Electron-transfer Photochemistry of Endoperoxides

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Derivatives of 1,2-dioxacyclohex-4-ene and 2,3-dioxabicyclo[2.2.2]oct-5-ene (endoperoxides, EPs) form EDA complexes with tetracyanoethylene (TCNE). The phenyl-substituted EPs **3a**, **4a**, **4b** and **6** undergo electron-transfer-induced reactions when the EDA complexes are irradiated. Two types of reactions are observed depending on the ring system. Monocyclic EPs (**3a**, **4a** and **4b**) afford furan derivatives, possibly through the Criegee-type rearrangement, and dehydration, whereas the bicyclic EP **6** undergoes cycloreversion through the C–O bond cleavage.

Endoperoxides (EPs) rank among the most important class of organic peroxides and much attention has been paid to their chemical and biochemical properties.[1] Since EPs are readily available from the photooxygenation of 1,3-dienes,[2] their synthetic applications have also been developed.[3] An intriguing property possessed by EPs is that the oxygen–oxygen bond or the carbon–oxygen bond can be readily cleaved by thermolysis or photolysis.

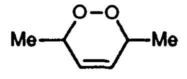
Although the thermolyses,[4] photoreactions,[5] and acid-,[6] base-,[7] or metal-catalysed[8] reactions of EPs have been extensively studied, little work has been done on their electron-transfer reactions. In this study we examined the electron-transfer photochemistry of monocyclic EPs **1**–**4** and bicyclic EPs **5** and **6**.† We have observed that these EPs form electron donor-acceptor (EDA) complexes[9] with tetracyanoethylene (TCNE), which is known to form EDA complexes with various electron donors.[9,10] The technique employed in this study is photoexcitation of the TCNE EDA complexes of the EPs.

Photoexcitation of weak EDA complexes [D, A] formed from a donor (D) and an acceptor (A) results in electron-transfer from D to A to generate ionic EDA complexes [D$^{\bullet+}$, A$^{\bullet-}$].[9] Although the back electron-transfer reaction (k_b) of the photogenerated ion pair is generally very fast,[11] reactive donors can undergo chemical reactions[12] competing with the back electron-transfer deactivation process [eqn. (1)]. We found that several EPs can serve as reactive donors and undergo electron-transfer-induced reactions.

$$\mathrm{D} + \mathrm{A} \rightleftharpoons [\mathrm{D}, \mathrm{A}] \underset{k_b}{\overset{h\nu_{CT}}{\rightleftharpoons}} [\mathrm{D}^{\bullet+}, \mathrm{A}^{\bullet-}] \longrightarrow \text{Products} \quad (1)$$

Results

The EPs examined in this study were synthesized by the photooxygenation of the corresponding dienes.[13] These diene EPs are good electron donors and form weak EDA complexes with TCNE. When a colourless solution of TCNE in dichloromethane was mixed with *cis*-3,6-dimethyl-1,2-dioxacyclohex-4-ene (**1**) or 3,3,6,6-tetramethyl-1,2-dioxacyclohex-4-ene (**2**), the solution turned faint yellow. Clear yellow colourations were observed upon similar mixing of TCNE with a phenyl-substituted EP such as 3,6-diphenyl-1,2-dioxacyclohex-4-ene (**3a**) or 3-phenyl-1,2-dioxacyclohex-4-ene (**4a**). An orange to red brown colour resulted from more strongly electron donating EPs such as **3b**–**d** and **4c**–**d**. The colour change is due to the appearance of the charge-transfer (CT) absorption bands of the EDA complexes. As shown in Fig. 1 only the tail absorptions were observed for the EDA complexes of **1** and **2**. In the case of **3a** a distinct absorption maximum was observed at 368 nm. As a whole 3,6-diaryl and 3-aryl derivatives (**3** and **4**) exhibited clear and significant CT absorption bands (Fig. 2, Table 1).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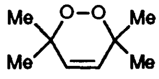
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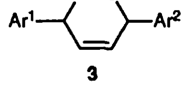
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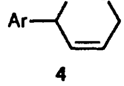
a: Ar^1 = Ar^2 = C_6H_5
b: Ar^1 = Ar^2 = 4-MeC_6H_4
c: Ar^1 = 4-$MeOC_6H_4$; Ar^2 = C_6H_5
d: Ar^1 = Ar^2 = 4-$MeOC_6H_4$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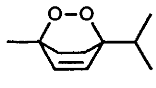
a: Ar = C_6H_5
b: Ar = 4-ClC_6H_4
c: Ar = 4-MeC_6H_4
d: Ar = 4-$MeOC_6H_4$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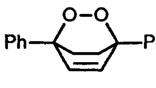
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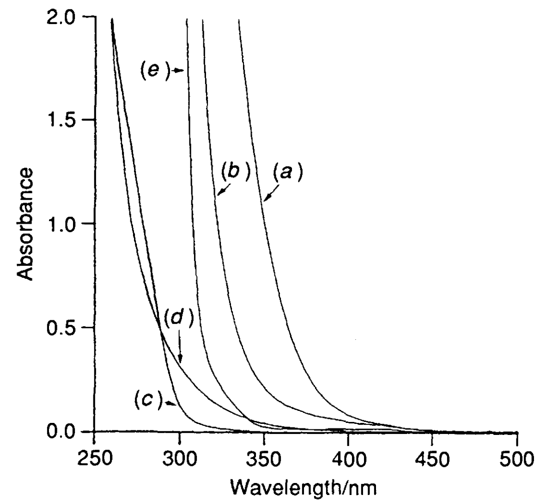

Fig. 1 The CT absorption spectra of the EDA complexes of **1** and **2** with 0.05 mol dm^{-3} of TCNE in dichloromethane: (*a*) TCNE and 0.07 mol dm^{-3} of **1**; (*b*) TCNE and 0.05 mol dm^{-3} of **2**. Also shown are the absorption spectra of the uncomplexed **1**, **2**, and TCNE [(*c*), (*d*) and (*e*), respectively].

In contrast to the monocyclic EPs **1** and **2**, bicyclic ascaridole **5** is a much better electron donor, as can be recognized by

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† We used the term 'endoperoxide' to refer to the monocyclic as well as bicyclic derivatives.

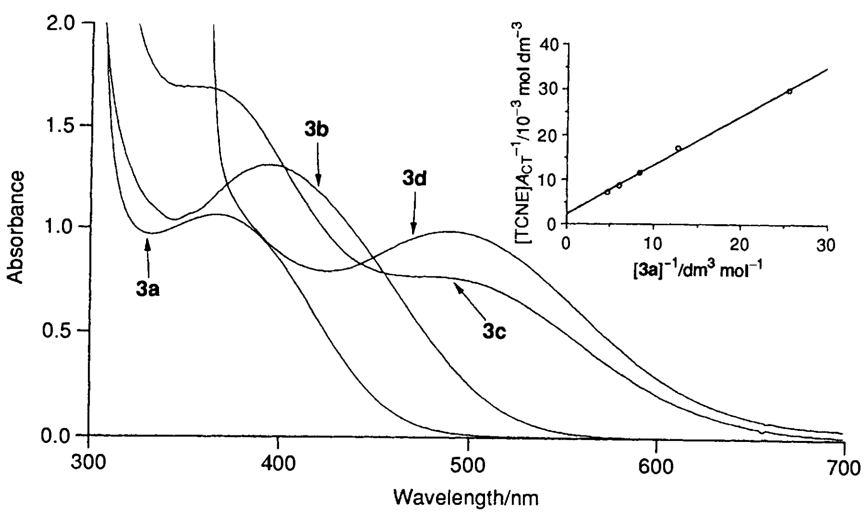


Fig. 2 The CT absorption spectra of the EDA complexes of **3a**, **3b**, **3c** and **3d** (0.03 mol dm^{-3} each) with 0.05 mol dm^{-3} of TCNE in dichloromethane. The inset is the Benesi–Hildebrand plot for **3a** monitored at 368 nm.

Table 1 Oxidation potentials (E^{ox})[a] of the EP donors and the CT absorption maxima (λ_{max})[b] of the TCNE EDA complexes

EP	E^{ox}/V *vs.* SCE	λ_{max}/nm
1	>2.5	tail[c]
2	>2.5	tail
3a	2.35	368
3b	2.12	394
3c	1.75	475, 352 sh[d]
3d	1.67	492
4a	*ca.* 2.4	375 sh
4b	*ca.* 2.4	392 sh
4c	2.14	392
4d	1.86	494
5	1.92	448
6	1.80	362 sh, 418 sh

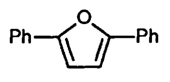
[a] Measured in acetonitrile. The values are all irreversible. [b] Measured in CH_2Cl_2. [c] Tail absorption. [d] A shoulder.

comparing their oxidation potentials. It is noteworthy that the oxidation potential of **5** is lower than those of the phenyl-substituted monocyclic EPs **3a** and **4a**. Thus the CT absorption spectrum of the ascaridole **5**–TCNE complex shown in Fig. 3 appears with a broad intense band at λ_{max} 448 nm, which is lower in energy than those of **3a** and **4a**. The CT absorption spectrum of the TCNE EDA complex of 1,4-diphenyl-2,3-dioxabicyclo[2.2.2]oct-5-ene (**6**) appears with two partially resolved bands: a shorter wavelength shoulder around 362 is due to the phenyl groups and the other shoulder around 418 nm is due to the dioxabicyclooctane skeleton. In Table 1 are summarized the observed CT absorption maxima of the EPs.

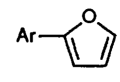
The formation constants (K) of the TCNE EDA complexes of **3a** and **5** were determined according to the spectrophotometric procedure of Benesi and Hildebrand.[14] Owing to the limited solubility of TCNE in dichloromethane, the CT absorbance A_{CT} (at the λ_{max} 368 nm for **3a**, or at the λ_{max} 448 nm for **5**) was measured with the EP donors in excess. Under these conditions the Benesi–Hildebrand relationship for the concentration dependence of A_{CT} is given in eqn. (2). As shown in the insets of Figs. 2 and 3, linear fits for the Benesi–Hildebrand plots were obtained. For **3a**, the formation constant K and the extinction coefficient ε_{CT} at 368 nm were determined to be 2.1 dm^3 mol^{-1} and 442 dm^3 mol^{-1} cm^{-1}, respectively, by linear least square analysis. For **5**, K and ε_{CT} at 448 nm were determined to be 2.3 dm^3 mol^{-1} and 628 dm^3 mol^{-1} cm^{-1}, respectively. The small K values indicate that the EDA complexes are weak.

$$\frac{[\mathrm{TCNE}]}{A_{CT}} = \frac{1}{\varepsilon_{CT}} + \frac{1}{K\varepsilon_{CT}[\mathrm{EP}]} \qquad (2)$$

Photolyses of the EDA complexes in dichloromethane solutions were performed by using a 2 kW xenon lamp with an IR-filter and a glass cut-off filter. Even after several hours of irradiation, the EDA complexes of **1**, **2**, **3b–d**, **4c–d**, and ascaridole (**5**) failed to undergo photochemical reactions. However, similar photolyses with **3a**, **4a**, **4b** and **6** resulted in net chemical transformations (Table 2). Thus, a yellow solution of **3a** and TCNE in dichloromethane gradually turned green upon photolysis and 2,5-diphenylfuran (**7a**) was obtained with recovery of TCNE. The colour change can be assigned as being due to the formation of the EDA complex between the resulting furan and the remaining TCNE. The small decrease in the yield of recovered TCNE seems to be due to a secondary reaction of TCNE with the resulting water.[15] Photoreactions with **4a** and **4b** were also accompanied by similar colour changes and resulted in the formation of 2-arylfurans **8a** and **8b**. Control experiments showed that no reaction was observed either in the dark or under irradiation without TCNE.



