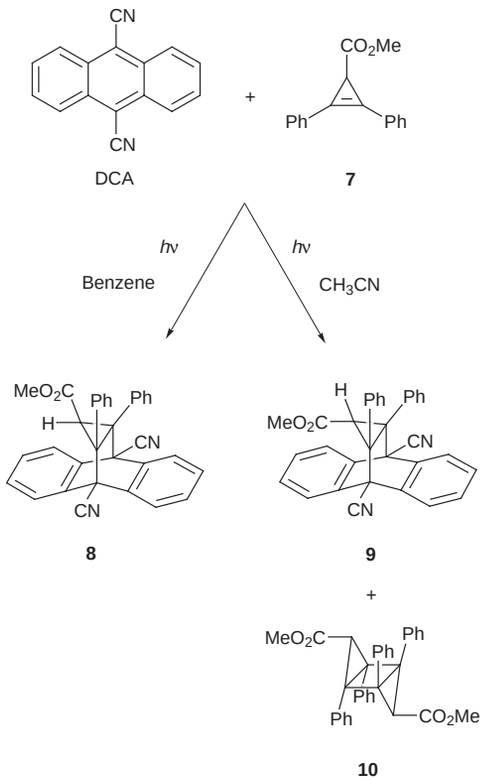
In the present study, the photocycloaddition of DCA to tropone **1** was performed in benzene and in a 1 : 1 mixed solution of acetonitrile and dichloromethane. The result revealed a marked difference with respect to the formation of an [8+4]π cycloadduct in CH_3CN–CH_2Cl_2. The formation of the [8+4]π adduct was enhanced by co-sensitizer biphenyl (BP) and was quenched by 1,4-dimethoxybenzene (DMB), which involves the indirect ET mechanism.

Results and discussion

Photocycloaddition in benzene

The nature of the medium is quite influential in a photochemical reaction.[15] At first, the photoaddition was examined in a nonpolar solvent; when a benzene solution of tropone **1** and DCA (**1** : DCA = 1 : 1.2) was irradiated by means of a 400 W high-pressure mercury lamp through a filter to cut off light of $\lambda < 400$ nm, four products (**11**–**14**) were obtained (Scheme 3). The ^{1}H NMR spectrum of product **11** is characterized by the signals of a couple of methine groups, *i.e.* δ 2.90 (1 H, ddd, *J* 10.3, 3.7 and 2.2 Hz),† 2.96 (1 H, d, *J* 10.3), and the signals of four vinyl protons at δ 6.08, 6.19, 6.67 and 6.69. The

† Throughout this paper, *J*-values are given in Hz.



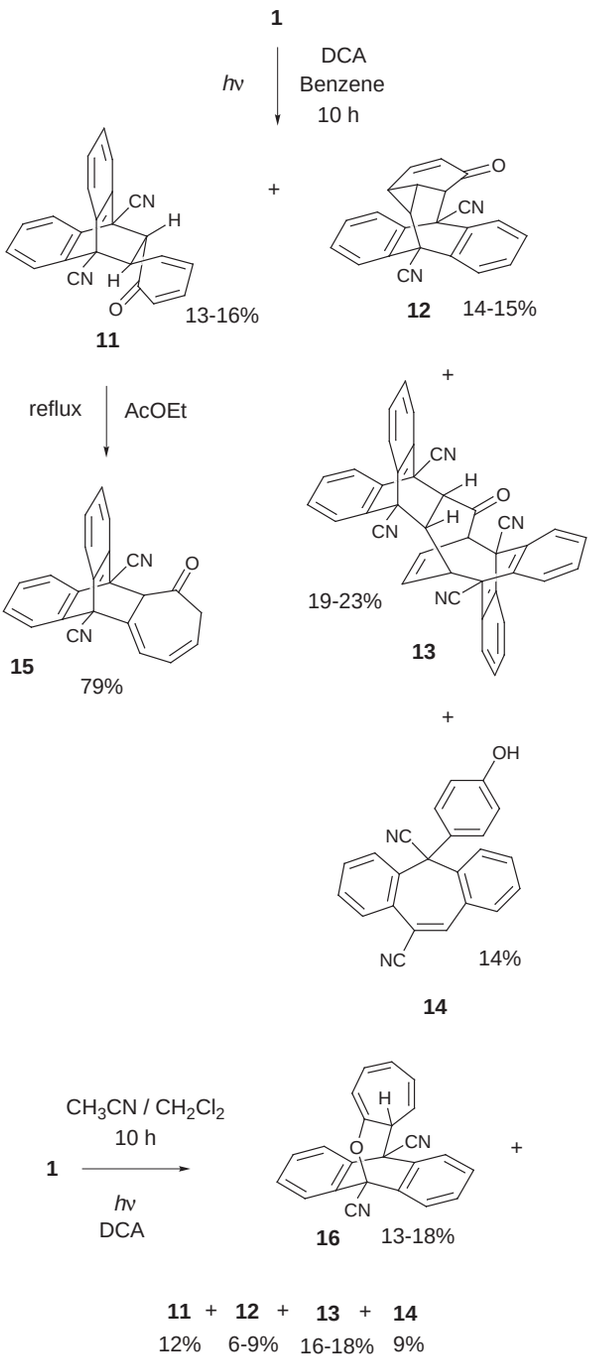
Scheme 2

stereostructure of product **11** was clarified by an intensive NMR spectral analysis. The *trans* relationship for the ring juncture of the [2+4]π addition was deduced from the coupling constant of the two methine protons at the juncture, *J* 10.3, since the corresponding methine protons of the *trans*-[4+2]π photodimer **3** of tropone **1** showed the vicinal coupling constant, *J* 11.0.[4]

Refluxing of adduct **11** in an ethyl acetate solution for 6 h led to a [1,5] hydrogen-shift resulting in the formation of an isomer **15** in 79% yield. The ^{1}H NMR spectrum of product **15** revealed that the signals at δ 2.65 and 3.26, ascribable to a methylene group, possess a distinct coupling constant (*J* 18.5). No more isomerization of compound **15** occurred under the conditions used. This was consistent with the results that the dihydro derivative of tropone **1** prepared by $LiAlH_4$ reduction exists as cyclohepta-3,5-dienone[16] and that cyclohepta-3,5-dienone is the product of the acid-catalysed ketonization of cyclohepta-1,3,5-trien-3-ol.[17]

The structural assignment for product **12** agreed well with the ^{1}H NMR spectral data. It showed four methine proton signals at δ 1.48 (1 H, ddd, *J* 10.6, 9.5, 8.8 and 0.7), 1.76 (1 H, dddd, *J* 9.5, 8.8, 4.0 and 0.7) and 1.99 (1 H, t, *J* 9.5), which indicated the presence of a cyclopropane ring, and δ 3.36 (1 H, d, *J* 10.6) ascribable to the proton at the neighbouring carbon to the carbonyl group, and two olefinic protons at δ 5.32 (1 H, dd, *J* 10.3 and 0.7) and 6.09 (1 H, ddd, *J* 10.3, 4.0 and 0.7). The ^{13}C NMR spectrum also revealed three cyclopropane carbon signals at δ_C 14.5, 18.4 and 32.0 and an α,β-unsaturated carbonyl signal (δ_C 195.3) to confirm the structure. From these data, compound **12** is considered to be an adduct as shown in Scheme 3.

