THE PHOTOCHEMICAL PREPARATION OF OZONIDES BY ELECTRON-TRANSFER PHOTO-OXYGENATION OF EPOXIDES

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Abstract-9,10-Dicyanoanthracene (DCA) sensitizes the electron-transfer photo-oxygenation of epoxides in oxygen-saturated acetonitrile to form ozonides. Epoxides with oxidation potentials lower than 2 V vs SCE quench the fluorescence of DCA and are converted to the ozonides with DCA alone. Epoxides which do not quench the singlet excited state of DCA are unreactive under these conditions. However, the photooxygenation of these epoxides can be effected by addition of biphenyl (BP) as a catalyst or co-sensitizer. Investigations of the stereochemistry of the reactions of cis- and trans-2,3-diaryloxiranes has shown that both isomeric epoxides are converted exclusively to the corresponding cis-ozonides. Co-sensitized photooxygenation of cis- and trans-2,3-diphenyloxirane affords only cis-3,5-diphenyl-1,2,4-trioxolane. The same stereochemical course is followed for the electron-transfer photo-oxygenation of more easily oxidized 2,3dinaphthyloxiranes that do not require BP co-sensitization. The stereochemistry of the naphthyl-substituted ozonides has been unequivocably assigned by an X-ray structure of cis-3,5-bis(2'-naphthyl)-1,2,4-trioxolane. The corresponding trans-ozonide was prepared by ozonation of cis-1,2-bis(2'-naphthyl)ethene and stereochemically identified by chromatographic resolution using high-performance liquid chromatography with optically active (+)-poly(triphenylmethyl methacrylate) as the stationary phase. These stereochemical results have been interpreted in terms of a mechanism involving addition of singlet oxygen as a dipolarophile to intermediate carbonyl ylides.

Electron-transfer photo-oxygenation with 9,10dicyanoanthracene (DCA) has, recently, been utilized for the photochemical conversion of epoxides,¹⁻³ aziridines⁴ and cyclopropanes^{1e,3-7} to 1,2,4-trioxolanes (ozonides), 1,2,4-dioxazolidines and 1,2-dioxolanes, respectively. The initial step in DCA-sensitized photo-oxygenations is the fluorescence quenching in polar solvents of singlet excited DCA by the substrate to generate DCA⁻⁻ and the substrate radical cation. Eriksen and Foote⁸ have calculated that electrontransfer quenching of singlet excited DCA should be exothermic for substrates with oxidation potentials less than 2 V relative to SCE in acetonitrile. Subsequent steps in the proposed mechanism for electron-transfer photo-oxygenation involve transfer of an electron from DCA⁻⁻ to oxygen to generate O₂⁻⁻ and reaction of O₂⁻⁻ with the substrate radical cation to yield the peroxidic products.

The above process is, of course, limited to those substrates that are capable of quenching the fluorescence of DCA. We have, however, recently developed a method for the electron-transfer photooxygenation of compounds that have oxidation potentials greater than 2 V and that, consequently, do not quench singlet excited DCA.1,5 To effect the photooxygenation of such compounds, a non-lightabsorbing aromatic hydrocarbon (biphenyl, BP) is added to the reaction solution as a catalyst or cosensitizer. We have recently utilized co-sensitized photo-oxygenation to form ozonides from epoxides that are unreactive under standard DCA-sensitized conditions. An investigation of the stereochemistry of the DCA-BP co-sensitized photo-oxygenation of cisand trans-2,3-diphenyloxiranes has shown that both epoxides are converted exclusively to the cis-ozonide.1c We have also observed that the same stereochemical course is followed for the electron-transfer photooxygenation of more easily oxidized 2,3-dinaphthyloxiranes that do not require BP co-sensitization.¹ In contrast, the photo-oxygenation of 2,3-diaryl-2,3-dimethyloxiranes yields mixtures of cis- and transozonides. In this paper, we provide a full description of these results and offer a mechanistic interpretation.

RESULTS

DCA-BP co-sensitized conversion of epoxides to ozonides

With the exception of 2,3-diphenylindene oxide (7), the epoxides shown in Table 1 exhibit oxidation potentials greater than 2 V vs the saturated calomel electrode (SCE) in acetonitrile and, as a result, do not measurably quench the fluorescence of DCA. They are, therefore, relatively unreactive towards photooxygenation with DCA alone. However, in the presence of both DCA and BP, the epoxides are converted to the corresponding ozonides in high yields. Photooxygenations were carried out in dry acetonitrile with 1 $\times 10^{-2}$ M epoxide, 1×10^{-2} M BP and 6×10^{-4} M DCA. The solutions were irradiated at 10° under oxygen with a 450 W medium-pressure mercury lamp using a CuSO₄-filter solution. Under these conditions only DCA is excited by absorption of the mercury emissions at 405 and 436 nm. The reactions were monitored by reverse-phase HPLC and further analysed by removal of the solvent at 0° under vacuum and acquisition of the 300 MHz ¹H-NMR spectra in CDCl₁. The ozonides were isolated by chromatography over silica gel and further characterized by reduction with Ph₃P.