7a



8a: Ar = C_6H_5
b: Ar = 4-ClC_6H_4

We have also investigated the photoreactions of the EPs **9**–**14** under the CT-irradiation conditions (Table 3). Of these EPs **9** and **10** were reactive and afforded the furan derivatives **15** and **16**, whereas **11**–**13** were unreactive. In the case of **14**, which possesses a benzylic proton, the reaction proceeded and **14** was consumed significantly. However, no formation of distinct products could be observed. These results suggest that the presence of both a benzylic proton at C3 (C6) and a methine proton at C6 (C3) is essential for clean productive photoreactions. As will be discussed later, a few reaction pathways shown in Scheme 1 are conceivable for the transformation of a cation radical of EP ($EP^{\bullet +}$).

The bicyclic EP **6**, on the other hand, underwent a different type of reaction upon CT-irradiation. When a yellow solution of **6** and TCNE in dichloromethane was irradiated (λ > 390 nm), the colour gradually faded and gas evolution was observed. Analysis, followed by isolation of the photoproduct, showed that the cycloreversion reaction, as shown in eqns. (3) and (4),

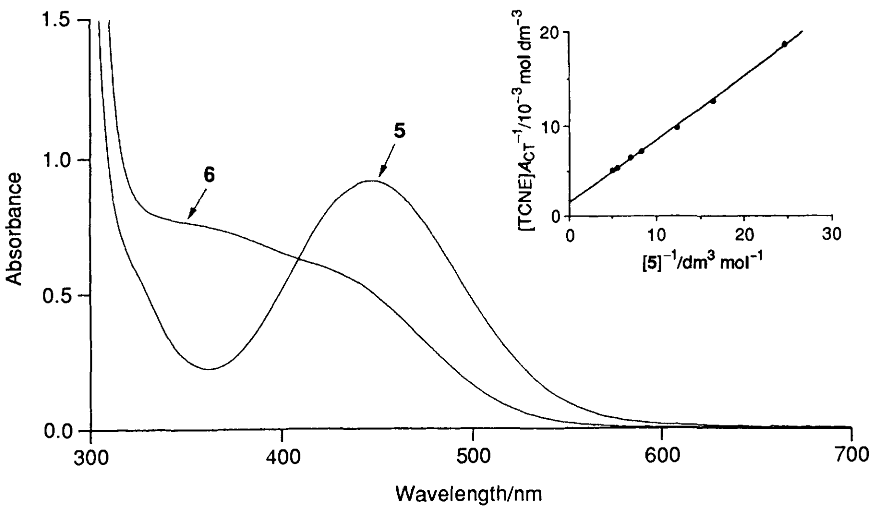
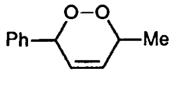


Fig. 3 The CT absorption spectra of the EDA complexes of **5** and **6** in dichloromethane: [**5**] = [TCNE] = 0.025 mol dm^{-3}; [**6**] = 0.03 mol dm^{-3} and [TCNE] = 0.05 mol dm^{-3}. The inset is the Benesi–Hildebrand plot for **5** monitored at 448 nm.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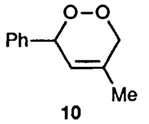
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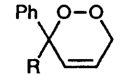
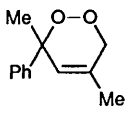

11a: R = Me
b: R = Ph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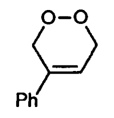
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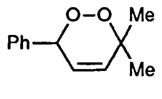
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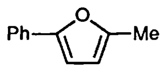
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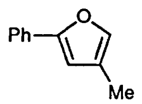
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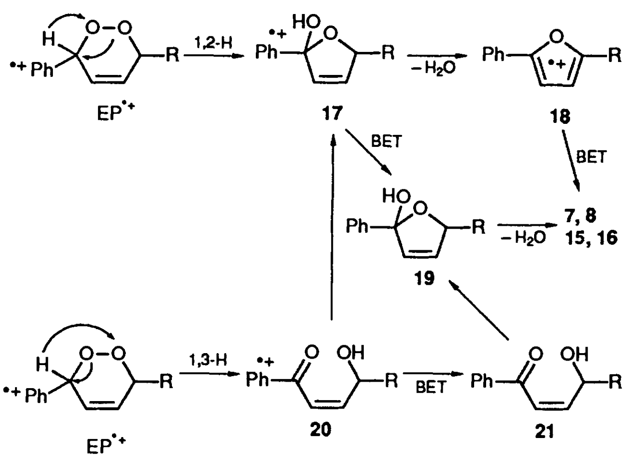
$$\text{EP} + \text{TCNE} \rightleftharpoons [\text{EP, TCNE}] \underset{k_b}{\overset{h\nu_{CT}}{\rightleftharpoons}} [\text{EP}^{\bullet+}, \text{TCNE}^{\bullet-}]$$



Scheme 1

Table 2 Photolysis of the TCNE EDA complexes of EP donors[a]

EP	λ (irradiation)/nm	t/h	Product, yield (%)	Recovery yield (%) EP	TCNE
3a	>340	2	**7a**, 25	72	86
3a	>390	4	**7a**, 36	63	82
4a	>390	4	**8a**, 16	84	98
4b	>390	4	**8b**, 21	64	89
6[b]	>390	0.5	**23**, 70	30	14
6[b,c]	>390	0.5	**23**, 46	53	52

[a] A 5 cm^3 CH_2Cl_2 solution containing an EP (5 × 10^{-2} mol dm^{-3}) and TCNE (5 × 10^{-2} mol dm^{-3}) was irradiated. [b] A 3 cm^3 CH_2Cl_2 solution containing **6** (6 × 10^{-2} mol dm^{-3}) and TCNE (6 × 10^{-2} mol dm^{-3}) was irradiated. [c] Contains tetramethylethylene (**24**) (6 × 10^{-2} mol dm^{-3}).

Table 3 Photolysis of the TCNE EDA complexes of EP donors **9**–**14**[a]

EP	λ_{max}[b]/nm	Product, yield (%)	Recovery yield (%) EP	TCNE
9	366 sh	**15**, 29	63	95
10	352 sh	**16**, 39	30	—[d]
11a	368 sh	none	100	99
11b	379	none	99	95
12	361 sh	none	97	98
13	478, 388	none	98	—[d]
14[c]	367 sh	none	70	60

[a] A 3 cm^3 CH_2Cl_2 solution of an EP (6 × 10^{-2} mol dm^{-3}) and TCNE (6 × 10^{-2} mol dm^{-3}) was irradiated for 2 h (λ > 340 nm). [b] CT absorption maxima of the EDA complexes. [c] Irradiated for 6 h. [d] Not determined.

occurred to give molecular oxygen and diene **22**, which was obtained as the TCNE adduct **23** in 70% yield with 30% recovery of **6** (Table 2). It is interesting to examine the spin multiplicity of the evolved oxygen. Since CT-irradiation of the EDA complex of **6** would generate a singlet ion radical pair [$\mathbf{6}^{\bullet+}$, $\text{TCNE}^{\bullet-}$], singlet oxygen ($^1O_2$) may be generated from $\mathbf{6}^{\bullet+}$ by a concerted fission of the C–O bonds. If $^1O_2$ is formed, it can be trapped by a suitable trapping reagent. Thus we carried out the reaction in the presence of tetramethylethylene **24**, which is known as a good $^1O_2$ acceptor ($k = 2.4 \times 10^7$ dm^3 mol^{-1})^{16} and reacts with $^1O_2$ to give hydroperoxide **25** [eqn. (5)]. However, no formation of hydroperoxide **25** was observed while the retro-Diels–Alder reaction proceeded normally (Table 2).*

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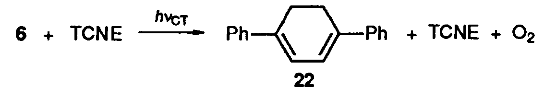
* The reaction in the presence of tetramethylethylene (**24**) is slower since **24** also forms an EDA complex with TCNE and some fraction of the incident light is absorbed by the complex, whose $\lambda_{max\,CT}$ is 538 nm and K is 0.079 dm^3 mol^{-1}.

The result suggests that the oxygen extrusion may proceed in a stepwise manner. A possible mechanism for the photoreaction of **6** is shown in Scheme 2. No formation of $^1O_2$ suggests that an efficient intersystem crossing process should occur in an intermediate state such as the primary ion radical pair [$6^{\bullet+}$, TCNE$^{\bullet-}$], the secondary ion radical pair [**26**, TCNE$^{\bullet-}$], or biradical **27**. If the intersystem crossing of the initially formed ion radical pair [$6^{\bullet+}$, TCNE$^{\bullet-}$] is efficient, triplet excited **6** may be generated and the triplet state reaction could be involved.



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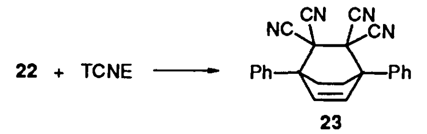

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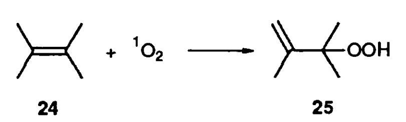

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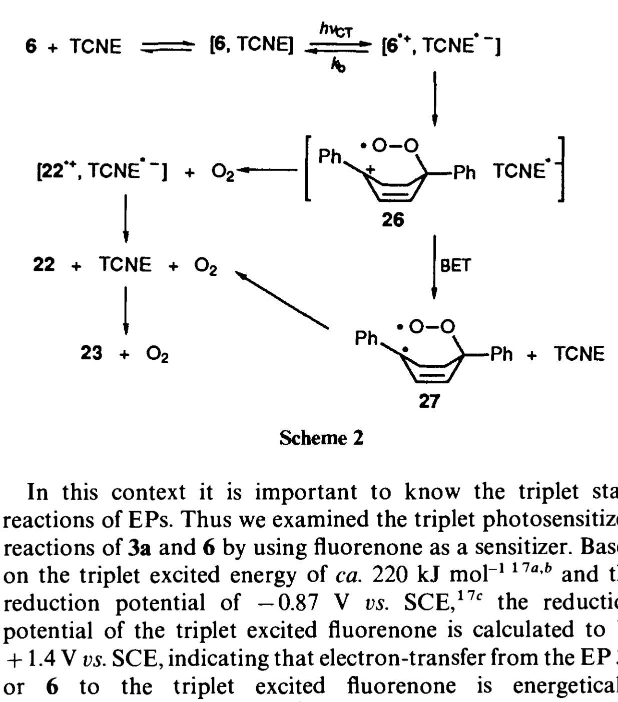

Scheme 2

In this context it is important to know the triplet state reactions of EPs. Thus we examined the triplet photosensitized reactions of **3a** and **6** by using fluorenone as a sensitizer. Based on the triplet excited energy of *ca.* 220 kJ mol^{-1} [17a,b] and the reduction potential of -0.87 V *vs.* SCE,[17c] the reduction potential of the triplet excited fluorenone is calculated to be $+1.4$ V *vs.* SCE, indicating that electron-transfer from the EP **3a** or **6** to the triplet excited fluorenone is energetically unfavourable. When a 3 cm^3 dichloromethane solution of **3a** (0.185 mmol) was irradiated with fluorenone (0.02 mmol) for 1 h ($\lambda > 340$ nm), diepoxide **30** was obtained in 8% yield with the concomitant formation of furan **7a** in 10% and the recovery of **3a** in 72% yield. It is significant that the diepoxide was formed in substantial yield in the triplet photosensitized reaction. Analogous sensitized photolysis of EP **6** for 1 h ($\lambda > 390$ nm) produced diepoxide **31** in 98% yield. The exclusive formation of diepoxide **31** by the triplet sensitized photolysis of **6** stands in sharp contrast to the cycloreversion reaction induced by the CT-irradiation. These results strongly suggest that the triplet excited state of **3a** or **6** is not involved in the CT-photoreactions. The triplet state reactions can best be explained by the direct cleavage of the O–O bond of EPs as shown in eqns. (6) and (7).