A 1:2 adduct **13** of tropone **1** and DCA was also obtained. The structure of product **13** was elucidated to be a [4+4]–[2+4]π cycloadduct on the basis of spectroscopic evidence. The ^{1}H NMR spectrum revealed four well separated methine proton signals, two of which [δ 1.70 (1 H, dd, *J* 9.5 and 0.7) and 2.72 (1 H, dd, *J* 9.5 and 2.2)] can be ascribed to the methine protons at the juncture of the [2+4]π addition, and other two protons (δ 3.92 and 4.28) belong to the protons on the carbon of the



Scheme 3

juncture of [4+4]π addition between tropone **1** and DCA. Since the proton at δ 2.72 showed a positive nuclear Overhauser effect (NOE) with the neighbouring proton (δ 1.70), the stereochemistry of the [2+4] junction was deduced to be *cis*. The structure was further verified by ^{13}C NMR spectroscopy including the signals of 39 carbons, in which a carbonyl carbon appeared at δ_C 196.9.

The structure of compound **14** was deduced to be 5,10-dicyano-5-(4-hydroxyphenyl)-5*H*-dibenzo[*a*,*d*]cycloheptene from the spectral data; the ^{1}H NMR spectrum indicated the presence of a *para*-substituted phenol and a singlet signal at δ 7.35 together with eight aromatic proton signals. A singlet signal at δ 4.91, ascribable to a phenolic hydroxy group, disappeared on the addition of a drop of deuterium oxide. The ^{13}C NMR spectrum showed an sp^3-carbon signal at δ_C 56.4 and two cyano groups at δ_C 118.5 and 119.6.

When a benzene solution of DCA and tropone **1** was heated to 40 °C in the dark for 10 h, TLC and HPLC analyses

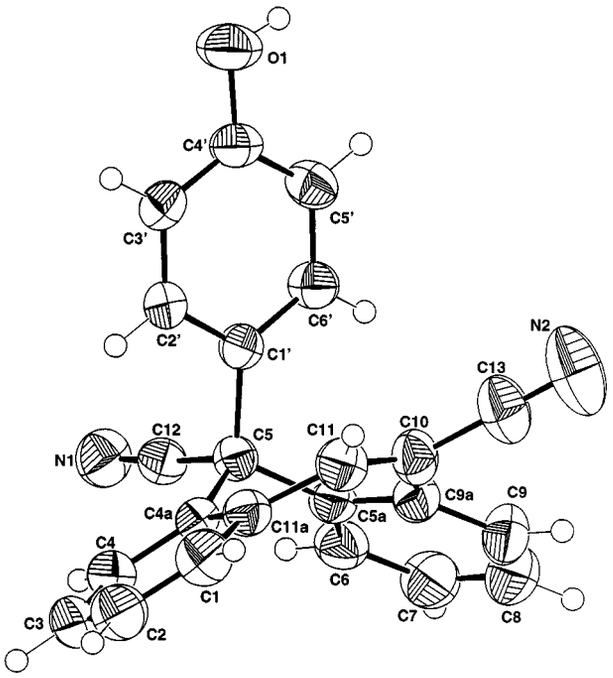


Fig. 1 The ORTEP drawing with thermal ellipsoids scaled to enclose 50% probability. Heteroatoms are shown as cross-hatched. Hydrogen atoms are shown as spheres with their arbitrary radii of 0.10 Å.

indicated no reaction. This showed that the cycloaddition proceeded only under the photosensitization conditions.

X-Ray analysis of compound 14

A single crystal of compound **14** was obtained from a mixed solution of benzene and CH_3CN by allowing the solvent to evaporate off slowly. The crystal structure is shown in Fig. 1. The cycloheptatriene moiety is puckered; the angle between the mean-square planes of the two benzene rings is 123.06(7)°. The stereochemistry of the phenol group is axial not only to avoid the steric repulsion with the two *peri*-hydrogen atoms but also to form hydrogen bonding of the hydroxy group with the nitrogen atom of an adjacent molecule.

Photoreaction of DCA and tropone 1 in CH_3CN–CH_2Cl_2

When a CH_3CN–CH_2Cl_2 solution of DCA and tropone **1** (1.2:1) was irradiated under similar conditions as those in benzene, an [8+4]π adduct **16** was obtained together with the four adducts (**11**–**14**). The structure of product **16** could be identified according to the ^{1}H NMR spectrum, *i.e.* the presence of five olefinic protons at δ 5.55, 6.42, 6.64, 6.69 and 6.95 indicated the structure to be a 1-substituted cycloheptatriene derivative, and a methine proton signal at δ 1.75 could be assigned to the *exo*-proton on C-7. There is no ambiguity in the structure of the cycloheptatriene derivative. Since the ^{13}C NMR spectrum of compound **16** exhibited no carbonyl carbon, the structure of product **16** was further confirmed. The products and the yields in polar and nonpolar solvents are summarized in Table 1.

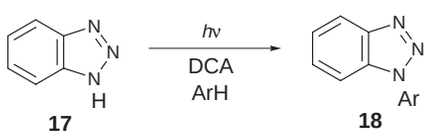
Comparison of the photocycloaddition reactions in benzene and in CH_3CN–CH_2Cl_2 showed that compound **16** is produced only in CH_3CN–CH_2Cl_2. The solvent effect is a sign that the formation of compound **16** may be formed *via* an ET mechanism. A decisive influence of the medium on the photochemical reaction is especially true for an ET process that leads to the generation or disappearance of polar species.[15] The solvent stabilization effects of the ET intermediates formed in ET reactions are significant.[15]

Co-sensitization by biphenyl

The use of a co-sensitizer having an appropriate oxidation potential as a relay in the photoinduced ET process between a donor substrate and an acceptor sensitizer has recently received increasing attention. Often not only is a rate acceleration in ET reactions observed, but, in many cases, endothermic ET, which is not a facile process, is made feasible by adding a suitable co-sensitizer. Schaap *et al.*[18] have published a method of co-sensitization by DCA–BP that can efficiently initiate the ET photooxygenation for a number of less reactive compounds such as phenyl-substituted cyclopropanes, epoxides and aziridines. It was also reported[19] that the photoinduced ET reactions between DCA and benzotriazole **17** were co-sensitized by aromatic hydrocarbons and the subsequent addition reaction led to the formation of the corresponding 1-arylbenzotriazoles **18** (Scheme 4). It is clear that direct ET between singlet excited