HPLC analysis indicated that BP is not significantly consumed during these photo-oxygenations. Control experiments have shown that no oxygenation occurs in the presence of BP without DCA. Further, epoxides 1 and 9 are not converted to the ozonides upon irradiation for periods of 30 hr with a 400 W high-

Epoxide [*]	Irradiation tim c (min)	Ozonide	Yield (%)
Ph Ph Ph 1	12	^{ዎh} O ^{Ph} የሰላ ፖዖክ O_O 2	93 ^b
Ph Ph Ph Bh	40	Ph O Ph Ph O H O O 4	90 [»]
S Ph	15	e Ph e Ph	88°
Or Ph 7 Ph	30		85 ⁶
Ph H H	180	Ph Ph Ph Ph H	65ª
H Ph Ph H	180	Phy Ph H H H 11	65ª
R_1 R_2 R_3		$\begin{array}{ccc} Ph & Ph & R_1 & O & Ph \\ R_1 & O & R_2 & Ph & O & R_2 \\ 15 & 16 & 16 \end{array}$	
13a: $R_1 = R_2 = Mc$ 13b: $R_1 = H; R_2 = Mc$ $R_{10} = Mc$	90 100	(ratio of isomers) ^d 37:63 24:76	88 ^{d,e} 84 ^{d.e}
Ph R		(
$14a: R_1 = R_2 = Me$	45	(ratio of isomers) ^o 34:66	90 ^{d,e}
14b : $R_1 = H$; $R_2 = Me$	60	25:75	90 ^{d,e}

Table 1. DCA-BP co-sensitized photo-oxygenation of epoxides

* The epoxides are relatively unreactive towards prolonged photo-oxygenation with DCA in the absence of BP with the exception of 7 which produced the ozonide, 8 in 4 h in 70% yield. Compound 7 quenches DCA fluorescence as efficiently as BP (k_e for 7 = $3.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$).

^b Isolated yields.

^e Yield determined by HPLC.

^d Yields and ratios of isomers determined by 300 MHz ¹H-NMR.

* Combined yields of both isomers.

pressure sodium lamp in oxygenated acetonitrile containing Rose Bengal, indicating that they do not react with singlet oxygen directly.

Of special interest is the observation that the cosensitized photo-oxygenation of cis- and trans-2,3diphenyloxiranes (9 and 10) leads exclusively to the cis-ozonide, 11. Authentic samples of cis- and trans-3,5diphenyl-1,2,4-trioxolanes (11 and 12) were prepared by ozonation of stilbene and were shown to be stable to the photo-oxygenation conditions. In addition, no isomerization of the epoxides was detected by HPLC or ¹H-NMR at partial conversion of 9 or 10. In the absence of BP, only 7% benzaldehyde and no ozonide was obtained after 20 hr irradiation.

In contrast to the above stereochemical results, photo-oxygenation of tri- and tetra-substituted epoxides leads to mixtures of cis- and trans-ozonides.

Reaction of cis- and trans-2,3-dimethyl-2,3-diphenyloxiranes (13a and 14a) under co-sensitized photooxygenation conditions affords a mixture of ozonides 15a and 16a in approximately a 35:65 cis-trans ratio of isomers (88-90% combined yields of ozonides). Analysis by 'H-NMR at partial conversion revealed that the trans-epoxide, 14a, undergoes very slow isomerization (<3%) during the photo-oxygenation. The cis-epoxide, 13a, on the other hand, exhibited no isomerization during the reaction. In the absence of biphenyl, photo-oxygenation for 15 hr showed 40% conversion to the ozonides in a 55:45 isomeric ratio. Ozonides 15a and 16a were separated by preparative TLC over silica and recrystallized to afford pure samples (15a is a liquid while 16a melts at 95-96°). In order to establish the stereochemistry of these ozonides, we have conducted experiments utilizing highperformance liquid chromatography (HPLC) with optically active (+)-poly(triphenylmethyl methacrylate) as the stationary phase.⁹ Chromatography of ozonide 16a with methanol as eluant shows two peaks of equal area corresponding to the resolved enantiomers of the chiral *trans*-ozonide. The achiral *cis*-ozonide, 15a, however, exhibits only one peak under the same chromatographic conditions. The use of HPLC for the stereochemical identification of ozonides is described in more detail below.