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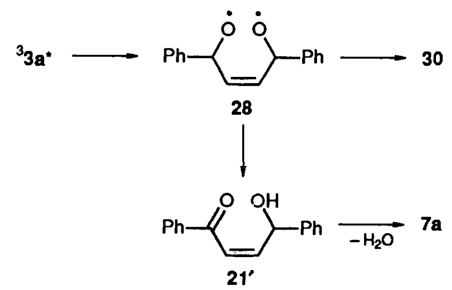

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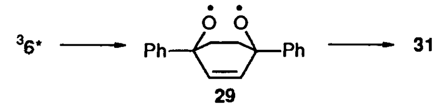

(7)

Discussion

TCNE, a typical electron acceptor, is known to form EDA complexes with a wide variety of electron donors.[9,10] Formation of the EDA complexes is often associated with colour changes, which are easily discernible by the appearance of new absorption bands on the electronic absorption spectra. The EPs examined in this study also form EDA complexes with TCNE in solution and the new CT absorption bands were observed. The CT absorptions can be assigned as being due to the electronic transitions from high-lying occupied molecular orbitals of the EP donors to the lowest unoccupied molecular orbital (LUMO) of TCNE. Accordingly the electron-transfer from the EP donors to TCNE can occur upon photoirradiation of the EDA complexes.

As shown in Figs. 1, 2 and 3, the shape and the maxima of the CT absorption bands vary with the structure of EPs and the attachment of aryl-substituent(s). The absorption maxima of the EDA complexes of **1** and **2** were obscured by the tail absorptions of the uncomplexed EPs and TCNE. On the other hand the CT absorption spectrum of the ascaridole (**5**)–TCNE complex shown in Fig. 3 appears with a broad intense band at λ_{max} 448 nm. It is important to note that these three EPs possess only alkyl substituents. The difference in appearance of the spectra is due to the difference in the electron donating ability between dioxacyclohexenes (**1** and **2**) and ascaridole (**5**) as qualitatively indicated by their oxidation potentials (Table 1). The degree of electron donating ability of EPs is dependent on their structure, as discussed below.

Organic peroxides have several high-lying occupied molecular orbitals owing to the atomic p-orbitals around the O–O bond.[18] Antisymmetric combinations of the orbitals result in the highest occupied molecular orbital (HOMO) and the next (NHOMO) being designated as π_- and n_-, respectively,* while the symmetric combination leads to inner MOs such as π_+ and n_+. Photoelectron spectroscopic (PES) studies, in conjunction with theoretical studies, have shown that the energy levels are dependent on the dihedral angle θ around the peroxide bond (C–O–O–C).[18d,f] For example, dioxabicycloalkanes having θ of nearly 0 possess lower ionization potentials[18c,d,f] and can even be oxidized electrochemically to the corresponding cation radicals.[19]

In the case of an EP derived from a 1,3-diene, the double bond may function as an additional electron donating site. Ionization potentials (E_i) of certain diene EPs have been determined by PES.[18c,20] Tanimoto and co-workers studied microwave

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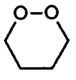
* The orbital designation is according to Gleiter.[18f] According to Salomon *et al.*[18d] the HOMO and the NHOMO are symbolized as n_o^- and σ^-, respectively.

spectroscopy and PES of 1,2-dioxacyclohex-4-ene (**32**). They reported that its dihedral angle is 80° and the vertical ionizations occur at 9.66 eV and 10.37 eV.[20] Based on the dihedral angle of 80° and the theoretical calculations, they concluded that π_- and π_+ are the two upper MOs around the peroxide bond, and the ionization occurs at 10.37 eV from both of them since they are almost degenerate. Ionization from the double bond occurs at 9.66 eV. The assignment is in accord with the observation that the ionization of dioxacyclohexane **33** occurs at 10.0 and 10.2 eV.[18d] In the case of ascaridole (**5**), it can be expected that the orbital derived from an antisymmetric combination (π_-) would be significantly destabilized since its dihedral angle is 0°. Indeed the HOMO has been assigned to an orbital derived from an anti-bonding combination of p-orbitals around the O–O bond (π_-) and the ionization from π_- occurs at 8.42 eV whereas ionization from the double bond occurs at 10.71 eV.[18c]

32

10.37 eV
9.66 eV (C=C)



33

10.0, 10.2 eV

Although the E_i data for **1** and **2** are not available, it seems reasonable that their HOMOs are localized on the double bonds, and that the peroxide MOs are subjacent as is the case for **32**. Accordingly we assign the tail absorptions of the EDA complexes **1** and **2** as being mainly due to the electronic transitions from the double bonds to TCNE. While these electronic transitions would produce cation radicals ($\mathbf{1}^{\cdot+}$ and $\mathbf{2}^{\cdot+}$), whose spin and charge are localized on the double bonds, they may not be reactive enough to compete with the back electron-transfer deactivation since we did not observe any photochemical transformation.

Based on the PES data for **5**, the CT absorption of **5** at λ_{max} 448 nm can be attributed to the electronic transition from the π_- orbital to the LUMO of TCNE. Despite the intense CT absorption band of the **5**–TCNE complex, no appreciable photoreaction was observed and **5** and TCNE were recovered when the CT band was irradiated with visible light (λ > 390 nm). This is not surprising since electron-transfer from the HOMO (π_-) of **5** to the LUMO of TCNE attendant upon CT-photolysis would not result in a considerable decrease in the O–O bond strength since it is antibonding in character.

For the series of monoaryl- and diaryl-dioxacyclohexenes **3** and **4**, the CT absorptions were progressively red-shifted with increasing electron donating ability of the aryl substituent(s) as shown in Fig. 2 and Table 1, which is in accord with the decreasing order of E_i for chlorobenzene (9.31 eV),[21] benzene (9.25 eV,[22] 9.23 eV[23]), toluene (9.0 eV,[22] 8.85 eV[23]) and anisole (8.39 eV,[24] 8.54 eV[21]). Although electron-transfer from an aryl group is possible in these cases, the phenyl- or 4-chlorophenyl-substituted dioxacyclohexenes **3a**, **4a** and **4b** turned out to be reactive upon electron-transfer and furan derivatives were produced whereas the 4-methylphenyl or 4-methoxyphenyl derivatives **3b–d** and **4c–d** were unreactive. It is known that arene cation radicals undergo deprotonation at the benzylic positions.[25] For instance, cation radicals of toluene and xylene are relatively strong acids. The acidity is dependent on the electron donating ability of the parent arenes. Less electron donating arenes can be stronger acids upon electron detachment. Thus phenyl or 4-chlorophenyl derivatives can be activated upon CT-excitation and the proton transfer reaction can proceed, competing with the back electron-transfer. On the other hand cation radicals from 4-methyl or 4-methoxy derivatives are expected to be much less acidic and the proton transfer reaction would not compete with the fast back electron transfer. It is also known that the lifetime of an ion radical pair generated by photoexcitation of an EDA complex is dependent on the ion pair energy gap for the back electron-transfer and that the lifetime is shorter when the gap is smaller.[11c,d,e,g] For example, the lifetime for the benzene–TCNE system is 100–200 ps whereas those for the toluene- and xylene–TCNE systems have upper limits of 100 ps and 50 ps, respectively.[11f] Thus faster back electron-transfer rates are expected for the 4-methyl or 4-methoxy derivatives, and prevent them from chemical reactions.

As mentioned before, there are a few possibilities as to the mechanism for the formation of furans (Scheme 1). We presume at this stage that the ion radical reactions may proceed within the solvent cage since we could not detect any free transient species by nanosecond laser flash photolysis. The initial involvement of the 1,2-proton transfer for the Criegee type reorganization of $EP^{\cdot+}$ to **17** appears to be more economical than the longer range 1,3-proton transfer and seems to be in accord with the least motion principle. Dehydration of **17** to give furan cation radical **18** and sequential back electron-transfer from $TCNE^{\cdot-}$ would afford furans.* Similar facile dehydration was also observed in the mass spectrometry of **3** and **4**, which showed consistent strong peaks due to the dehydrating fragmentation of the molecular ion peaks.

In acid-catalysed reactions of EPs, hemiketals and keto-alcohols such as **19** and **21** have been postulated as precursors to furans.[1b] In the present case it may also be possible that **19** and **21** are produced from **17** and **20**, respectively, through the back electron-transfer processes (BET). We expected that in the case of EP **14** the two methyl substituents would prohibit the otherwise possible dehydration to form a furan so that the corresponding hemiketal and/or ketoalcohol might be detected. Unfortunately it was not successful.

It is interesting that the bicyclic EP **6** reacted in a different way. As shown in Fig. 3, the CT absorption spectrum of **6** appears with two shoulders around 362 nm and 418 nm. The longer wavelength shoulder corresponds to electronic transition from π_- around the peroxide bond and the shorter wavelength shoulder can be attributed to electronic transition from the phenyl group. This assignment is supported by the E_i values and the CT absorption maxima of ascaridole (8.42 eV, 448 nm) and of benzene (9.25 eV, 380 nm). Since the dihedral angle of the peroxide bond is 0°, as in the case for ascaridole (**5**), electron-transfer from the peroxide MO (π_-) does not seem to be responsible for the reaction. However, electron-transfer from the phenyl group to TCNE is also possible by the photo-irradiation and it would be effective. The observed cycloreversion can be explained as a consequence of the orbital interaction between the singly occupied π-orbital localized on the phenyl group and the C–O σ-bond in the cation radical state $\mathbf{6}^{\cdot+}$. Since $^1O_2$ is not produced by the CT-photoreaction of **6**, the reaction sequence can be described by a stepwise mechanism as shown in Scheme 2. Efficient intersystem crossing may occur in the intermediate state(s) such as the secondary ion radical pair [**26**, $TCNE^{\cdot-}$], and/or diradical **27**. It is unlikely that the intersystem crossing of the initially formed ion radical pair [$\mathbf{6}^{\cdot+}$, $TCNE^{\cdot-}$] is efficient and leads to generation of the triplet excited **6** since we have confirmed that the triplet sensitized reaction of **6** results in the formation of diepoxide **31** instead of the cycloreversion.

While production of a locally excited triplet state by photoexcitation of a TCNE EDA complex is less obvious,† a singlet

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* Proton transfer from $EP^{\cdot+}$ to $TCNE^{\cdot-}$ is also plausible. The O–O bond fission of the resulting benzyl-type radical followed by $H^{\cdot}$ transfer from $TCNEH^{\cdot}$ would afford **20** as a precursor for a furan.

† EDA complexes from weaker acceptors such as tetracyanobenzene[26a,b] or fumaronitrile[26c,e] are known to produce locally excited triplet states when optically excited. See ref. 26.

exciplex generated by diffusional quenching may produce a triplet excited state through intersystem crossing.[27] Relevant to this is the photosensitized reaction of rubrene EP reported by Stevens and Liu.[28] They found that the cycloreversion of rubrene EP can be sensitized by 9,10-dicyanoanthracene or chloranil as a sensitizer. Based on the photokinetic studies and magnetic field effect, they proposed a mechanism involving a triplet excited state (π_{oo}*, σ_{co}*) of rubrene EP which was generated by triplet recombination of the photo-generated ion pairs.† Generally the triplet state reactions of EPs seems to proceed *via* the (π_{oo}*, σ_{oo}*) state to give O–O cleavage products. Indeed we did observe that the O–O bond cleavage is characteristic of the triplet state reactions of diene EPs such as **3a** and **6**. In this respect the involvement of the specific triplet state (π_{oo}*, σ_{co}*) proposed by Stevens and Liu is interesting since it may be akin to the diradical **27** in Scheme 2.