Table 1 Product distributions of the reactions of tropone **1** and DCA

	Yield of products (%)				
Solvent	**11**	**12**	**13**	**14**	**16**
Benzene	13–16	14–15	19–23	14	
CH_3CN–CH_2Cl_2	12	6	16	9	13



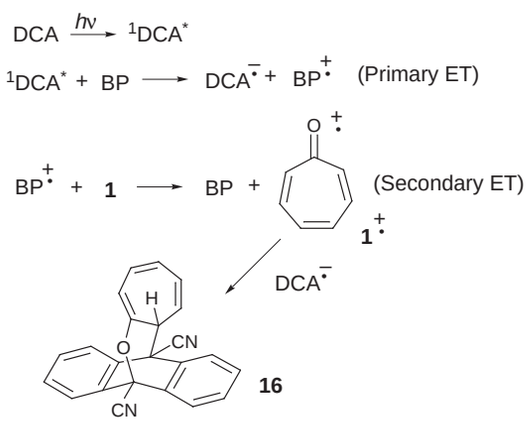
17 **18**

ArH = BP, Naphthalene, Anisole

Scheme 4

DCA and compound **17** (E^{ox} = 2.56 V *vs.* SCE) is unfavourable since it is a strongly endothermic reaction (ΔG_{ET} = 13.6 kcal mol^{-1}).‡ But an addition of aromatic hydrocarbons could initiate indirect ET to produce the radical cation and the subsequent reaction to form products.

A CH_3CN–CH_2Cl_2 solution containing DCA, tropone **1** and a co-sensitizer, BP, was irradiated for 2 h. Only [8+4]π adduct **16** was obtained, in 31% yield (see Scheme 5). By adding BP, the



Scheme 5

yield of product **16** as well as the rate of the reaction was apparently enhanced and the product distribution changed considerably from that without BP. BP does not absorb light and is chemically unreactive. It works only as a co-sensitizer under the above reaction conditions. The rate enhancement was deduced to be based on the following indirect ET mechanism. Primary ET of singlet excited DCA and BP had already been verified in the investigation of photoinduced oxygenation[18] or

‡ 1 cal = 4.184 J.

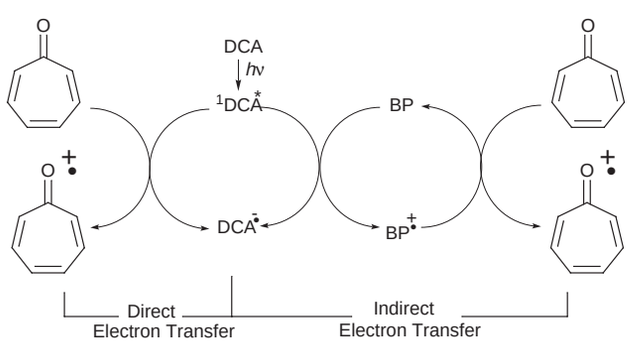
Table 2 Product distributions of the reactions of tropone **1** and DCA with and without DMB in CH_3CN–CH_2Cl_2

		Yield of products (%)				
1	DMB	**11**	**12**	**13**	**14**	**16**
1×10^{-2} M		see Table 1				
1×10^{-2} M	1.2×10^{-3} M	11	8	8	20	

coupling reaction.[19] It is favourable not only in the thermodynamic sense ($\Delta G = -2.8$ kcal mol^{-1}), but also in the considerable separation efficiency of the $DCA^{\bullet -}/BP^{\bullet +}$ ion pair ($F_{sep} = 0.75$).[20] Farid[20] has observed the transient absorption spectra of $DCA^{\bullet -}$ and $BP^{\bullet +}$ upon pulsed laser excitation of DCA in the presence of 0.2 M BP in CH_3CN. This is direct evidence for the occurrence of the ET process between DCA and BP.

Thus, in the case of the reaction of DCA and tropone **1** in the presence of BP, the second ET from tropone **1** to $BP^{\bullet +}$ would occur efficiently to give $\mathbf{1}^{\bullet +}$ and regenerated BP since the radical cation $BP^{\bullet +}$ has a longer lifetime[18,19] than singlet excited DCA. The subsequent irreversible reaction of $DCA^{\bullet -}$ and $\mathbf{1}^{\bullet +}$ would lead to adduct **16**.

The exclusive formation of compound **16** in the presence of BP verified its formation through an ET mechanism. Therefore, it can be concluded that, in the absence of BP, adduct **16** was formed *via* a direct ET pathway and, in the presence of BP, its formation involved two pathways; direct and indirect ET processes (Scheme 6).

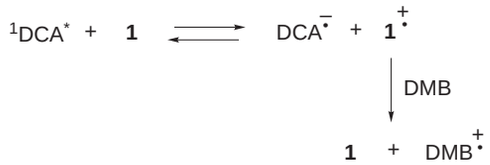


Scheme 6

Quenching reaction of the [8+4]π cycloaddition by DMB

One method of identifying intermediates is to trap or scavenge them with appropriate compounds. In many cases, it is possible to find specific scavengers for radical cations, radical anions, or excited state.[21,22] In sensitized ET photooxygenation, addition of a small amount of donor molecules with an oxidation potential less than that of the substrate should quench the oxygenation reactions by ET from a donor molecule to a substrate radical cation. This involves a competitive ET process. In general, the free-energy change involved in this ET is given by the difference in the oxidation potential between that of the substrate and that of the donor molecule. The ET photooxygenation of phenyl-substituted alkenes was reported to be quenched by methoxybenzene[13] and use of 1,4-dimethoxynaphthalene is known to quench the ET addition of DCA to 2,3-diphenylcyclopropanecarboxylate.[14]

Herein, DMB was used as a donor to quench product formation *via* the radical cation of tropone **1**. When a CH_3CN–CH_2Cl_2 solution containing DCA, tropone **1** and DMB was irradiated, the [8+4]π adduct **16** was not detected; the yields of adducts **11** and **12** were similar, the 1:2 adduct **13** was diminished and compound **14** was increased, compared with the reaction in the absence of DMB. These results are listed in Table 2. The apparent quenching effect of DMB on the formation of compound **16** resulted from efficient quenching of a radical cation intermediate of tropone **1** by DMB (Scheme 7).