Co-sensitized photo-oxygenation of *cis*- and *trans*-2methyl-2,3-diphenyloxiranes (13b and 14b) leads to a mixture of ozonides in a 25:75 *cis*-trans ratio of isomers (84-90% combined yields of ozonides). It was shown that the ratio of ozonides remains constant throughout photo-oxygenation. Compound 14b undergoes slow isomerization (<3%) during photo-oxygenation, while no isomerization is observed for 13b. Photooxygenation of 14b for 15 hr in the absence of biphenyl produces 50% of 13b and 42% of the ozonides in an isomeric ratio of 22:78. Ozonides 15b and 16b have been stereochemically assigned by comparisons of the ¹H-NMR chemical shifts to those observed for ozonides 11, 15a and 16a.

DCA-sensitized conversion of epoxides to ozonides

Insight into the mechanism of DCA-BP cosensitized photo-oxygenation of epoxides has been provided by investigations of the stereochemistry of the reaction. Of concern, however, was the possible influence of the co-sensitizer on the stereochemical course of this reaction. We have, therefore, conducted a complimentary study of the stereochemistry of the DCA-sensitized photo-oxygenation of more easily oxidized epoxides which do not require the use of BP.

Unlike the 2,3-diphenyloxiranes, cis- and transdinaphthyloxiranes (17 and 18) quench the fluorescence of DCA in acetonitrile (Tables 2 and 3). We have observed that photo-oxygenation of these epoxides proceeds rapidly in the absence of BP to vield exclusively the cis-ozonides, 19. The reactions were carried out as described above and the products analysed in CD₂Cl₂ by 300 MHz ¹H-NMR. Spectra exhibited absorptions for only the cis-isomers, 19, of the ozonides in 80-89% yield. The ozonides were isolated by preparative TLC on silica gel. Reduction of these ozonides with Ph₃P gave 1- or 2-naphthaldehyde. Control experiments have shown that the ozonides are stable to the photo-oxygenation conditions with less than 5% decomposition after 2 hr irradiation with DCA. Reactions run to partial conversion show no detectable amount of the isomeric trans-ozonides nor any isomerization of the starting epoxides.

For comparison, mixtures of cis- and transdinaphthyl ozonides were prepared by ozonation of the corresponding alkenes in pentane at low temperature. Treatment of cis- and trans-1,2-bis(1'-naphthyl)ethene with ozone in pentane at -78° , removal of the solvent at 0° and analysis in CD₂Cl₂ by NMR indicated a 15% yield of isomeric ozonides in a ratio of 25:75. The minor isomer exhibited the same chemical shift (δ 7.138) for the ring protons as the photo-ozonide, 19a, from 17a and 18a. Ozonation of cis-1,2-bis(2'-naphthyl)ethene gave a 40:60 mixture of ozonides in 92% yield with the same chemical shift (δ 6.555) for the minor isomer as for the photo-ozonide, 19b (m.p. 172–174°) obtained from 17b and 18b. In order to isolate the major isomer (trans-3,5-bis(2'-naphthyl)-1,2,4-trioxolane, 20b), the mixture

Epoxide	Irradiation time (min)	Ozonide	Yield (%)"
Np, , Np, Np, N, 17			
17a: $Np_1 = Np_2 = 1$ -naphthyl 17b: $Np_1 = Np_2 = 2$ -naphthyl 17c: $Np_1 = 1$ -naphthyl $Np_2 = 2$ -naphthyl	15 5 15		89 89 80
H , NP, NP, 18			
18a: $Np_1 = Np_2 = 1$ -naphthyl 18b: $Np_1 = Np_2 = 2$ -naphthyl 18c: $Np_1 = 1$ -naphthyl Np_2 = 2-naphthyl	30 15 15		80 ° 79
Ar, Ar Me 21 Me	60	Ar O Ar Me O Ar Me O Me Ar O Me	94 ⁶
$ \begin{array}{c} \text{Me} \\ \text{Ar} \\ \text{Z2} \\ \text{Ar} \\ \text{T} \\ \text{HeOC}_{\text{c}} H_{\text{c}} \end{array} $	40	(ratio of isomers) 15:85 15:85	96°

Table 2. DCA-sensitized photo-oxygenation of epoxides

* Yields were determined by 300 MHz ¹H NMR using an internal standard.