We expect that further studies with not only diene EPs but also arene EPs will reveal additional features of the structure–reactivity relationship for the electron-transfer reactions and the triplet state reactions.

Conclusions

Although relatively weak, EPs possess electron donating ability and can form EDA complexes with TCNE. Photoexcitation of the TCNE EDA complexes is a useful method for electron-transfer reactions of EPs. This exploratory study has shown an intriguing facet of the reactivities of EPs in a cation radical manifold. Regardless of the ring system, *i.e.* monocyclic or bicyclic, cation radicals of the alkyl-substituted EPs such as **1**, **2** and **5**, are not reactive enough to compete with the back electron-transfer deactivations. On the other hand the phenyl-substituted EPs **3a**, **4a**, **4b** and **6** are reactive upon CT-irradiation and two types of reactions were observed depending on the ring system. The monocyclic EPs **3a**, **4a** and **4b** afford furan derivatives while the bicyclic EP **6** undergoes the cycloreversion reaction. In these cases, electron-transfer from the phenyl rings results in active cation radicals, in which spin and charge are localized on the phenyl rings. The orbital interaction between the phenyl SOMO and the C–H σ-bond is favoured in the monocyclic systems **3a**, **4a** and **4b** while that with the C–O σ-bond plays a key role in the bicyclic EP **6**.

Experimental

General.—Melting points were determined on a Yamato MP-21 apparatus and are uncorrected. IR spectra were measured on a Shimadzu IR-435 spectrometer. Electronic spectra were measured on a Hewlett-Packard HP 8452 diode array spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Varian XL-200 spectrometer operating at 200 MHz for ^{1}H and 50 MHz for ^{13}C. A Varian EM-390 spectrometer was also used for ^{1}H NMR measurement (90 MHz). ^{1}H Chemical shifts are reported in ppm downfield from a TMS internal standard. *J* values are in Hz. ^{13}C chemical shifts in ppm are based on the $CDCl_3$ resonance (77.0 ppm). Cyclic voltammetric measurements were carried out in acetonitrile with 0.1 mol dm^{-3} tetraethylammonium perchlorate as a supporting electrolyte and SCE as a reference electrode by using a Yanagimoto P-1000 voltammetric analyser equipped with a function generator. Mass spectra were measured on a Hitachi M-52 or Hitachi M-2500S spectrometer. TCNE was purchased from Wako Chemical Co. and purified by sublimation. Commercially available spectroscopic grade dichloromethane was distilled over calcium hydride prior to use. Photolyses were carried out by using a 2 kW xenon lamp with a water IR-filter and a glass cut-off filter.

Syntheses of the Endoperoxides.—As summarized in Table 4, the EPs, **1**–**6** and **9**–**14**, were synthesized by the photooxygenation of the corresponding dienes according to analogous procedures as reported in the literature. Typically, a CCl_4 solution containing a diene and 0.01 mmol of a sensitizer (tetraphenylporphine, TPP or rose bengal, RB) was irradiated at 15 °C by using a 2 kW xenon lamp with a Toshiba Y-50 glass filter (λ > 490 nm) while the solution was agitated with a slow stream of oxygen. After irradiation the solvent was removed and the resulting photolysate was chromatographed on a silica gel column (at low temperature, if necessary) eluted with hexane containing an appropriate amount of dichloromethane or diethyl ether. If necessary, florisil was also used to separate an EP from TPP. The resulting EP was purified by recrystallization at lower temperature or bulb-to-bulb vacuum distillation.

cis-3,6-Dimethyl-1,2-dioxacyclohex-4-ene (**1**), colourless oil.[13a,b,c] δ_H(200 MHz, $CDCl_3$) 1.29 (6 H, d, *J* 6.2, CH_3), 4.61 (2 H, q, *J* 6.2, H-3,6), 5.85 (2 H, s, H-4,5). δ_C(50 MHz, $CDCl_3$) 18.5 (2 C, CH_3), 74.3, (2 C, C-3,6), 128.6 (2 C, C-4,5). ν_{max}(neat)/cm^{-1} 3030, 2980, 2920, 2860, 1443, 1366, 1081, 1035, 718.

3,3,6,6-Tetramethyl-1,2-dioxacyclohex-4-ene (**2**), colourless prisms (from CH_2Cl_2–MeOH), m.p. 56–58 °C (lit.[13d] 57–58 °C).

cis-3,6-Diphenyl-1,2-dioxacyclohex-4-ene (**3a**), colourless needles (from EtOH), m.p. 80–81 °C (lit.[13f] 81–82 °C). δ_C(50 MHz, $CDCl_3$) 80.2 (2 C, C-3,6), 127.4 (2 C, C-4,5), 128.4 (4 C, phenyl C-3,5 or C-2,6), 128.6 (4 C, phenyl C-2,6 or C-3,5), 128.7 (2 C, phenyl C-4), 137.7 (2 C, phenyl C-1). *m/z* (25 eV) 238 (M^+, 10%), 220 ($M^+ - H_2O$, 100), 206 ($M^+ - O_2$, 28), 191 (15), 180 (11), 133 (36), 131 (18), 115 (40), 105 (93).

cis-3,6-Bis(4-methylphenyl)-1,2-dioxacyclohex-4-ene (**3b**), colourless plates (from CH_2Cl_2–hexane), m.p. 62–63 °C. δ_H(200 MHz, $CDCl_3$) 2.34 (6 H, s, CH_3), 5.59 (2 H, br s, H-3,6), 6.28 (2 H, br s, H-4,5), 7.17 (4 H, AA′BB′, *J* 8), 7.33 (4 H, AA′BB′, *J* 8). δ_C(50 MHz, $CDCl_3$) 21.2 (2 C, CH_3), 80.0 (2 C, C-3,6), 127.4 (2 C, C-4,5), 128.5 (4 C, tolyl C-2,6), 129.2 (4 C, tolyl C-3,5), 134.8 (2 C, tolyl C-1), 138.6 (2 C, tolyl C-4). ν_{max}(KBr)/cm^{-1} 3040, 2920, 2900, 2860, 1612, 1515, 1300, 1246, 1180, 1113, 1061, 1003, 946, 902, 819, 766, 539, 514. *m/z* (70 eV) 266 (M^+, 6%), 249 ($M^+ - OH$, 22), 248 ($M^+ - H_2O$, 100), 234 ($M^+ - O_2$, 29), 219 (14), 208 (12), 131 (17), 119 ($CH_3C_6H_4CO^+$, 58), 105 (16), 91 ($CH_3C_6H_4{}^+$, 39). Although the ^{1}H NMR analysis showed that **3b** was pure, the elemental analysis for carbon was not satisfactory (Found: C, 79.7; H, 6.85. Calc. for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81%).

cis-3-(4-Methoxyphenyl)-6-phenyl-1,2-dioxacyclohex-4-ene (**3c**), colourless prisms (from CH_2Cl_2–hexane), m.p. 60–61 °C. δ_H(200 MHz, $CDCl_3$) 3.80 (3 H, s, OCH_3), 5.60 (2 H, br s, H-3,6), 6.22–6.38 (2 H, m, H-4,5), 6.85–7.49 (9 H, m). δ_H(50 MHz, $CDCl_3$) 55.3 (CH_3O), 79.8 (C-3), 80.1 (C-6), 114.0 (2 C, anisyl C-3,5), 127.3 (C-5), 127.6 (C-4), 128.4 (2 C, phenyl C-3,5 or C-2,6), 128.5 (2 C, phenyl C-2,6 or C-3,5), 128.6 (phenyl C-4), 129.6 (anisyl C-1), 130.0 (2 C, anisyl C-2,6), 138.0 (phenyl C-1), 160.1 (anisyl C-4). ν_{max}(KBr)/cm^{-1} 3040, 2850, 1610, 1514, 1452, 1274, 1250, 1170, 1067, 1025, 921, 823, 746, 695, 558. *m/z* (70 eV) 268 (M^+, 15%), 251 ($M^+ - OH$, 19), 250 ($M^+ - H_2O$, 100), 236 ($M^+ - O_2$, 80), 235 ($M^+ - O_2H$, 61), 144 (21), 135 ($CH_3OC_6H_4CO^+$, 82), 121 (26), 115 (26), 105 ($C_6H_5CO^+$, 30), 91 (15), 77 ($C_6H_5{}^+$, 57). Although the ^{1}H NMR analysis showed that **3c** was pure, the elemental analysis for carbon was not satisfactory (Found: C, 75.55; H, 6.15. Calc. for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01%).

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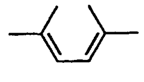
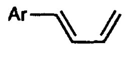
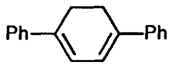
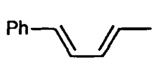
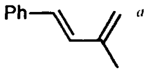
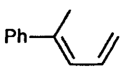
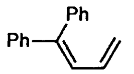
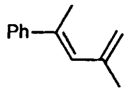
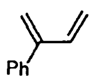
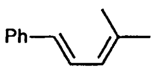
† It is not clear whether Stevens and Liu observed the other products due to the O–O bond cleavage which may more possibly occur through the other triplet state (π_{oo}*, σ_{oo}*) in addition to the proposed triplet cycloreversion (C–O bond cleavage) through the (π_{oo}*, σ_{co}*) state.

Table 4 Synthesis of EPs by photooxygenation of dienes

Diene	(mmol)	Sensitizer	Solvent (cm^3)	Irrad. time/h	EP yield (%)	Ref.
	(9.01)	TPP	CCl_4 (30)	6	**1** 53	13*a*,*b*,*c*
	(30.0)	RB	MeOH (30)	3	**2** 2	13*d*,*e*
						
a: (Ph, Ph)	(3.97)	TPP	CCl_4 (20)	2	**3a** 75	13*b*,*f*,*g*
b: (4-MePh, 4-MePh)	(1.99)	TPP	CCl_4 (10)	3	**3b** 69	
c: (4-MeO-Ph, Ph)	(0.948)	TPP	CCl_4 (20)	1	**3c** 78	
d: (4-MeOPh, 4-MeOPh)	(2.01)	TPP	CCl_4 (20)	10	**3d** 59	13*g*
						
a: (C_6H_5)	(20.0)	TPP	CCl_4 (100)	8	**4a** 57	13*b*
b: (4-ClC_6H_4)[a]	(4.00)	TPP	CCl_4 (20)	4	**4b** 40	
c: (4-MeC_6H_4)[a]	(2.00)	TPP	CCl_4 (10)	6	**4c** 51	
d: (4-$MeOC_6H_4$)[a]	(4.00)	TPP	CCl_4 (20)	6	**4d** 34	
α-Terpinene	(22.0)	RB	MeOH (70)	5	**5** 90	13*h*
	(2.80)	TPP	CCl_4 (100)	1	**6** 74	13*i*
 [a]	(4.04)	RB	CCl_4 (20)[b]	6.5	**9** 48	13*b*
 [a]	(0.971)	TPP	CCl_4 (5)	1.5	**10** 54	
	(6.04)	TPP	CCl_4 (30)	4	**11a** 18	
	(1.60)	TPP	CCl_4 (24)	12	**11b** 35	
	(2.04)	TPP	CCl_4 (10)	1.3	**12** 89	13*b*
	(10.0)	RB	CH_2Cl_2 (20)[b]	8.5	**13** 27	13*b*
	(5.05)	TPP	CCl_4 (60)	4.5	**14** 30	8*e*, 13*b*

[a] A mixture of *cis*- and *trans*-isomer (*ca.* 1:1) was used. The *cis*-isomer was recovered. [b] Contains 5% MeOH (v/v).

cis-3,6-Bis(4-methoxyphenyl)-1,2-dioxacyclohex-4-ene (**3d**), colourless needles (from CH_2Cl_2–EtOH), m.p. 80–82 °C. δ_H(200 MHz, $CDCl_3$) 3.80 (6 H, s, OCH_3), 5.57 (2 H, br s, H-3,6), 6.28 (2 H, br s, H-4,5), 6.90 (4 H, AA′BB′, *J* 8.7), 7.37 (4 H, AA′BB′, *J* 8.7). δ_C(50 MHz, $CDCl_3$) 55.3 (2 C, CH_3O), 79.7 (2 C, C-3,6), 114.0 (4 C, anisyl C-3), 127.6 (2 C, C-4,5), 129.9 (2 C, anisyl C-1), 130.0 (4 C, anisyl C-2), 160.0 (2 C, anisyl C-4). ν_{max}(KBr)/cm^{-1} 3010, 2970, 2890, 2830, 1608, 1512, 1242, 1173, 1020, 901, 827. *m*/*z* (13.5 eV: 298 (M^+, 4%), 280 ($M^+ - H_2O$, 100) (Found: C, 72.45; H, 6.15. Calc. for $C_{18}H_{18}O_4$: C, 72.47; H, 6.08%).