Scheme 7

This strongly supported the idea that **16** is formed *via* an ET mechanism. The efficient ET from DMB to $\mathbf{1}^{\bullet +}$ may be favoured in free-energy change (DMB, $E^{ox}_{1/2} = 1.34$ V *vs.* SCE) and the resultant radical cation $\mathbf{1}^{\bullet +}$ might have a longer lifetime. It has been reported that the quenching of a radical cation by a donor with a lower oxidation potential is inefficient for radical cations with shorter lifetimes.[13] It should be noted that DMB can also quench the fluorescence of DCA in competition with tropone **1**. However, the amount of DCA in the mixture was kept high (10:1) and this competitive quenching by DMB should be minimal.

Fluorescence quenching and electrochemical considerations

In a degassed CH_3CN or benzene solution, the fluorescence quenching of DCA by tropone **1** was efficient as shown in Fig. 1. From the slopes of the Stern–Volmer plot of I_o/I *vs.* [**1**] and the lifetime of DCA in CH_3CN (15.3 ns)[23] and in benzene (12.4 ns),[24] the quenching constants k_q were obtained. The k_q-values (9.37×10^9 l mol^{-1} s^{-1} in CH_3CN and 6.46×10^9 l mol^{-1} s^{-1} in benzene) indicated an apparent quenching effect in both polar and nonpolar solvents. In CH_3CN, the quenching rate was approximately diffusion controlled, which implies that the ET quenching process is operative.

On the other hand, tropone **1** is a representative non-alternant aromatic ketone. The electron-donating ability of tropone **1** was estimated from the oxidation potential measured by means of cyclic voltammetry (CV). The oxidation potential of tropone **1** was 1.95 V *vs.* Ag/AgCl and the reduction potential of DCA was −1.05 V *vs.* Ag/AgCl. According to Weller's equation, the ET process from tropone **1** to DCA is estimated to be endothermic ($\Delta G = +1.2$ kcal mol^{-1}). Although this ET process is energetically unfavoured, it is driven by the subsequent irreversible coupling reaction between $DCA^{\bullet -}$ and $\mathbf{1}^{\bullet +}$. As has been discussed, the enhancement effect of BP and the quenching effect of DMB in the formation of adduct **16** provided evidence for the ET process. Meanwhile, the experimental result that compound **16** was obtained in 13–18% yield implied that ET occurred but not so efficiently.

Concentration effect on the reaction of tropone 1 and DCA

As described in the preceding section, a significant medium effect was observed; in a polar solvent, ET took part in formation of the [8+4]π adduct **16**; whereas it did not do so in a nonpolar solvent. In this section, the concentration effect in the photochemical reaction of tropone **1** and DCA will be discussed.

A benzene solution of tropone **1** and DCA (**1**:DCA = 3:1) was irradiated under similar conditions to those above to give the adducts **11**–**14** as well as two tropone dimers, the [6+4]π dimer **2** and the [4+2]π dimer **3**. The difference is the formation of the dimers of tropone **1** under the conditions of increased donor concentration. The results are summarized in Table 3. On the other hand, the concentration effect in CH_3CN–CH_2Cl_2 was remarkable; with increased donor concentration, the [8+4]π adduct **16**, which was the product obtained *via* an ET mechanism under dilute concentration, was not formed. The

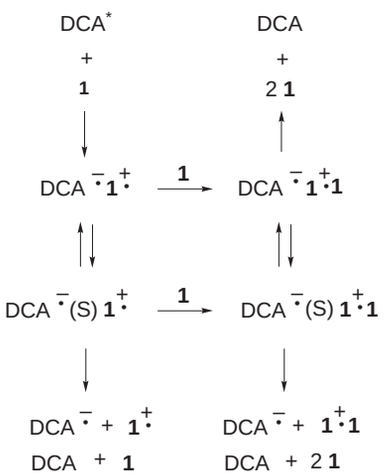
Table 3 Concentration effect on the product distributions of the reactions of tropone **1** and DCA

			Yield of products (%)						
1	DCA	Solvent[a]	**11**	**12**	**13**	**14**	**16**	**2**	**3**
1	1.2	A	see Table 1						
		B	see Table 1						
3	1	A	38	16	8	8		11	19
		B	35	11	14	9		17	10

[a] A: Benzene, B: CH_3CN–CH_2Cl_2 = 1 : 1.

product distribution between nonpolar and polar solvents was similar except for the yields of the dimers.

It is known[25] that the fluorescence quantum yields and lifetimes decrease with increasing donor concentration for some exciplexes of DCA with naphthalenes and phenanthrenes as donors; the primary contact radical-ion pair ($DCA^{\bullet-}$**1**$^{\bullet+}$) was intercepted by another donor molecule (**1**) to form a 1 : 2 radical-ion complex, $DCA^{\bullet-}$**1**$^{\bullet+}$**1**, and the rate of energy-wasting back-ET competed with solvation to form a solvent-separated 1 : 2 radical-ion pair, $DCA^{\bullet-}$(S)**1**$^{\bullet+}$**1** (Scheme 8).



Scheme 8

From this, back-ET to an acceptor (DCA) and 2 **1** and separation to $DCA^{\bullet-}$ and **1**$^{\bullet+}$**1** are competing. Therefore, it was the case that adduct **16** was not formed in a polar solvent when donor concentration was higher. In other words, the ET mechanism to compound **16** is operative under the conditions of dilute concentration.

It is noteworthy that the photoreaction of tropone **1** and DCA revealed a significant concentration effect. At higher donor concentration, two tropone dimers were formed: the [6+4]π dimer **2** was a major product in a polar solvent while the [4+2]π dimer **3** was a major one in a nonpolar solvent. It has been reported that dimer **2** was formed by a stepwise process *via* triplet intermediates.[7] The formation of dimer **3** could be explained by a concerted process according to the Woodward–Hoffmann rules.[26] As a plausible mechanism, the dimeric radical cation **1**$^{\bullet+}$**1** might be involved in forming compound **2** in a polar solvent. This is consistent with the fact that compound **16** was not formed at higher donor concentration and that ET was responsible for the reaction of tropone **1** and DCA in a polar solvent.

Mechanistic considerations

As mentioned above, the adducts **11**–**14** were formed in the cycloaddition *via* an exciplex intermediate, and in CH_3CN–CH_2Cl_2 an ET process to give the [8+4]π adduct **16** competed with the formation of the adducts **11**–**14**. It was observed that irradiation of either adduct **11** or **12** in the presence of DCA gave no product. Then, it was concluded that the adducts did not interchange photochemically. Furthermore, a *meta*-cycloaddition of tropone **1** was also observed, suggesting the possibility of a photochemical equilibrium between tropone **1** and tropovalene **19**.[27,28] The valence isomer **19** might be concerned in the formation of not only adduct **12** but also adduct **14**; from MM2 calculations[29] on compound **19**, the C^1–C^7 bond length is shorter than the C^1–C^2 (= C^2–C^7) and the C^1–C^6 (= C^6–C^7) bond lengths.