^b Combined yields of both isomers.

^c The yield of 19b from 18b was not determined due to low solubility of this epoxide in McCN. However, no *trans*-ozonide, 20b, was detected by ¹H NMR.

Quencher	E ^{ox} (V vs SCE) ^a	ke (1010 M-1 s-1)b	ΔG (kcal mol ⁻¹)
17a	1.55	1.24	-9.7
17b	1.59	1.37	-8.8
17c	1.54	1.26	- 9.9
18a	1.50	1.53	- 10.9
1 8b	1.53	4	-10.2
18c	1.52	1.52	10.4
21	1.28	1.47	-15.9
22	1.24	2.19	-16.9
Biphenyl	1.90	0.31	- 1.6

Table 3. Oxidation potentials (E_{σ}^{*}) , fluorescence quenching rate constants (k_{σ}) , and free energies for electron transfer (ΔG) .

^a Peak potentials for the irreversible oxidation of the epoxides and biphenyl were obtained by cyclic voltammetry in acetonitrile vs SCE using a platinum electrode, 0.1 M tetraethylammonium perchlorate and a scan rate of 300 m V s⁻¹.

^bRate constants for the quenching of DCA fluorescence in nitrogensaturated acetonitrile.

^c Approximate free energies for electron-transfer fluorescence quenching using oxidation peak potentials and the Weller equation (see text and Refs 8 and 12).

^d Not determined because of limited solubility in acetonitrile.

of ozonides was recrystallized several times from acetone. Examination by NMR of the material in the mother liquor after the fifth recrystallization showed enrichment (>90%) of **20b** exhibiting an absorption at δ 6.606. This material was further purified by preparative TLC and, subsequently, recrystallized from acetone to yield pure *trans*-ozonide, **20b** (m.p. 166-168°). Ozonation of *cis*- and *trans*-1-(1'-naphthyl)-2-(2'-naphthyl)ethenes in pentane at -40° gave a complex mixture of peroxidic products. The NMR spectrum of the mixture showed absorptions for the four ozonides, described above, as well as absorptions expected for *cis*- and *trans*-ozonides, **19c** and **20c**.

[†] Murray et al.¹¹ had earlier used kinetic resolution by brucine to identify the *trans* isomer of diisopropyl ozonide.

In our study of the co-sensitized photo-oxygenation of cis- and trans-2,3-diphenyloxiranes, we compared the resulting photo-ozonide to authentic cis- and transozonides prepared by ozonation of stilbene.1e The stereochemistry of these ozonides has been assigned by Criegee and Horber¹⁰ by chromatography over cellulose acetate. The chiral trans-ozonide was identified by its partial resolution on this stationary phase.[†] In order to establish the stereochemistry of the naphthyl-substituted ozonides, we conducted similar experiments utilizing HPLC over optically active (+)poly(triphenylmethyl methacrylate).⁹ As anticipated, obtained from ozonation of 2,3-bis-(2'-20b naphthyl)ethene was resolved by chromatography over this stationary phase (Fig. 1a), confirming the transdinaphthyl stereochemistry of this ozonide.



Fig. 1. (a) Chromatographic resolution of *trans*-3,5-bis-(2'-naphthyl)-1,2,4-trioxolane (20b) on a μ S-Chiralpak OT(+) column [1.5 (i.d.) × 250 mm] and Varian 5000 liquid chromatograph equipped with a UV detector. Flow rate of methanol was 0.2 ml/min. Peak 1 results from a trace impurity of 2-naphthaldehyde; the extinction coefficient at 254 nm is much larger for the aldehyde than the ozonides. Peaks 2 and 3 show the separated enantiomers of the *trans*-ozonide. (b) X-ray structure of *cis*-3,5-bis-(2'-naphthyl)-1,2,4-trioxolane (19b).

Chromatography of the photo-ozonides 19a and 19bexhibited only one peak consistent with the proposed *cis* stereochemistry. An X-ray structure of 19b has also confirmed the *cis* stereochemical assignment (Fig. 1b),†

An investigation of the stereochemistry of the reaction with *cis*- and *trans*-2,3-bis-(4'-methoxyphenyl)-2,3-dimethyloxiranes (21 and 22) has also been carried out. The electron-donating methoxy groups lower the oxidation potentials of these epoxides and, as a result, they are also reactive in the absence of BP. As expected, the ratio of the *cis*- and *trans*-ozonides, 23 and 24, is similar to that obtained from the DCA-BP co-sensitized photo-oxygenation of epoxides 13 and 14 (Table 2). Ozonides 23 and 24 have been stereochemically identified by comparison of ¹H-NMR chemical shifts to the data obtained for 15 and 16.