3-Phenyl-1,2-dioxacyclohex-4-ene (**4a**), colourless oil.[13b] δ_H(200 MHz, $CDCl_3$) 4.57 (1 H, m, H-6), 4.75 (1 H, m, H-6), 5.62 (1 H, m, H-3), 6.06–6.22 (2 H, m, H-4,5), 7.32–7.43 (5 H, m, phenyl). δ_C(50 MHz, $CDCl_3$) 69.8 (C-6), 80.6 (C-3), 124.8 (C-5), 126.9 (C-4), 128.5 (4 C, phenyl C-2,3,5,6), 128.8 (phenyl C-4), 137.1 (phenyl C-1). *m*/*z* (70 eV) 162 (M^+, 7%), 160 ($M^+ - 2$ H, 33), 144 ($M^+ - H_2O$, 45), 130 ($M^+ - O_2$, 8), 115 (51), 105 ($C_6H_5CO^+$, 100), 77 ($C_6H_5^+$, 69).

3-(4-Chlorophenyl)-1,2-dioxacyclohex-4-ene (**4b**), colourless leaflets (from hexane), m.p. 61–62 °C. δ_H(200 MHz, $CDCl_3$) 4.61 (1 H, dddd, *J* 16.6, 2.8, 2.2, 1.6, H-6), 4.72 (1 H, dddd, *J* 16.6, 2.6, 2.2, 1.8, H-6), 5.57 (1 H, dddd, *J* 2.2, 2.2, 2.2, 2.2, H-3), 6.08 (1 H, dddd, *J* 10.2, 2.2, 1.8, 1.6, H-5), 6.19 (1 H, dddd, *J* 10.2, 2.8, 2.6, 2.2, H-4), 7.33 (4 H, br s, aryl). δ_C(50 MHz, $CDCl_3$) 69.9 (C-6), 79.8 (C-3), 125.2 (C-5), 126.4 (C-4), 128.7 (2 C, aryl C-3,5), 129.9 (2 C, aryl C-2,6), 134.8 (aryl C-4 or C-1), 135.8 (aryl C-1 or C-4). ν_{max}(KBr)/cm^{-1} 3050, 2890, 2820, 1599, 1495, 1415, 1383, 1086, 1057, 1031, 1017, 994, 931, 884, 837, 821, 801, 792, 638, 523. *m*/*z* (70 eV): 198 ($M^+ + 2$, 1%), 196 (M^+, 11), 194 ($M^+ - 2$ H, 25), 180 (18), 178 ($M^+ - H_2O$, 35), 164 ($M^+ - O_2$, 6), 159 (15), 151 (18), 149 (17), 141 (32), 140 (15), 139 ($^{35}ClC_6H_4CO^+$, 100), 115 (39), 113 (18), 111 ($^{35}ClC_6H_4^+$, 42), 75 (43).

3-(4-Methylphenyl)-1,2-dioxacyclohex-4-ene (**4c**), colourless oil. δ_H(200 MHz, $CDCl_3$) 2.35 (s, 3 H, CH_3), 4.55 (1 H, dddd, *J* 16.0, 2.6, 2.4, 1.8, H-6), 4.76 (1 H, dddd, 16.0, 3.0, 2.4, 1.8, H-6), 5.60 (1 H, dddd, *J* 2.4, 2.4, 2.0, 1.8, H-3), 6.09 (1 H, dddd, *J* 10.4, 1.8, 1.8, 1.8, H-5), 6.16 (1 H, dddd, *J* 10.4, 3.0, 2.6, 2.0, H-4), 7.17 (2 H, AA′BB′, *J* 8.2), 7.27 (2 H, AA′BB′, *J* 8.2). δ_C(50 MHz, $CDCl_3$) 21.2 (CH_3), 69.9 (C-6), 80.5 (C-3), 124.7 (C-5), 127.1 (C-4), 128.5 (2 C, tolyl C-2,6), 129.2 (2 C, tolyl C-3,5), 134.1 (tolyl C-1), 138.8 (tolyl C-4). ν_{max}(neat)/cm^{-1} 3040, 3020, 2880, 1615, 1513, 1058, 1033, 994, 930, 882, 815, 792, 768, 656, 604. *m/z* (70 eV) 176 (M^+, 7%), 174 ($M^+ - 2$ H, 33), 158 ($M^+ - H_2O$, 66), 144 ($M^+ - O_2$, 9), 131 (29), 129 (41), 119 ($CH_3C_6H_4CO^+$, 100), 115 (28), 91 ($CH_3C_6H_4{}^+$, 66).

3-(4-Methoxyphenyl)-1,2-dioxacyclohex-4-ene (**4d**), colourless leaflets (from CH_2Cl_2–hexane), m.p. 46 °C. δ_H(200 MHz, $CDCl_3$) 3.80 (3 H, s, OCH_3), 4.55 (1 H, dddd, *J* 16.5, 2.8, 2.2, 1.6, H-6), 4.77 (1 H, dddd, *J* 16.5, 3.0, 2.2, 2.0, H-6), 5.59 (1 H, dddd, *J* 2.2, 2.2, 2.2, 2.2, H-3), 6.08 (1 H, dddd, *J* 10.2, 2.2, 2.0, 1.6, H-5), 6.17 (1 H, dddd, *J* 10.2, 3.0, 2.8, 2.2, H-4), 6.89 (2 H, AA′BB′, *J* 8.9), 7.31 (2 H, AA′BB′, *J* 8.9). δ_C(50 MHz, $CDCl_3$) 55.3 (CH_3O), 69.8 (C-6), 80.3 (C-3), 113.9 (2 C, anisyl C-3,5), 124.8 (C-5), 127.2 (C-4), 129.0 (anisyl C-1), 130.1 (2 C, anisyl C-2,6), 160.2 (anisyl C-4). ν_{max}(KBr)/cm^{-1} 3010, 2950, 2910, 2830, 1613, 1515, 1280, 1251, 1172, 1106, 1055, 1030, 997, 926, 882, 792, 766, 661, 536. *m/z* (70 eV) 192 (M^+, 2%), 190 ($M^+ - 2$ H, 40), 174 ($M^+ - H_2O$, 39), 161 (8), 160 ($M^+ - O_2$, 8), 159 (26), 147 (25), 135 ($CH_3OC_6H_4CO^+$, 100), 131 (17), 115 (12), 107 ($CH_3OC_6H_4{}^+$, 17), 92 (20), 77 (42). Although the ^1H NMR analysis showed that **4d** was pure, the elemental analysis for carbon was not satisfactory (Found: C, 68.05; H, 6.4. Calc. for $C_{11}H_{12}O_3$: C, 68.74; H, 6.29%).

1,4-Diphenyl-2,3-dioxabicyclo[2.2.2]oct-5-ene (**6**), slightly yellow leaflets (from EtOH), m.p. 149–150 °C (lit.[13i] 156 °C). δ_H(200 MHz, $CDCl_3$) 1.96–2.27 (2 H, m, H-7,8), 2.59–2.70 (2 H, m, H-7,8), 6.89 (2 H, s, H-5,6), 7.31–7.58 (10 H, m, phenyl). δ_C(50 MHz, $CDCl_3$) 29.6 (2 C, C-7,8), 78.4 (2 C, C-1,4), 126.1 (4 C, phenyl C-3,5), 128.4 (2 C-5,6), 128.6 (4 C, phenyl C-2,6), 136.6 (2 C, phenyl C-4), 139.5 (2 C, phenyl C-1). ν_{max}(KBr)/cm^{-1} 3060, 3020, 2930, 1600, 1490, 1445, 1362, 1265, 1230, 1180, 1160, 1130, 1060, 1015, 970, 928, 910, 755, 720, 695, 530. *m/z* (13.5 eV) 264 (M^+, 7%), 249 (17), 247 (7), 237 (12), 236 (15), 234 (13), 233 (58), 232 (36), 231 (75), 230 (100), 221 (10), 220 (37), 218 (5), 206 (6), 144 (22) (Found: C, 81.85; H, 6.0. Calc. for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10%).

cis-3-Methyl-6-phenyl-1,2-dioxacyclohex-4-ene (**9**), colourless oil.[13b] δ_H(200 MHz, $CDCl_3$) 1.36 (3 H, d, *J* 6.8, CH_3), 4.76 (1 H, br q, *J* 6.8, H-3), 5.48 (1 H, m, H-6), 6.02–6.14 (2 H, m, H-4,5), 7.32–7.43 (5 H, m, phenyl). δ_C(50 MHz, $CDCl_3$) 18.4 (CH_3), 74.5 (C-3), 80.0 (C-6), 126.0 (C-5), 128.46 (2 C, phenyl C-3,5 or C-2,6), 128.49 (2 C, phenyl C-2,6 or C-3,5), 128.6 (phenyl C-4), 129.8 (C-4), 137.9 (phenyl C-1). ν_{max}(neat)/cm^{-1} 3030, 2970, 2860, 1492, 1454, 1382, 1366, 1255, 1174, 1135, 1090, 1053, 1033, 938, 916, 886, 821, 786, 751, 716, 696, 636. *m/z* (70 eV) 176 (M^+, 4%), 174 ($M^+ - 2$ H, 5), 158 ($M^+ - H_2O$, 100), 144 ($M^+ - O_2$, 4), 138 (13), 129 (19), 115 (44), 105 ($C_6H_5CO^+$, 72), 77 ($C_6H_5{}^+$, 53).

5-Methyl-3-phenyl-1,2-dioxacyclohex-4-ene (**10**), colourless plates (from hexane), m.p. 40–41.5 °C. δ_H(200 MHz, $CDCl_3$) 1.82 (3 H, dddd, *J* 2.2, 2.2, 1.0, 1.0, CH_3), 4.40 (1 H, dddq, *J* 15.8, 2.2, 1.8, 1.0, H-6), 4.60 (1 H, dddq, *J* 15.8, 2.2, 2.0, 1.0, H-6), 5.57 (1 H, qddd, *J* 2.2, 2.2, 2.2, 2.2, H-3), 5.78 (1 H, dddq, 2.2, 2.0, 1.8, 2.0, H-4), 7.32–7.39 (5 H, m, phenyl). δ_C(50 MHz, $CDCl_3$) 18.2 (CH_3), 73.0 (C-6), 80.4 (C-3), 120.8 (C-4), 128.5 (4 C, phenyl C-2,3,5,6), 128.7 (phenyl C-4), 132.4 (C-5), 137.8 (phenyl C-1). ν_{max}(KBr)/cm^{-1} 3030, 2870, 1457, 1080, 1018, 956, 929, 919, 757, 698. *m/z* (13.5 eV) 176 (M^+, 2.3%), 158 ($M^+ - H_2O$, 1.4), 144 ($M^+ - O_2$, 100), 129 (21). Although the ^1H NMR analysis showed that **10** was pure, the elemental analysis for carbon was not satisfactory (Found: C, 73.85; H, 6.6. Calc. for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86%).