The C^1–C^2 bond would break to give a diradical intermediate **A**, from which the radical combination *via* 'path a' would afford the adduct **12**. Alternatively, the C–C bond of the cyclopropane ring would cleave to give a benzyl radical intermediate **B**, which would lead to a norcaradiene derivative **C**. From the cycloheptatriene **D**, the migration of the phenol group would give compound **14**. It has been reported that 7-phenylcycloheptatriene gave a mixture of 3-, 1- and 2-isomers on heating, *i.e.* a hydride shifted faster than a phenyl group.[30] In the intermediate **D**, since the phenol group should be axial due to the reduction in steric hindrance between the *peri*-hydrogen and the cyano group, the phenol group would migrate faster than the hydride to give product **14** (see Scheme 9).

In conclusion, tropone **1**, as a contribution of a polarized 6π-aromatic structure, *i.e.* a cycloheptatrienylium oxide, behaved as an electron donor in its photochemical reactions with an electron-accepting DCA in a polar solvent. Furthermore, energy transfer from excited DCA to tropone **1** occurred to give a valence isomer, **19**, which reacted with DCA to afford adducts.

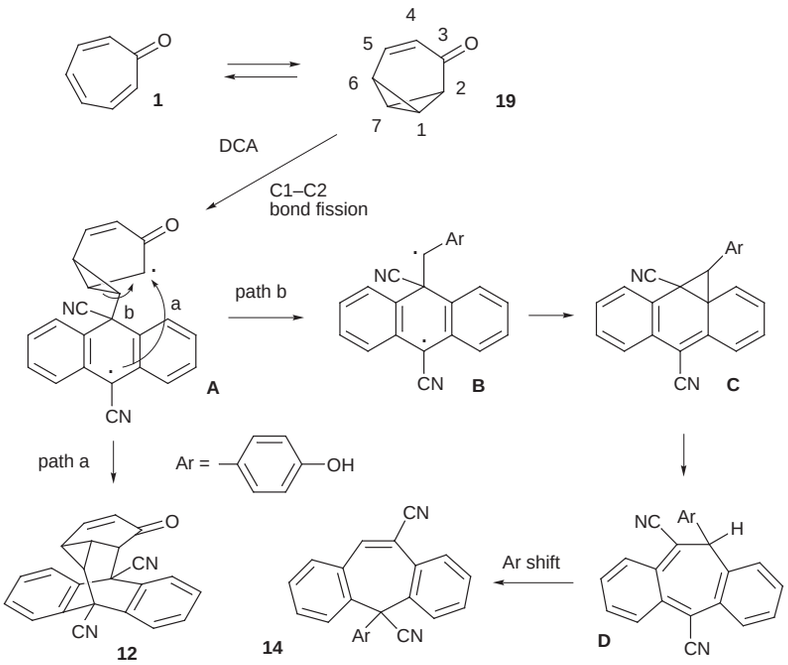
Conclusions

The photocycloaddition of DCA with tropone **1**, a representative non-benzenoid aromatic ketone, was shown to give a *trans*-[2+4]π adduct **11**, a [4+4]–[2+4]π adduct **13**, an adduct **12** of DCA and compound **19**, as well as a dibenzo[*a*,*d*]cycloheptene derivative **14** in benzene. In a polar solvent, a new cycloadduct **16** was formed. Although it is energetically unfavoured (ΔG = 1.2 kcal mol^{-1}), the ET process could occur since it is driven by the subsequent irreversible coupling reaction between $DCA^{\bullet-}$ and **1**$^{\bullet+}$. As has been discussed, the enhancement by BP and the quenching effect of DMB on the formation of adduct **16** provided evidence for the ET process. The results from experiments at the high concentrations of tropone **1** also supported this conclusion. This is the first example of ET in the photochemistry of troponoids. The reactions with substituted troponoids promise to provide more interesting results.

Experimental

NMR spectra were measured on a GSX 270H Model spectrometer for samples in $CDCl_3$ solution, unless otherwise stated, and chemical shifts are expressed in δ-units. IR spectra were recorded on a JASCO IR A102 spectrometer with KBr disks. FAB mass spectra and high-resolution mass spectra were obtained with a JEOL SX/SX102A spectrometer in the Faculty of Pharmaceutical Science, Kyushu University. Mps were determined on a Yanagimoto Micro Melting Apparatus. The stationary phase for column chromatography was Wakogel C-300 and eluent was a mixture of AcOEt and hexane, unless otherwise stated. Acetonitrile was refluxed over diphosphorus pentaoxide and distilled, then the same procedure was performed over calcium hydride. Benzene was washed successively with conc. sulfuric acid, water, aq. Na_2CO_3 and water. After drying over Na_2SO_4, the solvent was distilled over Na-wire. DCA from Tokyo Kasei Organic Chemicals was purified by recrystallization (toluene), and tropone **1**, which was prepared by reported procedures,[31] was purified by distillation (bp 105 °C/10 mmHg) for fluorescence quenching and CV measurements.

Photochemical reactions were carried out with a 400 W high-pressure Hg lamp. A 0.6 cm path-length filter solution (0.7 M



Scheme 9

aq. $NaNO_2$) was used to cut off light with $\lambda < 400$ nm. A reaction solution was bubbled with argon for 1 h and irradiated for 10 h. After irradiation, the solution was filtered to remove unchanged DCA. The solvent was removed and the residue was chromatographed.

Photoreaction of DCA and tropone 1 (DCA : 1 = 1.2 : 1) in benzene

A benzene solution (100 ml) of DCA (273 mg, 1.2 mmol) and tropone **1** (106 mg, 1 mmol) was saturated with argon and irradiated. The reaction mixture was separated by chromatography to give adducts **11** (26 mg, 15%), **12** (24 mg, 14%), **13** (58 mg, 20%) and seven-membered adduct **14** (24 mg, 14%) together with unchanged tropone **1** (52 mg).