Oxidation potentials and fluorescence quenching

Peak potentials for the irreversible oxidation of the epoxides and biphenyl (Table 3) were obtained by cyclic voltammetry in acctonitrile vs a saturated calomel electrode (SCE). Quenching of the fluorescence of DCA by these substrates was measured in nitrogen-saturated acetonitrile using the Stern-Volmer equation:

$$I_0/I_q = 1 + k_q \tau [Q]$$

where I_0 and I_q are relative fluorescence intensities in the absence and presence of quencher (Q), τ is the lifetime of the singlet excited state of the fluorescer. Plots of I_0/I_q vs the concentration of the quencher provided values for $k_q \tau$ from which quenching rate constants (k_q) were calculated (τ for DCA in acetonitrile = 15.2 ns).⁸

The free energy change (ΔG) involved in the electrontransfer fluorescence quenching of singlet excited DCA by a quencher (Q) may be calculated by the Weller equation:¹²

$$\Delta G = 23.06[E(Q/Q^+) - E(DCA^{--}/DCA) - e_0^2/a\epsilon - \Delta E_{0,0}]$$

where
$$E(Q/Q^+)$$
 is the oxidation potential of the
quencher, $E(DCA^-/DCA)$ is the reduction potential of
DCA (-0.98 V vs SCE in acetonitrile), $e_0^2/a\epsilon$ is the
energy gained by bringing the two radical ions to
encounter distance, *a*, in the solvent of dielectric
constant, ϵ (*ca* 0.06 eV in acetonitrile) and $\Delta E_{0,0}$ is the
electronic excitation energy of DCA (2.89 eV).⁸
Although reversible oxidation potentials were not
observed with the quenchers listed in Table 3, ΔG for
electron-transfer fluorescence quenching can, never-
theless, be estimated by using the oxidation peak
potentials.

DISCUSSION

Epoxides which quench the fluorescence of DCA can undergo photo-oxygenation to form ozonides in high yield (Table 2). Kirschenheuter and Griffin³ have similarly found that a strained bicyclic epoxide can be converted to the corresponding ozonide. Futamura *et* al.² have reported that *p*-methoxyphenyl-substituted epoxides also yield ozonides.[‡]

We have observed that biphenyl (BP) can be used to co-sensitize the photo-oxygenation of various arylsubstituted epoxides which are unreactive in the presence of DCA alone. Although the mechanism for BP co-sensitization has not yet been fully elucidated, we have offered the following explanation. BP is more easily oxidized than the epoxides shown in Table 1 and consequently, quenches singlet excited DCA more efficiently to generate BP⁺⁻ and DCA⁻⁻ (Scheme 1). Although subsequent electron-transfer from these epoxides is endothermic, this process is favoured by the longer lifetime of BP+ compared to singlet excited DCA. Mattes and Farid¹³ have made a similar suggestion for the co-sensitization by phenanthrene and 9-cyanoanthracene of the electron-transfer dimerization of phenyl vinyl ether. We have pointed out that co-sensitization by BP may be considered mechanistically analogous to homogeneous redox catalysis of electrode reactions.¹⁴ For example, direct electroreductions of aliphatic halides (RX) generally occur at very slow rates and require large overvoltages. However, electrochemically generated radical anions of aromatic hydrocarbons can be employed as catalytic agents. Electron-transfer from this species to RX forms

$${}^{1}\text{DCA}^{\ddagger} + \text{BP} \longrightarrow \text{BP}^{\ddagger} + \text{DCA}^{\intercal}$$

$${}^{1}\text{DCA}^{\ddagger} + \bigwedge_{\substack{Ar & Ar \\ 9,10 \text{ } ar = \text{Ph} \\ 17,18 \text{ } Ar = \text{Np} \\ DCA^{\intercal} + 0_{2} \longrightarrow 0_{2}^{\intercal} + 0_{2}^{\intercal} + \text{DCA}$$

$${}^{Ar} + 0_{2}^{\intercal} \longrightarrow 0_{2}^{\intercal} + 0_{2} \longrightarrow 0_{2}^{\intercal} + \text{DCA}$$

$${}^{Ar} + 0_{2}^{\intercal} \longrightarrow 0_{2}^{\intercal} + 0_{2} \longrightarrow 0_{2}^{\intercal} + 0_{2} \longrightarrow 0_{2}^{\intercal} + 0_{2}^{\intercal} \longrightarrow 0_{2}^{$$

[†] Full details of the X-ray structure of ozonide, 19b will be published separately.