3-Methyl-3-phenyl-1,2-dioxacyclohex-4-ene (**11a**), colourless oil. δ_H(200 MHz, $CDCl_3$) 1.56 (3 H, s, CH_3), 4.40 (1 H, ddd, *J* 16.4, 3.4, 2.0, H-6), 4.73 (1 H, ddd, *J* 16.4, 2.2, 2.2, H-6), 6.03 (1 H, ddd, *J* 10.2, 3.4, 2.2, H-5), 6.31 (1 H, ddd, *J* 10.2, 2.2, 2.0, H-4), 7.23–7.49 (5 H, m, phenyl). δ_C(50 MHz, $CDCl_3$) 26.2 (CH_3), 69.4 (C-6), 81.0 (C-3), 123.2 (C-5), 125.8 (2 C, phenyl C-2,6), 127.5 (phenyl C-4), 128.3 (2 C, phenyl C-3,5), 131.2 (C-4), 143.5 (phenyl C-1). ν_{max}(neat)/cm^{-1} 3040, 2980, 2880, 1491, 1443, 1362, 1229, 1093, 1071, 1035, 999, 915, 880, 762, 696. *m/z* (70 eV) 176 (M^+, 5%), 174 ($M^+ - 2$ H, 4), 162 (22), 161 ($M^+ - CH_3$, 100), 133 (99), 131 (30), 129 (37), 128 (20), 115 (68), 105 ($C_6H_5CO^+$, 98), 103 (53), 91 (27), 78 (24), 77 ($C_6H_5{}^+$, 85).

3,3-Diphenyl-1,2-dioxacyclohex-4-ene (**11b**), colourless prisms (from hexane), m.p. 73.5–74 °C. δ_H(200 MHz, $CDCl_3$) 4.68 (2 H, dd, *J* 3.0, 2.0, H-6), 6.17 (1 H, dt, *J* 10.3, 3.0, H-5), 6.57 (1 H, dt, *J* 10.3, 2.0, H-4), 7.24–7.40 (10 H, m, phenyl). δ_C(50 MHz, $CDCl_3$) 69.6 (C-6), 85.4 (C-3), 123.4 (C-5), 127.5 (4 C, phenyl C-2,6), 127.9 (2 C, phenyl C-4), 128.2 (4 C, phenyl C-3,5), 130.8 (C-4), 142.0 (2 C, phenyl C-1). ν_{max}(KBr)/cm^{-1} 3050, 2880, 1490, 1449, 1057, 1032, 1008, 964, 916, 761, 743, 694, 608, 491. *m/z* (70 eV) 238 (M^+, 4%), 236 ($M^+ - 2$ H, 16), 193 (25), 182 (13), 178 (11), 165 (16), 161 (13), 133 (31), 131 (21), 115 (29), 105 ($C_6H_5CO^+$, 100), 91 (13), 77 ($C_6H_5{}^+$, 57).

3,5-Dimethyl-3-phenyl-1,2-dioxacyclohex-4-ene (**12**), colourless plates (from hexane), m.p. 50–51 °C (lit.,[13b] 51.5–52.5 °C). δ_H(200 MHz, $CDCl_3$) 1.52 (3 H, s, 3-CH_3), 1.77 (3 H, ddd, *J* 1.6, 1.0, 1.0, 5-CH_3), 4.20 (1 H, br d, *J* 15.8, H-6), 4.59 (1 H, qdd, *J* 1.0, 15.8, 1.8, H-6), 5.98 (1 H, qdd, *J* 1.6, 1.8, 1.8, H-4), 7.20–7.49 (5 H, m, phenyl). δ_C(50 MHz, $CDCl_3$) 18.1 (5-CH_3), 26.7 (3-CH_3), 72.5 (C-6), 80.7 (C-3), 125.2 (C-4), 125.8 (2 C, phenyl C-2,6), 127.3 (phenyl C-4), 128.2 (2 C, phenyl C-3,5), 130.8 (C-5), 144.3 (phenyl C-1). *m/z* (70 eV) 190 (M^+, 3%), 175 ($M^+ - CH_3$, 100), 147 (82), 129 (46), 128 (24), 105 ($C_6H_5CO^+$, 69), 77 ($C_6H_5{}^+$, 48).

4-Phenyl-1,2-dioxacyclohex-4-ene (**13**), colourless prisms (from MeOH), m.p. 50–51 °C (lit.,[13b] 50–50.5 °C). δ_H(200 MHz, $CDCl_3$) 4.77 (2 H, dt, *J* 3.2, 2.2, H-6), 4.95 (2 H, td, *J* 1.8, 2.2, H-3), 6.31 (1 H, tt, *J* 3.2, 1.8, H-5), 7.26–7.43 (5 H, m, phenyl). δ_C(50 MHz, $CDCl_3$) 70.2 (C-6), 71.3 (C-3), 119.8 (C-5), 124.8 (2 C, phenyl C-2,6), 128.1 (phenyl C-4), 128.7 (2 C, phenyl C-3,5), 134.6 (C-4), 136.4 (phenyl C-1). *m/z* (70 eV) 162 (M^+, 6%), 160 ($M^+ - 2$ H, 15), 145 (17), 144 ($M^+ - H_2O$, 100), 138 (13), 131 (14), 115 (76), 105 (13), 103 (21), 89 (16), 77 ($C_6H_5{}^+$, 15).

3,3-Dimethyl-6-phenyl-1,2-dioxacyclohex-4-ene (**14**), colourless prisms (from hexane), m.p. 58–58.5 °C (lit.[8e,13b] not mentioned). δ_H(200 MHz, $CDCl_3$) 1.34 (3 H, s, CH_3-3), 1.44 (3 H, s, CH_3-3), 5.53 (1 H, dd, *J* 1.9, 1.8, H-6), 5.92 (1 H, dd, *J* 10.2, 1.8, H-4), 6.02 (1 H, dd, *J* 10.2, 1.9, H-5), 7.32–7.42 (5 H, m). δ_C(50 MHz, $CDCl_3$) 24.9 (CH_3), 25.5 (CH_3), 77.8 (C-3), 79.8 (C-6), 125.1 (C-5), 128.5 (4 C, phenyl C-2,3,5,6), 128.8 (phenyl C-4), 133.5 (C-4), 137.4 (phenyl C-1). ν_{max}(KBr)/cm^{-1} 3040, 2970, 1455, 1359, 1136, 1044, 762, 731, 699. *m/z* (70 eV) 190 (M^+, 20%), 175 ($M^+ - CH_3$, 35), 173 ($M^+ - OH$, 59), 158 (22), 147 (36), 143 (21), 138 (63), 132 (51), 131 (84), 129 (26), 117 (23), 115 (24), 105 ($C_6H_5CO^+$, 100), 97 (22), 91 (34), 83 (31), 78 (29), 77 ($C_6H_5{}^+$, 94).

Determination of the Formation Constants of the TCNE *EDA Complexes of* **3a** *and* **5**.—A known amount of **3a** was placed in a 1 cm quartz cuvette and a 3 cm^3 stock solution of TCNE (4.00×10^{-3} mol dm^{-3}) in dichloromethane was added. The solution was mixed well prior to spectrophotometric measurement at 368 nm. The procedure was repeated with varied amounts of **3a**. The concentration of **3a** varied from 3.92×10^{-2} mol dm^{-3} to 2.12×10^{-1} mol dm^{-3}. Plots of [TCNE]/A_{CT} against $[\mathbf{3a}]^{-1}$ were linear as shown in the inset of Fig. 2. The values of K and $\varepsilon_{\mathrm{CT}}$ at 368 nm were evaluated from the slope ($K\,\varepsilon_{\mathrm{CT}})^{-1}$ and the intercept $(\varepsilon_{\mathrm{CT}})^{-1}$ obtained by linear least squares fitting ($r = 0.999$).

A 3 cm^3 solution of TCNE (9.99×10^{-4} mol dm^{-3}) in dichloromethane was placed in a 1 cm quartz cuvette and **6** was added in 10 mm^3 increments with a microlitre syringe. On each addition the solution was mixed well prior to spectrophotometric measurement at 448 nm. The concentration of **6** varied from 4.06×10^{-2} mol dm^{-3} to 2.03×10^{-1} mol dm^{-3}. Plots of $[\mathrm{TCNE}]/A_{\mathrm{CT}}$ against $[\mathbf{6}]^{-1}$ were linear as shown in the inset of Fig. 4. The linear fit by linear least squares ($r = 0.999$) led to the evaluation of K and $\varepsilon_{\mathrm{CT}}$.

General Procedure for Photolyses of the TCNE *EDA Complexes of the* EPs.—Typically a 5 cm^3 dichloromethane solution containing 0.25 mmol of EP and 0.25 mmol of TCNE was irradiated by using a 2 kW xenon lamp through a glass filter (a Toshiba UV-35 for wavelengths $\lambda > 340$ nm, or a Toshiba L-42 for wavelengths $\lambda > 390$ nm). Then the solvent was evaporated and and 0.3 mmol of α-terpinene was added. The resulting mixture was analysed by a 90 MHz or 200 MHz ^{1}H NMR spectroscopy with 1,1,1,2-tetrachloroethane (4.27 ppm in CDCl$_3$) or 1,1,2,2-tetrachloroethane (5.92 ppm in CDCl$_3$) as an internal standard. Products, if any, were isolated by preparative TLC.

Photolysis of the TCNE *EDA complex of* EP **3a**. A 5 cm^3 solution containing 0.25 mmol of **3a** and 0.25 mmol of TCNE in dichloromethane was irradiated as described above ($\lambda >$ 390 nm). After irradiation for 4 h the solvent was evaporated and 0.3 mmol of α-terpinene was added. The resulting mixture was analysed by 90 MHz ^{1}H NMR spectroscopy with 1,1,2,2-tetrachloroethane as an internal standard. The analysis showed that furan **7a** was formed in 36% yield and **3a** was recovered in 63% yield. TCNE could be recovered as an α-terpinene–TCNE adduct in 82% yield. Furan **7a** and the α-terpinene–TCNE adduct were isolated by preparative silica gel TLC in 32% and 80% yield, respectively. Furan **7a**, colourless powder (from EtOH), m.p. 84–85.5 °C (lit.,[13f] 87–88, lit.,[29] 88–89 °C). δ_{H}(90 MHz, CDCl$_3$) 7.90–7.57 (m, 4 H), 7.50–7.20 (m, 6 H), 6.70 (s, 2 H). $\nu_{\max}$(KBr)/cm^{-1} 1610, 1489, 1445, 1210, 1155, 1080, 1020, 925, 910, 795, 760, 690, 670. m/z (25 eV) 221 (M$^+$ + 1, 20%), 220 (M$^+$, 100), 192 (3), 191 (19), 115 (45), 105 (25), 77 (4). α-Terpinene–TCNE adduct, colourless powder, m.p. 175–175.5 °C (from diethyl ether). δ_{H}(90 MHz, CDCl$_3$) 1.18 (3 H, d, J 7.2), 1.28 (2 H, d, J 7.2), 1.67 (3 H, s), 1.50–1.86 (2 H, m), 1.97–2.26 (2 H, m), 2.47 (1 H, qq, J 7.2, 7.2), 6.35 (2 H, s). $\nu_{\max}$(KBr)/cm^{-1} 2980, 2240, 1464, 1380, 1208, 1137, 1060, 992, 940, 900, 720 (Found: C, 72.8; H, 6.2; N, 21.15. Calc. for $C_{16}H_{16}N_4$: C, 72.70; H, 6.10; N, 21.19%).