Adduct **11**: crystals, mp 240–242 °C; δ 2.90 (1 H, ddd, *J* 10.3, 3.7 and 2.2), 2.96 (1 H, d, *J* 10.3), 6.08 (1 H, d, *J* 12.5), 6.19 (1 H, ddd, *J* 10.6, 7.0 and 2.2), 6.67 (1 H, dd, *J* 10.6 and 3.7), 6.69 (1 H, dd, *J* 12.5 and 7.0), 7.32–7.46 (4 H, m), 7.64 (1 H, dd, *J* 7.3 and 1.5), 7.73–7.82 (2 H, m) and 7.96 (1 H, dd, *J* 7.3 and 1.5); δ_C 44.7, 45.6, 48.1, 58.4, 116.1, 116.4, 121.5, 122.5, 123.9, 125.6, 127.3, 128.2, 128.5, 128.7, 128.9, 130.2, 132.8, 132.9, 137.4, 137.5, 137.6, 139.4 and 194.0; ν_{max}(KBr) 2246, 1679, 1460, 1413, 1383 and 758 cm^{-1}; FAB MS (*m*/*z*, %) 335 (30), 334 (5), 307 (76), 154 (100), 136 (77), 107 (42), 89 (30) and 77 (23) [Found: (FAB MS): 335.1176 $(M + H)^+$. Calc. for $C_{23}H_{15}N_2O$: *m*/*z*, 335.1183].

Adduct **12**: crystals, mp 260 °C; δ 1.48 (1 H, dddd, *J* 10.6, 9.5, 8.8 and 0.7), 1.76 (1 H, dddd, *J* 9.5, 8.8, 4.0 and 0.7), 1.99 (1 H, t, *J* 9.5), 3.36 (1 H, d, *J* 10.6), 5.32 (1 H, dd, *J* 10.3 and 0.7), 6.09 (1 H, ddd, *J* 10.3, 4.0 and 0.7), 7.33–7.42 (3 H, m), 7.52–7.58 (2 H, m) and 7.8–8.1 (3 H, m); δ_C 14.5, 18.4, 32.0, 46.3, 46.7, 49.7, 117.9, 119.1, 123.6, 126.2, 126.9, 127.2, 129.0, 129.1, 129.4, 129.7, 132.0, 133.6, 137.8, 138.2 (3 C) and 195.3; ν_{max}(KBr) 1682, 1475, 1456, 1242, 756 and 738 cm^{-1}; FAB MS (*m*/*z*, %) 335 (6), 307 (71), 241 (28), 194 (23) and 154 (100) [Found: (FAB MS): 335.1180 $(M + H)^+$].

Adduct **13**: crystals, mp 303–304 °C; δ 1.70 (1 H, dd, *J* 9.5 and 0.7), 2.72 (1 H, dd, *J* 9.5 and 2.2), 3.92 (1 H, br d, *J* 9.5), 4.28 (1 H, ddm, *J* 10.3 and 2.2), 4.60 (1 H, ddd, *J* 10.3, 9.5 and 0.7), 4.93 (1 H, td, *J* 10.3 and 1.1), 7.22–7.28 (2 H, m), 7.35–7.58 (8 H, m) and 7.71–7.93 (6 H, m); δ_C 30.9, 49.2, 49.8, 50.1, 51.9, 52.3, 56.6, 63.3, 115.7, 116.0, 119.5, 120.4, 122.4, 123.5, 123.6, 124.3, 124.8, 126.4, 126.7, 128.1, 128.5, 128.8 (4 C), 129.6, 129.7, 130.1, 130.9, 131.5, 132.6 (2 C), 133.2, 134.1, 134.2, 134.3, 135.4, 136.0 and 196.9; ν_{max}(KBr) 2924, 1693, 1463, 762 and 737 cm^{-1}; FAB MS (*m*/*z*, %) 563 (1), 228 (100) and 106 (45) (Found: C, 83.3; H, 4.4; N, 10.0. Calc. for $C_{39}H_{22}N_4O$: C, 83.25; H, 3.94; N, 9.96%).

Adduct **14**: crystals, mp 277–278 °C; δ 4.91 (1 H, s), 6.45 (2 H, dm, *J* 8.5), 6.59 (2 H, dm, *J* 8.5), 7.35 (1 H, s), 7.43 (1 H, dm, *J* 7.7), 7.48 (1 H, tm, *J* 7.2), 7.52 (1 H, tm, *J* 7.2), 7.63–7.67 (2 H, m), 7.82 (1 H, dd, *J* 7.7 and 1.2) and 8.23 (2 H, br d, *J* 6.8); δ_C 56.4, 115.1, 115.5 (2 C), 118.5, 119.6, 127.5, 127.7, 128.4, 128.5 (2 C), 128.7, 129.2, 129.3, 130.3, 130.7, 131.0, 131.1, 131.6, 137.5, 138.6, 142.8 and 155.9; ν_{max}(KBr) 3432, 1609, 1511, 1436, 1275, 1207, 838 and 758 cm^{-1} [Found: (FAB MS): 335.1172 $(M + H)^+$, 334.1115 $(M)^+$. Calc. for $C_{23}H_{15}N_2O$: *m*/*z*, 335.1183 and for $C_{23}H_{14}N_2O$: *M*, 334.1105].

Thermal reaction of *trans*-adduct 11 to adduct 15

An ethyl acetate solution (10 ml) of *trans*-adduct **11** (10 mg) was refluxed for 6 h under nitrogen. The reaction mixture was chromatographed with a mixed solvent of hexane, benzene and ethyl acetate (9 : 6 : 1) to give isomer **15** in 79% yield as crystals, mp 233–236 °C; δ 2.65 (1 H, dm, *J* 18.5), 3.26 (1 H, dd, *J* 18.5 and 7.7), 3.50 (1 H, td, *J* 2.6 and 1.1), 5.90 (1 H, ddd, *J* 11.0, 7.7 and 3.7), 6.28 (1 H, dddd, *J* 11.0, 5.1, 2.6 and 1.1), 6.82 (1 H, ddd, *J* 5.1, 2.6 and 1.1), 7.30–7.40 (4 H, m), 7.65 (1 H, dd, *J* 7.3 and 1.1), 7.74–7.81 (2 H, m) and 7.96 (1 H, dd, *J* 7.3 and 1.1); ν_{max}(KBr) 2860, 1724, 1459, 1253, 751 and 720 cm^{-1}; FAB MS (*m*/*z*, %) 335 (30), 334 (8), 307 (34), 154 (100), 137 (59), 107 (25) and 77 (17) [Found: (FAB MS): 335.1186 $(M + H)^+$. Calc. for $C_{23}H_{15}N_2O$: *m*/*z*, 335.1183].

Photoreaction of DCA and tropone 1 (DCA : 1 = 1.2 : 1) in CH_3CN–CH_2Cl_2

The photoreaction of DCA (273 mg, 1.2 mmol) and tropone **1** (106 mg, 1 mmol) in 100 ml of CH_3CN–CH_2Cl_2 was carried out in the same manner. The reaction mixture was separated by chromatography to give adducts **11** (22 mg, 12%), **12** (12 mg, 6%), **13** (48 mg, 16%), **14** (17 mg, 9%) and adduct **16** (23 mg, 13%) together with unchanged tropone **1** (48 mg).