[‡] Our stereochemical results with 2,3-diaryloxiranes stand in contrast to those of Futamura *et al.*³ in which the formation of *trans*-ozonides was suggested.

the unstable RX^{-1} and regenerates the hydrocarbon. Although this reversible step is energetically unfavourable, it is driven by the irreversible decomposition of RX^{-1} . A similar mechanism may be involved in co-sensitization by BP. Endothermic electron-transfer from epoxides, such as 9 and 10, to BP⁺⁺ would generate the unopened epoxide radical cation. This step would be driven by the subsequent generation of the ring-opened radical cation and trapping by superoxide to form the ozonide.

The stereochemistry of these reactions provides additional insight into the mechanism. DCA-BP co-sensitized photo-oxygenation of *cis*- and *trans*-2,3diphenyloxirane (9 and 10) yields exclusively *cis*ozonide 11. The same course is followed for the DCA-sensitized photo-oxygenation of the 2,3-dinaphthyloxiranes, 17 and 18, which do not require BP co-sensitization. These striking stereochemical results would seem to rule out a mechanism involving attack of O_2^{-1} on the epoxide radical cation to give long-lived biradical or zwitterion intermediates as such intermediates should lead to a mixture of isomeric ozonides.

The stereochemistry of these reactions is, however, consistent with the intermediacy of ring-opened radical cations which may be formed either directly by epoxide quenching of singlet excited DCA or indirectly by electron-transfer from the epoxide to BP⁺⁺ (Scheme 1). As barriers to rotation in these species are quite low,^{15,16} equilibration can occur to afford the most stable E,E-conformation. Back electron transfer from O_2^{-} or DCA⁻ to the radical cations would yield the corresponding carbonyl ylides. Subsequent concerted addition of singlet oxygen as a dipolarophile to the ylides would give the observed products. Manring et al.¹⁷ have shown that singlet oxygen is formed in DCAsensitized photo-oxygenations by energy transfer from singlet and triplet excited DCA to oxygen. Singlet oxygen may also be generated as a result of back electron-transfer from O_2^- to the radical cation.18

In contrast to the stereoselective formation of cisozonides from 2,3-diaryloxiranes, photo-oxygenation of the tri- and tetra-substituted epoxides affords mixtures of cis- and trans-ozonides (Tables 1 and 2). Formation of the isomeric ozonides may involve an equilibrium mixture of E,E and E,Z conformers of the ring-opened radical cations. Subsequent reduction would yield the corresponding carbonyl ylides which would be trapped by singlet oxygen to give the mixture of ozonides. The proposed intermediacy of carbonyl ylides and their reaction with singlet oxygen to form ozonides is consistent with the previously reported reaction of photogenerated carbonyl ylides with dipolarophiles.¹⁹ Of particular relevance are the observations of Wong et al.15 and Albini and Arnold.20 1,4-Dicyanonaphthalene was used as a sensitizer to generate carbonyl ylides by electron-transfer processes. These ylides could be trapped to yield tetrahydrofurans. Reaction of epoxides 9, 10, 17 and 18, gave products with a cis-diaryl relationship.

Investigations are currently in progress on the mechanistic details of BP co-sensitization. However, we have found that rate enhancements in the presence of BP can be obtained for a variety of DCA-sensitized photo-oxygenations. Results of these studies will be reported shortly.

EXPERIMENTAL

General. ¹H-NMR spectra were taken on a Nicolet 300 MHz instrument. Chemical shifts are reported in δ -values downfield from TMS. Mass spectra were taken on an AEI MS-902 mass spectrometer. HPLC analyses were carried out on a Varian 5000 instrument interfaced with a Vista 401 data section. An AUTECH C-18 reverse phase column (25 cm × 4.6 mm, 5 µm) eluted with a gradient of 30–100% acetonitrile in water was used for HPLC. Absorption spectra were recorded on a Cary 219 UV-visible spectrometer. An Aminco-Bowman spectrophotofluorometer was used for fluorescence quenching studies. All m.ps were determined with a Thomas Hoover m.p. apparatus and are reported uncorrected. Elemental analyses were performed by Midwest Microlab, Ltd.