Similar irradiation with shorter wavelength light ($\lambda > 340$ nm) afforded a similar result, which is also shown in Table 2. No reaction was observed when the photolysis was carried out either in the dark or under irradiation ($\lambda > 340$ nm) without TCNE.

Photolysis of the TCNE *EDA complex of* EP **4a**. A 5 cm^3 solution containing 0.25 mmol of **4a** and 0.25 mmol of TCNE in dichloromethane was irradiated for 4 h ($\lambda > 390$ nm) and worked up as described above. 90 MHz ^{1}H NMR analysis showed that furan **8a** was formed in 16% yield and that **4a** and TCNE were recovered in 84% and 98% yield, respectively. Furan **8a** was isolated in 12% yield by preparative TLC. No reaction was observed either in the dark or under similar irradiation without TCNE. **8a**, δ_{H}(90 MHz, CDCl$_3$) 6.41 (1 H, dd, J 4, 2, H-4), 6.61 (1 H, d, J 4, H-3), 7.1–7.7 (6 H, m, H-5, phenyl). **8a** has already been synthesized[7,30,31,32] and was identified by NMR spectral comparison with the authentic sample synthesized by the KOH catalysed dehydration of **4a** according to the reported method.[7]

Photolysis of the TCNE *EDA complex of* EP **4b**. A 5 cm^3 solution containing 0.25 mmol of **4b** and 0.25 mmol of TCNE in dichloromethane was irradiated for 4 h ($\lambda > 390$ nm) and worked up as described above. 90 MHz ^{1}H NMR analysis showed that furan **8b** was formed in 21% yield and that **4b** and TCNE were recovered in 64% and 89% yield, respectively. Furan **8b** was isolated in 21% yield by preparative TLC. No reaction was observed in the dark or under similar irradiation without TCNE. **8b**, δ_{H}(90 MHz, CDCl$_3$) 6.44 (1 H, dd, J 4, 2, H-4), 6.63 (1 H, d, J 4, H-3), 7.2–7.6 (5 H, m, H-5, aryl). **8b** was identified by NMR spectral comparison with the authentic sample synthesized previously.[31,32]

Photolysis of the TCNE *EDA complex of* EP **9**. A 3 cm^3 solution containing 0.18 mmol of EP **9** and 0.18 mmol of TCNE in dichloromethane was irradiated for 2 h ($\lambda > 340$ nm) and worked up as described above. 90 MHz ^{1}H NMR analysis showed that furan **15** was formed in 29% yield and that **9** and TCNE were recovered in 63% and 95% yield, respectively. Furan **15** was isolated in 30% yield by preparative TLC. No reaction was observed in the dark or under similar irradiation without TCNE. **15**, colourless oil δ_{H}(90 MHz, CCl$_4$) 2.36 (3 H, s, CH$_3$), 5.93 (1 H, m, H-3), 6.39 (1 H, dm, J 4, H-4), 7.0–7.6 (5 H, m, phenyl). **15** was identified by NMR spectral comparison with the authentic sample synthesized previously.[31,32]

Photolysis of the TCNE *EDA complex of* EP **10**. A 3 cm^3 solution containing 0.18 mmol of **10** and 0.18 mmol of TCNE in dichloromethane was irradiated for 2 h ($\lambda > 340$ nm). ^{1}H NMR analysis showed that furan **16** was formed in 39% yield, and **10** was recovered in 30% yield. No reaction was observed in the dark or under similar irradiation without TCNE. **16**, δ_{H}(90 MHz, CCl$_4$) 2.07 (3 H, s, CH$_3$), 6.37 (1 H, s, H-3), 7.0–7.6 (6 H, m, H-5, phenyl). Furan **16** was identified by NMR spectral comparison with the authentic sample synthesized previously.[33]

Photolysis of the TCNE *EDA complex of* EP **6**. A 3 cm^3 solution containing 48 mg (0.18 mmol) of **6** and 23 mg (0.18 mmol) of TCNE in dichloromethane was irradiated by using a 2 kW xenon lamp with a glass filter ($\lambda > 390$ nm). After 30 s irradiation gas evolution began and after 20 min irradiation a white deposit began to precipitate. After irradiation for 30 min the solvent was evaporated and the resulting mixture was analysed by 90 MHz NMR spectroscopy with 1,1,2,2-tetrachloroethane as an internal standard. The analysis showed that **6** was recovered in 30% yield. TCNE was recovered in 14% yield with α-terpinene as a trap. The TCNE adduct **23** could be isolated in 70% yield by digestion with diethyl ether. **23**, colourless powder, m.p. 195–197.5 °C (decomp.). δ_{H}(200 MHz, CDCl$_3$) 7.80–7.70 (4 H, m), 7.63–7.45 (6 H, m), 7.10 (2 H, s), 3.20–3.08 (2 H, m), 2.00–1.89 (2 H, m). $\nu_{\max}$(KBr)/cm^{-1} 3070, 3040, 2950, 2880, 2250, 1500, 1445, 1372, 1315, 1235, 1165, 1100, 1000, 955, 895, 745, 700, 630, 564, 489 (Found: C, 80.0; H, 4.6; N, 15.5. Calc. for $C_{24}H_{16}N_4$: C, 79.98; H, 4.47; N, 15.54%). The adduct **23** could be synthesized independently by the cycloaddition of 1,4-diphenylcyclohexa-1,3-diene with TCNE in dichloromethane at room temperature. No reaction was observed in the dark or under similar irradiation without TCNE.

A similar photoreaction in the presence of 0.18 mmol of tetramethylethylene (**24**) afforded 46% of **23** with recovery of 53% and 52% of **6** and TCNE, respectively. No formation of oxygenation product from tetramethylethylene was observed. The reaction in the presence of **24** is slower since **24** also forms an EDA complex with TCNE whose $\lambda_{\max\,\mathrm{CT}}$ is 538 nm and K is 0.079 dm^3 mol^{-1} and some fraction of the incident light is absorbed by this EDA complex.

Triplet Photosensitized Reaction of **3a**.—A 3 cm^3 solution containing 44.05 mg (0.185 mmol) of **3a** and 4 mg (0.02 mmol) of fluorenone in dichloromethane was irradiated with a

Toshiba UV-35 glass filter ($\lambda > 340$ nm). After irradiation for 1 h the solvent was evaporated and the resulting mixture was analysed by 90 MHz ^{1}H NMR spectroscopy with 1,1,1,2-tetrachloroethane as an internal standard. The analysis showed that furan **7a** and diepoxide **30** were formed in 10% and 8% yield, respectively, with recovery of **3a** in 72% yield. Products **7a** and **30** were isolated by preparative silica gel TLC and identified by NMR spectral comparison with the authentic data.[34] *meso*-1,2;3,4-bis(epoxy)-*trans*,*trans*-1,4-diphenylbutane (**30**), δ_H(200 MHz, CDCl$_3$) 3.17 (2 H, s), 3.92 (2 H, s), 7.25–7.35 (10 H, m).

Triplet Photosensitized Reaction of **6**.—A 5 cm^3 solution containing 26.4 mg (0.100 mmol) of **6** and 9 mg (0.05 mmol) of fluorenone in dichloromethane was irradiated with a Toshiba L-42 glass filter ($\lambda > 390$ nm). After irradiation for 1 h the solvent was evaporated and the resulting mixture was analysed by 200 MHz ^{1}H NMR spectroscopy with 1,1,1,2-tetrachloroethane as an internal standard. The analysis showed that diepoxide **31** was formed in 98% yield with a trace amount (1%) of recovered **6**. 20 mg (76%) of pure **31** was obtained by recrystallization of the photolysate from ethanol. *syn*-1,2;3,4-bis(epoxy)-1,4-diphenylcyclohexane (**31**), colourless plates, m.p. 121–121.5 °C (lit.[8d] not mentioned). δ_H(200 MHz, CDCl$_3$) 2.28 (2 H, AA′BB′, m), 2.54 (2 H, AA′BB′, m), 3.32 (2 H, s), 7.37 (10 H, m). δ_C(50 MHz, CDCl$_3$) 26.3 (2 C, C-4,6), 57.1 (2 C-1,4), 57.9 (2 C, C-2,3), 125.0 (4 C, phenyl C-3,5), 127.7 (2 C, phenyl C-4), 128.5 (4 C, phenyl C-2,6), 140.4 (2 C, phenyl C-1). ν_{max}(KBr)/cm^{-1} 3060, 2940, 1495, 1449, 913, 888, 745, 690, 631, 542. No reaction was observed in the absence of fluorenone at wavelengths > 390 nm.*

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* The direct photolysis of **6** is possible if irradiated at wavelengths > 340 nm since **6** has a weak absorption tailing up to *ca.* 400 nm (π^*_{OO}–σ^*_{OO} transition). Thus 1 h irradiation of a 5 cm^3 solution of 26 mg (0.10 mmol) of **6** in dichloromethane resulted in the formation of **31** in 73% yield with recovery of **6** in 22%. The details will be reported elsewhere.

References

1 (*a*) I. Saito and S. S. Nittala, in *The Chemistry of Peroxides*, ed. S. Patai, Wiley, New York, 1983, pp. 311–374; (*b*) A. A. Frimer, pp. 201–234.

2 (*a*) R. W. Denny and A. Nickon, *Org. React.*, 1973, **20**, 133; (*b*) I. Saito and T. Matsuura, in *Singlet Oxygen*, ed. H. H. Wasserman and R. W. Murray, Academic Press, New York, 1979, pp. 511–574.

3 (*a*) C. W. Jefford, J. Boukouvalas and S. Kohmoto, *J. Chem. Soc., Chem. Commun.*, 1984, 523; (*b*) G. Ohloff, *Pure Appl. Chem.*, 1975, **43**, 481; (*c*) H. H. Wasserman and J. L. Ives, *Tetrahedron*, 1981, **37**, 1825; (*d*) M. Balci, *Chem. Rev.*, 1981, **81**, 91; (*e*) C. H. Foster and G. A. Berchtold, *J. Am. Chem. Soc.*, 1972, **94**, 7939; (*f*) C. H. Foster and G. A. Berchtold, *J. Org. Chem.*, 1975, **40**, 3743.

4 (*a*) N. J. Turro, M.-F. Chow and J. Rigaudy, *J. Am. Chem. Soc.*, 1981, **103**, 7218; (*b*) H. H. Wasserman, J. R. Scheffer and J. L. Cooper, *J. Am. Chem. Soc.*, 1972, **94**, 4991; (*c*) H. H. Wasserman and J. R. Scheffer, *J. Am. Chem. Soc.*, 1967, **89**, 3073; (*d*) W. Adam and M. Balci, *Tetrahedron*, 1980, **36**, 833.

5 (*a*) E. Afshari, H.-D. Brauer, R. Schmidt, M. Lachgar and J. Rigaudy, *J. Photochem. Photobiol., A: Chem.*, 1992, **63**, 319; (*b*) K. K. Maheshwari, P. de Mayo and D. Wiegand, *Can. J. Chem.*, 1970, **48**, 3265; (*c*) N. P. Ernsting, R. Schmidt and H.-D. Brauer, *J. Phys. Chem.*, 1990, **94**, 5252; (*d*) K. B. Eisenthal, N. J. Turro, C. G. Dupuy, D. A. Hrovat, J. Langan, T. A. Jenny and E. V. Sitzmann, *J. Phys. Chem.*, 1986, **90**, 5168; (*e*) B. Stevens and W. A. Glauser, *Chem. Phys. Lett.*, 1986, **129**, 120; (*f*) R. Srinivasan, K. H. Brown, J. A. Ors, L. S. White and W. Adam, *J. Am. Chem. Soc.*, 1979, **101**, 7424; (*g*) J. Rigaudy, C. Breliere and P. Scribe, *Tetrahedron Lett.*, 1978, 687; (*h*) J. Rigaudy, A. Defoin and J. Baranne-Lafont, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 413.