Adduct **16**: pale yellow crystals, mp 104–106 °C; δ 1.75 (1 H, s), 5.55 (1 H, dd, *J* 10.2 and 0.5), 6.42 (1 H, ddm, *J* 10.2 and 6.0), 6.64 (1 H, ddm, *J* 11.0 and 6.8), 6.69 (1 H, ddm, *J* 11.0 and 6.0), 6.95 (1 H, d, *J* 6.8), 7.30 (1 H, td, *J* 7.5 and 1.2), 7.38 (1 H,

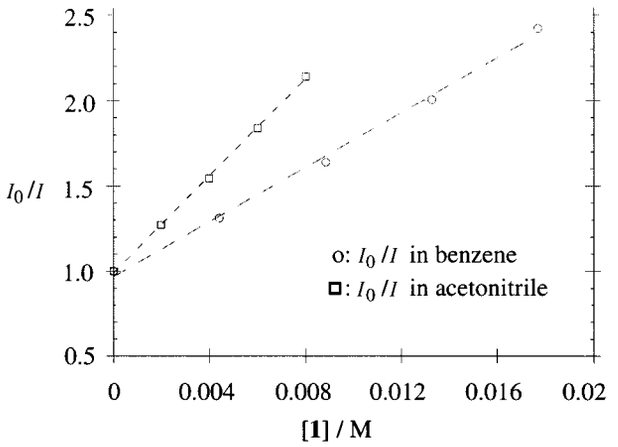


Fig. 2 Stern–Volmer plots of fluorescence quenching of DCA by tropone **1**

td, *J* 7.5 and 1.2), 7.41–7.45 (2 H, m), 7.65 (1 H, dm, *J* 7.5), 7.74–7.78 (1 H, m) and 7.82–7.86 (2 H, m); δ_C 53.2, 57.8, 74.3, 115.1, 116.0, 120.0, 122.0, 122.4, 125.0, 125.6, 128.1, 128.2, 128.3 (2 C), 128.6 (2 C), 128.9, 129.7, 133.8, 134.1, 135.6, 137.9 and 139.6; ν_{max}(KBr) 3024, 2248, 1461, 1071, 753 and 708 cm^{-1}; FAB MS (*m*/*z*, %) 334 (10), 317 (100), 154 (64), 136 (50), 107 (18) and 77 (13) [Found: C, 82.1; H, 4.45; N, 8.0%. (FAB MS): 334.1098 (M^+). Calc. for $C_{23}H_{14}N_2O$: C, 82.61; H, 4.22; N, 8.38%; *M*, 334.1105].

Photoreaction of DCA and tropone 1 in CH_3CN–CH_2Cl_2 in the presence of BP

A CH_3CN–CH_2Cl_2 solution (120 ml) contained DCA (273 mg), tropone **1** (106 mg) and BP (1.54 g, 10 mmol) was irradiated for 2 h. The reaction solution was filtered to remove unchanged DCA. The solvent was distilled off and the residue was chromatographed to give compound **16** (75 mg, 31%) and recovered substrate **1** (29 mg). Other products were polymeric materials and were not further characterized.

Photoreaction of DCA and tropone 1 in CH_3CN–CH_2Cl_2 in the presence of DMB

A CH_3CN–CH_2Cl_2 solution (120 ml) contained DCA (273 mg), tropone **1** (106 mg) and DMB (17 mg, 0.12 mmol) was irradiated for 10 h under the same conditions as those for the reaction in the absence of DMB. Products were adducts **11** (18 mg, 11%), **12** (13 mg, 8%), **13** (22 mg, 8%) and **14** (33 mg, 20%), together with unchanged tropone **1** (54 mg).

Fluorescence quenching

Fluorescence spectra and measurement of fluorescence quenching were recorded on a JSC, FP-700 spectrometer. The fluorescence quenching of DCA was measured by various concentrations of tropone **1** in CH_3CN and in benzene. The intensities at E_{ex} = 400 nm and E_{em} = 448 nm were obtained three times for each cell and an average value for each sample was used. The quenching results were analysed according to the Stern–Volmer equation and were shown in Fig. 2.

Determination of redox potentials

The oxidation potential of tropone **1** and the reduction potential of DCA were measured by CV, which was run with a three-electrode system. A platinum stick, a platinum wire and Ag/AgCl electrode were used as the working, counter and reference electrode, respectively. A cyclic voltammogram was obtained after 20 min of bubbling of N_2 into a CH_3CN solution of 0.1 M anhydrous lithium perchlorate and the compound under test.

Photoreaction of DCA and tropone 1 (DCA : 1 = 1 : 3) in benzene

A benzene solution (100 ml) of DCA (228 mg, 1 mmol) and tropone **1** (318 mg, 3 mmol) was saturated with argon and irradiated for 10 h. The reaction mixture was separated by chromatography to give compounds **11** (54 mg, 38%), **12** (23 mg, 16%), **13** (20 mg, 8%) and **14** (11 mg, 8%) together with two dimers **2** (20 mg, 11%) and **3** (34 mg, 19%) and unchanged substrate **1** (143 mg) and DCA (132 mg).

Table 4 Crystallographic data for compound **14**

Formula	$C_{23}H_{14}N_2O$
Relative molecular mass	M_r = 334.38
Crystal colour	Colourless
Crystal size/mm	0.25 × 0.15 × 0.07
Crystal system	Monoclinic
Space group	*C*2/*c*
a/Å	25.520(2)
b/Å	8.995(1)
c/Å	17.340(1)
β/deg	122.15(1)
V/Å^3	3370.1(6)
Z	8
D_{calc}/g cm^{-3}	1.318
μ/mm^{-1}	0.647
No. of reflections	2868
No. of observed reflections [$I > 2\sigma(I)$]	1761
Refined parameters	237
Refinement	F^2 (SHELXL93)
$R[F^2 > 2\sigma(F^2)]$	0.0404
$wR(F^2)$	0.1183

Photoreaction of DCA and tropone 1 (DCA : 1 = 1 : 3) in CH_3CN–CH_2Cl_2

A CH_3CN–CH_2Cl_2 solution (100 ml) of DCA (228 mg, 1 mmol) and tropone **1** (318 mg, 3 mmol) was saturated with argon and irradiated for 10 h. The reaction mixture was separated by chromatography to give adducts **11** (35 mg, 35%), **12** (11 mg, 11%), **13** (24 mg, 14%) and **14** (9 mg, 9%) together with two dimers **2** (24 mg, 17%) and **3** (14 mg, 10%) and unchanged substrate **1** (178 mg) and DCA (159 mg).

Irradiation of adduct 11 in the presence of DCA

A CH_3CN–CH_2Cl_2 solution (5 ml) of adduct **11** (4 mg) and DCA was irradiated for 7 h. The ^1H NMR spectrum showed that no reaction occurred.