Materials. The purification of acetonitrile, biphenyl and 9,10-dicyanoanthracene has been described previously.¹ Samples of *cis* and *trans* isomers of α -methylstilbene,²¹.²² 1,2-bis-(1'-naphthyl)ethene,¹⁵ 1,2-bis-(2'-naphthyl)ethene¹³ and 1-(1'-naphthyl)-2-(2'-naphthyl)ethene²³ were prepared by lit. methods. *cis*- and *trans*-2,3-Bis-(4-methoxyphenyl)-2-butenes were synthesized by coupling 4-methoxyacetophenone in the presence of TiCl₃ and lithium aluminum hydride in THF.²⁴ The physical characteristics of these alkenes are in agreement with their reported properties.²⁵

Preparation of epoxides. Epoxides 1, 3, 5, 7, 9 and 10 are known compounds and their physical characteristics have been reported previously.¹⁴ In general, the epoxides for this study were prepared by treatment of the appropriate alkene with *m*-chloroperbenzoic acid in dichloromethane at $10-15^{\circ}$ for 8-24 br. They were purified either by recrystallization alone or flash silica gel chromatography followed by recrystallization.

cis-2,3-Dimethyl-2,3-diphenyloxirane (13a): m.p. 52-53° (lit.²⁶ m.p. 50-51°); NMR (CDCl₃) & 7.052-7.252(10H, m) and 1.808 (6H, s). trans-2,3-Dimethyl-2,3-diphenyloxirane (14a): m.p. 110° (EtOH), (lit.²⁶ m.p. 106°); NMR (CDCl₃) δ 7.265-7.512 (10H, m) and 1.286 (s, 6H). cis-2-Methyl-2,3-diphenyloxirane (13b): m.p. $51-52^{\circ}$; NMR (CDCl₃) δ 7.043-7.257 (10H, m), 4.152 (1H, s) and 1.787 (3H, s). trans-2-Methyl-2,3-diphenyloxirane (14b): m.p. 46-47°; NMR (CDCl₃)δ 7.298-7.478 (10H, m), 3.976 (1H, s) and 1.467 (3H, s). cis-2,3-Bis-(1'-naphthyl)oxirane (17a): m.p. 169-171° (lit.²² m.p. 167.5-168.5°); NMR (CDCl₃) δ 7.179-8.236 (14H, m) and 5.122 (2H, s). trans-2,3-Bis-(1'-naphthyl)oxirane (18a): m.p. 145-146° (lit.²² m.p. 142-144°); NMR (CDCl₃) δ 7.249-8.051 (14H, m) and 4.511 (2H, s). cis-2,3-Bis-(2'-naphthyl)oxirane (17b): m.p. 113-114° (lit.¹⁵ m.p. 112-115°); NMR (CDCl₃) δ 7.141-7.828 (14H, m) and 4.597 (2H, s). trans-2,3-Bis-(2'naphthyl)oxirane(18b): m.p. 211-212° (lit. 15 m.p. 215°); NMR (CDCl₃) & 7.310-8.129 (14H, m) and 4.142 (2H, s). cis-2-(1'-Naphthyl)-3-(2'-naphthyl)oxirane (17c): m.p. $128-129^{\circ}$; NMR (CDCl₃) δ 7.200-8.215 (14H, m), 4.881 (1H, d, J = 4.4 Hz) and 4.734 (1H, d, J = 4.4 Hz); satisfactory analysis. trans-2-(1'-Naphthyl)-3-(2'-naphthyl)oxirane (18c): m.p. 101-102°; NMR (CDCl₃) & 7.372-8.212 (14H, m), 4.590 (1H, s) and 4.031 (1H, s); satisfactory analysis. cis-2,3-Dimethyl-2,3-bis-(4'methoxyphenyl)oxirane : oil; NMR (CDCl₃) & 7.008 (4H, d, J = 8.6 Hz), 6.604(4H, d, J = 8.6 Hz), 3.671(6H, s) and 1.759(6H, s); satisfactory analysis. trans-2,3-Dimethyl-2,3-bis-(4'methoxyphenyl)oxirane: m.p. 127.5-129°; NMR (CDCl₃) δ 7.329(4H, d, J = 8.49 Hz), 6.914(4H, d, J = 8.35 Hz), 3.828(6H, J)s) and 1.265 (6H, s); satisfactory analysis.