6 (*a*) C. W. Jefford, D. Jaggi, J. Boukouvalas and S. Kohmoto, *J. Am. Chem. Soc.*, 1983, **105**, 6497; (*b*) A. P. Schaap, P. A. Burns and K. A. Zaklika, *J. Am. Chem. Soc.*, 1977, **99**, 1270. See also ref. 1*a*, pp. 352–355, ref. 2*b*, pp. 528–530, and refs. cited therein.

7 K. Kondo and M. Matsumoto, *Chem. Lett.*, 1974, 701. See also ref. 1*a*, pp. 352–355, ref. 2*b*, pp. 528–530, and references cited therein.

8 (*a*) J. D. Boyd, C. S. Foote and D. K. Imagawa, *J. Am. Chem. Soc.*, 1980, **102**, 3641; (*b*) J. A. Turner and W. Herz, *J. Org. Chem.*, 1977, **42**, 1895; (*c*) S. Kohmoto, S. Kasai, M. Yamamoto and K. Yamada, *Chem. Lett.*, 1988, 1477; (*d*) M. Suzuki, H. Ohtake, Y. Kameya, N. Hamanaka and R. Noyori, *J. Org. Chem.*, 1989, **54**, 5292; (*e*) M. Suzuki, Y. Oda and R. Noyori, *Tetrahedron Lett.*, 1981, **22**, 4413; (*f*) D. Brown, B. T. Davis, T. G. Halsall and A. R. Hands, *J. Chem. Soc.*, 1962, 4492.

9 R. Foster, *Organic Charge-transfer Complexes*, Academic Press, New York, 1969; R. S. Mulliken and W. B. Pearson, *Molecular Complexes: A Lecture and Reprint Volume*, Wiley, New York, 1969.

10 L. R. Melby, in *The Chemistry of the Cyano Group*, ed. S. Patai, Wiley, New York, 1970, pp. 639–669.

11 (*a*) E. F. Hilinski, J. M. Masnovi, C. Amatore, J. K. Kochi and P. M. Rentzepis, *J. Am. Chem. Soc.*, 1983, **105**, 6167; (*b*) E. F. Hilinski, J. M. Masnovi, J. K. Kochi and P. M. Rentzepis, *J. Am. Chem. Soc.*, 1984, **106**, 8071; (*c*) H. Masuhara and N. Mataga, *Acc. Chem. Res.*, 1981, **14**, 312; (*d*) I. R. Gould, R. Moody and S. Farid, *J. Am. Chem. Soc.*, 1988, **110**, 7242; (*e*) I. R. Gould, R. H. Young, R. E. Moody and S. Farid, *J. Phys. Chem.*, 1991, **95**, 2068; (*f*) T. Takigawa, K. Kida, T. Okada and N. Mataga, presented at the Symposium on Photochemistry, Tokyo, 1979; abstract BII-212, p. 238; (*g*) T. Asahi and N. Mataga, *J. Phys. Chem.*, 1991, **95**, 1956. See also the refs. cited therein.

12 (*a*) S. Sankararaman, S. Perrier and J. K. Kochi, *J. Am. Chem. Soc.*, 1989, **111**, 6448; (*b*) G. Jones, II and W. G. Becker, *J. Am. Chem. Soc.*, 1983, **105**, 1276; (*c*) J. M. Masnovi and J. K. Kochi, *J. Am. Chem. Soc.*, 1985, **107**, 6781; (*d*) T. Miyashi, K. Wakamatsu, T. Akiya, K. Kikuchi and T. Mukai, *J. Am. Chem. Soc.*, 1987, **109**, 5270; (*e*) T. Miyashi, M. Kamata and T. Mukai, *J. Am. Chem. Soc.*, 1987, **109**, 2780; (*f*) Y. Takahashi and J. K. Kochi, *Chem. Ber.*, 1988, **121**, 253; (*g*) G. Jones, II, in *Photoinduced Electron Transfer, Part A*, ed. M. A. Fox and M. Chanon, Elsevier, Amsterdam, 1988, p. 245.

13 (*a*) K. Gollnick and A. Griesbeck, *Tetrahedron Lett.*, 1983, **24**, 3303; (*b*) M. Matsumoto, S. Dobashi, K. Kuroda and K. Kondo, *Tetrahedron*, 1985, **41**, 2147; (*c*) K. E. O'Shea and C. S. Foote, *J. Am. Chem. Soc.*, 1988, **110**, 7167; (*d*) L. E. Manring and C. S. Foote, *J. Am. Chem. Soc.*, 1983, **105**, 4710; (*e*) K. Gollnick and A. Griesbeck, *Tetrahedron*, 1984, **40**, 3235; (*f*) G. Rio and J. Berthelot, *Bull. Soc. Chim. Fr.*, 1969, 1664. See also ref. 13*g* for **3a**; (*g*) Y. Takahashi, K. Wakamatsu, K. Kikuchi and T. Miyashi, *J. Phys. Org. Chem.*, 1990, **3**, 509; (*h*) G. O. Schenck, K. Gollnick and O.-A. Neumüller, *Liebigs Ann. Chem.*, 1957, **603**, 46. See also ref. 8*f* and 13*f*; (*i*) K. Gollnick and G. O. Schenck, in *1,4-Cycloaddition Reactions*, ed. J. Hamer, Academic Press, New York, 1967, p. 271.

14 H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, 1949, **71**, 2703.

15 E. Ciganek, W. J. Linn and O. W. Webster, in ref. 10, p. 466.

16 K. Gollnick and A. Griesbeck, *Tetrahedron Lett.*, 1984, **25**, 725. See also K. Gollnick and H. J. Kuhn, in ref. 2*b*, p. 291.

17 (*a*) K. Yoshihara and D. R. Kearns, *J. Chem. Phys.*, 1966, **45**, 1994; (*b*) K. Kikuchi, unpublished result, Tohoku University; (*c*) C. K. Mann and K. K. Barnes, *Electrochemical Reactions in Nonaqueous Systems*, Marcel Dekker, New York, 1970, p. 185.

18 (*a*) K. Osafune and K. Kimura, *Chem. Phys. Lett.*, 1974, **25**, 47; (*b*) C. Batich and W. Adam, *Tetrahedron Lett.*, 1974, 1467; (*c*) R. S. Brown, *Can. J. Chem.*, 1975, **53**, 3439; (*d*) D. J. Coughlin, R. S. Brown and R. G. Salomon, *J. Am. Chem. Soc.*, 1979, **101**, 1533; (*e*) P. Rademacher and W. Elling, *Liebigs Ann. Chem.*, 1979, 1473; (*f*) R. Gleiter, W. Dobler, M. Eckert-Maksic, A. J. Bloodworth, H. J. Eggelte and D. Cremer, *J. Org. Chem.*, 1984, **49**, 3716.

19 (*a*) S. F. Nelsen, M. F. Teasley, A. J. Bloodworth and H. J. Eggelte, *J. Org. Chem.*, 1985, **50**, 3299; (*b*) S. F. Nelsen, M. F. Teasley, D. L. Kapp and R. M. Wilson, *J. Org. Chem.*, 1984, **49**, 1843.

20 T. Kondo, M. Tanimoto and M. Matsumoto, *Tetrahedron Lett.*, 1980, **21**, 1649.

21 A. D. Baker, D. P. May and D. W. Turner, *J. Chem. Soc., B*, 1968, 22.

22 G. Bieri, F. Burger, E. Heilbronner and J. P. Maier, *Helv. Chim. Acta*, 1977, **60**, 2213.

23 T. Kobayashi and S. Nagakura, *Chem. Lett.*, 1972, 903.

24 T. Kobayashi and S. Nagakura, *Bull. Chem. Soc. Jpn.*, 1974, **47**, 2563.

25 (*a*) C. J. Schlesener, C. Amatore and J. K. Kochi, *J. Am. Chem. Soc.*, 1984, **106**, 7472; (*b*) C. J. Schlesener, C. Amatore and J. K. Kochi, *J. Am. Chem. Soc.*, 1984, **106**, 3567; (*c*) J. M. Masnovi, S. Sankararaman and J. K. Kochi, *J. Am. Chem. Soc.*, 1989, **111**, 2263; (*d*) A. Yoshino, M. Ohashi and T. Yonezawa, *J. Chem. Soc., Chem. Commun.*, 1971, 97; (*e*) A. M. de P. Nicholas and D. R. Arnold, *Can. J. Chem.*, 1982, **60**, 2165; (*f*) A. M. de P. Nicholas, R. J. Boyd and D. R. Arnold, *Can. J. Chem.*, 1982, **60**, 3011; (*g*) A. Okamoto, M. S. Snow and D. R. Arnold, *Tetrahedron*, 1986, **42**, 6175; (*h*) M. M. Green, S. L. Mielke and T. Mukhopadhyay, *J. Org. Chem.*, 1984, **49**, 1276; (*i*) V. D. Parker and M. Tilset, *J. Am. Chem. Soc.*, 1986, **108**, 6371; (*j*) A. Albini, E. Fasani and A. Sulpizio, *J. Am. Chem. Soc.*, 1984, **106**, 3562; (*k*) A. Albini and S. Spreti, *Tetrahedron*, 1984, **40**, 2975; (*l*) F. D. Lewis and J. R. Petisce, *Tetrahedron*, 1986, **42**, 6207.

26 (*a*) S. Iwata, J. Tanaka and S. Nagakura, *J. Phys. Chem.*, 1967, **47**, 2203; (*b*) S. Iwata, J. Tanaka and S. Nagakura, *J. Am. Chem. Soc.*, 1967, **89**, 2813; (*c*) B. K. Adams and W. R. Cherry, *J. Am. Chem. Soc.*, 1981, **103**, 6904; (*d*) S. L. Mattes and S. Farid, *Acc. Chem. Res.*, 1982, **15**, 80; (*e*) D. R. Arnold and P. D. Wong, *J. Am. Chem. Soc.*, 1979, **101**, 1894.

27 (*a*) K. Kikuchi, M. Hoshi, T. Niwa, Y. Takahashi and T. Miyashi, *J. Phys. Chem.*, 1991, **95**, 38; (*b*) K. A. Brown-Wensley, S. L. Mattes and S. Farid, *J. Am. Chem. Soc.*, 1978, **100**, 4162; (*c*) L. E. Manring, C.-L. Gu and C. S. Foote, *J. Phys. Chem.*, 1983, **87**, 40; (*d*) R. C. Kanner and C. S. Foote, *J. Am. Chem. Soc.*, 1992, **114**, 682.

28 B. Stevens and T.-Y. Liu, *Mol. Cryst. Liq. Cryst.*, 1991, **194**, 133.

29 W. H. Perkin and A. Schloesser, *J. Chem. Soc.*, 1890, **57**, 944.

30 D. C. Ayres and J. R. Smith, *J. Chem. Soc., C*, 1968, 2737.

31 G. Dana, O. Convert, J.-P. Girault and E. Mulliez, *Can. J. Chem.*, 1976, **54**, 1827.

32 J. P. Girault, P. Scribe and G. Dana, *Bull. Soc. Chim. Fr.*, 1973, 1760.

33 M. Kosugi, I. Takano, I. Hoshino and T. Migita, *J. Chem. Soc., Chem. Commun.*, 1983, 989; H. Hagiwara and H. Uda, *J. Chem. Soc., Perkin Trans. 1*, 1984, 91.

34 M. A. Hashem, P. Weyerstahl and B. S. Green, *Tetrahedron*, 1984, **40**, 203.

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