Irradiation of adduct 12 in the presence of DCA

A CH_3CN–CH_2Cl_2 solution (8 ml) of adduct **12** (5 mg) and DCA was irradiated for 8 h. The ^1H NMR spectrum showed that no reaction occurred.

Attempted thermal reaction of DCA and tropone 1 in benzene

A benzene solution (10 ml) of DCA (27 mg) and tropone **1** (11 mg) was heated to 40 °C in the dark for 8 h. After removal of the solvent, the residue was dissolved in acetonitrile. The precipitate was filtered off and the filtrate was analysed by TLC and HPLC, which showed no reaction had occurred.

X-Ray crystallographic analysis of compound 14

A crystal of adduct **14** was obtained as a plate by recrystallization of the compound from a mixed solvent of benzene and CH_3CN. The measurements were made on an Enraf-Nonius FR590 diffractometer with graphite-monochromated Cu-Kα radiation (λ = 1.541 84 Å). Data were collected at a temperature of 23 ± 2 °C using the ω–2θ scan technique to a maximum 2θ-value of 129.9°. The structure was solved by a direct method (SIR92[32]), and was refined using full-matrix least squares (SHELXL93[33]) based on F^2 of all independent measured reflections. All H-atoms were located at ideal positions and were included in the refinement, but restrained to ride on the atom to which they were bonded. Isotropic thermal factors of H-atoms were held fixed to 1.2 times or 1.5 times (for the phenolic

proton) U_{eq} of the riding atoms. The crystallographic data are listed in Table 4.§

§ Full crystallographic details, excluding structure factor tables, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc.*, *Perkin Trans. 1*, available *via* the RSC Web page (http://www.rsc.org/authors). Any request to the CCDC for this material should quote the full literature citation and the reference number 207/240.

References

1 T. Mukai, T. Tezuka and Y. Akasaki, *J. Am. Chem. Soc.*, 1966, **88**, 5025.
2 A. S. Kende, *J. Am. Chem. Soc.*, 1966, **88**, 5026.
3 T. Tezuka, Y. Akasaki and T. Mukai, *Tetrahedron Lett.*, 1967, 1397.
4 T. Tezuka, Y. Akasaki and T. Mukai, *Tetrahedron Lett.*, 1967, 5003.
5 I. D. Reingold, K. S. Kwong and M. M. Menard, *J. Org. Chem.*, 1989, **54**, 708.
6 M. Cavazza, M. Zandomeneghi and F. Pietra, *J. Chem. Soc.*, *Chem. Commun.*, 1990, 1336; M. Cavazza, R. Cimiraglia, M. Persico, M. Zandomeneghi and F. Pietra, *J. Photochem. Photobiol. A*: *Chem.*, 1991, **61**, 329.
7 A. S. Kende and J. E. Lancaster, *J. Am. Chem. Soc.*, 1967, **89**, 5283.
8 T. Mukai, T. Sato, M. Takahashi and H. Mikuni, *Bull. Chem. Soc. Jpn.*, 1968, **41**, 2819.
9 T. S. Cantrell, *J. Am. Chem. Soc.*, 1971, **93**, 2540.
10 K. S. Feldman, J. H. Come, B. J. Kosmider, P. M. Smith, D. P. Rotelle and M.-J. Wu, *J. Org. Chem.*, 1989, **54**, 592.
11 S. Wu, A. Mori and H. Takeshita, *J. Chem. Soc.*, *Chem. Commun.*, 1994, 919.
12 J. Eriksen, C. S. Foote and T. L. Parker, *J. Am. Chem. Soc.*, 1977, **99**, 6455.
13 J. Eriksen and C. S. Foote, *J. Am. Chem. Soc.*, 1980, **102**, 6083.
14 K. A. Brown-Wensley, S. L. Mattes and S. Farid, *J. Am. Chem. Soc.*, 1978, **100**, 4162.
15 G. J. Kavarnos and N. J. Turro, *Chem. Rev.*, 1986, **86**, 401.
16 D. I. Schuster, J. M. Palmer and S. C. Dickerman, *J. Org. Chem.*, 1966, **31**, 4281.
17 C. S. Q. Lew and B. Capon, *J. Org. Chem.*, 1997, **62**, 5344.
18 P. Schaap. L. Lopez and S. D. Gabnon, *J. Am. Chem. Soc.*, 1983, **105**, 663.
19 J. H. Xu, J. P. He and Y. Qian, *J. Chem. Soc.*, *Chem. Commun.*, 1991, 714.
20 I. R. Gould, D. Ege, J. E. Moser and S. Farid, *J. Am. Chem. Soc.*, 1990, **112**, 4290.
21 P. G. Gassman and K. D. Olson, *J. Am. Chem. Soc.*, 1982, **104**, 3740.
22 A. J. Maroulis, Y. Shigemitsu and D. R. Arnold, *J. Am. Chem. Soc.*, 1978, **100**, 535.
23 J. Eriksen and C. S. Foote, *J. Phys. Chem.*, 1978, **82**, 2659.
24 W. R. Ware, J. D. Holms and D. R. Arnold, *J. Am. Chem. Soc.*, 1974, **96**, 7861.
25 I. R. Gould and S. Farid, *J. Am. Chem. Soc.*, 1983, **115**, 4814.
26 R. B. Woodward and R. Hoffman, *The Conservation of Orbital Symmetry*, Verlag Chemie GmbH, Weinheim, 1970, p. 126.
27 H. Prinzbach, H. Babisch and H. Fritz, *Tetrahedron Lett.*, 1976, 2129.
28 Y. Sugihara, N. Morokoshi and I. Murata, *Tetrahedron Lett.*, 1977, 3887.
29 Chem3D Plus program. Licenced from Cambridge Science Computing Inc.
30 A. P. Borg and H. Kloosterziel, *Recl. Trav. Chim. Pays-Bas*, 1963, **82**, 741.
31 P. Radlick, *J. Org. Chem.*, 1964, **29**, 960; T. Ikemi, T. Nozoe and H. Sugiyama, *Chem. Ind.*, 1960, 932; A. P. Ter Borg, R. van Helden, A. F. Bickel, W. Renold and A. S. Dreiding, *Helv. Chim. Acta*, 1960, **43**, 457.
32 M. C. Altomare, M. Burla, G. Camalli, C. Cascarano, A. Giacovazzo, G. Guagliardi and J. Polidori, *J. Appl. Crystallogr.*, 1994, **27**, 435.
33 G. M. Sheldrick, SHELXL93. Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1993.

Paper 8/03185A
Received 28*th April* 1998
Accepted 9*th July* 1998