General procedure for the photo-oxygenation of epoxides. A 450 W medium-pressure Hanovia lamp surrounded by a CuSO₄-filter soln¹ was employed for the photo-oxygenation reactions. An irradiation vessel fitted with a gas inlet tube was charged with the appropriate oxirane $(1 \times 10^{-2} \text{ M})$, biphenyl $(1 \times 10^{-2} \text{ M})$ if required, and 9,10-dicyanoanthracene (6 $\times 10^{-4} \text{ M})$ in dry acetonitrile and placed in a water bath at 0-5°. Dry O₂ was bubbled through the soln at a slow rate and the soln irradiated for a period of from 4 min to 3 hr. Aliquots were removed at regular intervals and analysed by HPLC and NMR. For analysis of the reaction mixture by NMR, the solvent was removed in vacuo at 0° and the products quantitated by adding an appropriate internal standard in either CDCl₃ or CD₂Cl₂. The ozonides were isolated by preparative TLC on silica and recrystallized. The characterization of ozonides 2, 4, 6, 8, 11 has been previously described.¹⁶

3-Methyl-3,5-diphenyl-1,2,4-trioxolanes 15b and 16b. A mixture of the ozonides 15b and 16b in a 25:75 cis-trans ratio was obtained by photo-oxygenation of either the cis- or trans-oxirane. The mixture was purified by preparative TLC over silica with hexane-benzene (1:4) followed by recrystallization for the trans isomer. cis-15b: liquid; NMR (CDCl₃) δ 7.262-7.425 (10H, m), 6.162 (1H, s) and 1.994 (3H, s). trans-16b: m.p. 52-53° (petrol ether); NMR (CDCl₃) δ 7.260-7.603 (10H, m), 6.231 (1H, s) and 1.852 (3H, s).

3,5-Dimethyl-3,5-diphenyl-1,2,4-trioxolanes 15a and 16a. A mixture of the ozonides 15a and 16a in approximately a 35:65 cis-trans ratio was obtained by photo-oxygenation of either the cis- or trans-oxirane. The mixture was purified by preparative TLC over silica with benzene-hexane (3:7) followed by recrystallization for the trans isomer. cis-15a: liquid; NMR (CDCl₃) δ 7.201-7.458 (10H, m) and 1.878 (6H, s). trans-16a: m.p. 95-96°; NMR (CDCl₃) δ 7.255-7.607 (10H, m) and 1.652 (6H, s).

cis-3,5-Bis-(1'-naphthyl)-1,2,4-trioxolane (19a). Isolated in 78% yield from epoxide 17a: m.p. $87-89^{\circ}$ (pentane); NMR (CD₂Cl₂) δ 7.409-8.272 (14H, m) and 7.138 (2H, s).

cis-3,5-Bis-(2'-naphthyl)-1,2,4-trioxolane (19b). Isolated in 75% yield from epoxide 17b: m.p. $172-174^{\circ}$ (acetone); NMR (CD₂Cl₂) δ 7.500–8.636 (14H, m) and 6.555 (2H, s).

cis-3-(1'-Naphthyl)-5-(2'-naphthyl)-1,2,4-trioxolane (19c). Isolated in 35% yield from epoxide 17c: m.p. 108-110° (pentane-CH₂Cl₂); NMR (CD₂Cl₂) δ 7.432-8.227 (14H, m), 7.077 (1H, s) and 6.614 (1H, s).

trans-3,5-Bis-(2'-naphthyl)-1,2,4-trioxolane (20b). This ozonide was obtained by purifying the mixture of ozonides prepared by ozonation of cis-1,2-bis-(2'-naphthyl)ethene in pentane at -40° . The mixture of isomers was repeatedly recrystallized from acetone. Analysis by NMR of the material in the mother liquor after the fifth recrystallization showed >90% of the desired trans isomer (ring proton at δ 6.606). This material was further purified by preparative TLC (benzene-hexane, 3:7) and, subsequently, recrystallized from acetone: m.p. 166-168°; NMR (CD₂Cl₂) δ 7.505-8.182 (14H, m) and 6.606 (2H, s).

Resolution of chiral ozonides by high-performance liquid with (+)-poly-(triphenylmethyl methacrylate) as the stationary phase. A JASCO μ s-Chiralpak OT(+)† reverse-phase column (250 × 1.5 mm) containing (+)-poly-(triphenylmethyl methacrylate) as the stationary phase was used on a Varian 5000 liquid chromatograph for resolution of chiral ozonides. The column was eluted with HPLC grade MeOH at a flow rate of 0.2 ml/min at ambient temp. trans-20b was completely resolved by this column as shown in Fig. 1(a). cis-19b, when subjected to the above conditions, led to a single peak in the chromatograph. Each of the above isomers showed a single peak with different retention times on standard C-18 reverse-phase columns. The Chiralpak column was also used to stereochemically identify cis and trans isomers of 15a and 16a.

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[†] This HPLC column is commercially available under the trade name Chiralpak OT(+) from Jasco Inc., 218 Bay Street, Easton, MD 21601, U.S.A.