

## Photoinduced Electron Transfer Reaction. Part 3.<sup>1</sup> 9,10-Dicyanoanthracene-sensitized Photo-oxidation of Electron-rich Stilbene Oxides

Shigeru Futamura, Shosaku Kusunose, Hiroyuki Ohta,\* and Yoshio Kamiya

Department of Reaction Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo, Japan 113

The 9,10-dicyanoanthracene (DCA)-sensitized photo-oxygenation of the electron-rich stilbene oxides (1) gives the ozonides (2) almost quantitatively. The fluorescence of DCA is quenched by (1) at a diffusion-controlled rate and the above reaction is quenched by polymethoxybenzenes which indicates that an electron transfer mechanism is involved. The quantum yield for ozonide formation varies from 0.5 for *trans*-2-(4-methoxyphenyl)-3-phenyloxirane (1d) to 2.4 for *trans*-2,3-bis(4-methoxyphenyl)-2,3-diethyloxirane (1h), suggesting a duplex reaction mechanism such as photo-oxygenation by superoxide and a Barton mechanism after the initial electron transfer from the epoxides (1) to the excited singlet state of DCA.

Recently, particular attention has been focused on photo-sensitized electron transfer reactions.<sup>2-4</sup> Singlet oxygen is widely accepted as the active oxygen species in extensive dye-sensitized photo-oxygenation reactions.<sup>5</sup> As Foote *et al.* have warned,<sup>6</sup> however, these reactions often involve an electron transfer from the substrate to the excited singlet state of the sensitizer. In these processes, oxygen is known to play an important role as an electron carrier which efficiently circulates in the catalytic system<sup>7</sup> and/or as an active oxygenating agent<sup>1,8-13</sup> such as the superoxide ion radical and triplet molecular oxygen.

In this work, 9,10-dicyanoanthracene (DCA) is used as an electron-deficient sensitizer. It can be excited at wavelengths >400 nm and can act as a good electron acceptor as it has a relatively low reduction potential [ $E_{1/2}^{\text{RED}}(\text{DCA}) - 0.97 \text{ V vs. SCE}$ ]. Because it is so widely applicable, a wide range of DCA-sensitized photo-oxidation reactions have already been reported for olefins,<sup>8</sup> acetylenes,<sup>9</sup> benzene derivatives,<sup>10</sup> phenols,<sup>1a</sup> and sulphides.<sup>11</sup>

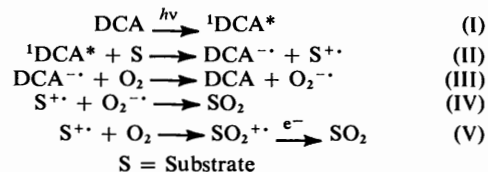
Two general mechanisms have been prepared to interpret these reactions depending on the substrate and the reaction conditions. An attractive mechanism (Scheme 1) is the photo-oxygenation of the substrate by superoxide, because the second electron transfer from DCA<sup>-•</sup> to O<sub>2</sub> rapidly affords O<sub>2</sub><sup>-•</sup> [equation (III)] and the oxidation is very likely to proceed catalytically [equations (I), (II), and (IV)].<sup>8a-c, 10b</sup> An alternative mechanism is also possible [equations (I), (II), and (V)], as some radical cations are known to react with triplet molecular oxygen,<sup>12,13</sup> thus competing effectively with the reactions in equations (I)–(IV), to afford photo-oxygenated products.

We were interested in the photo-sensitized electron transfer reactions of strained molecules, in particular of epoxide, in which the 2-oxapropyl radical cation is an intermediate.

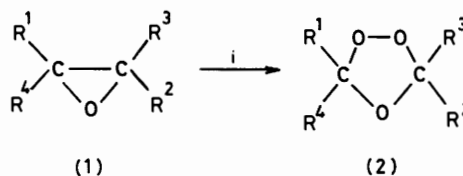
We have found that the DCA-sensitized photo-oxidation reaction of electron-rich stilbene oxides gives the corresponding ozonides almost quantitatively *via* an electron transfer mechanism.<sup>1b</sup>

### Results and Discussion

*trans*-2,3-Bis(4-methoxyphenyl)oxirane (1f) was irradiated in acetonitrile in the presence of DCA for 3 h to afford 3,5-bis(4-methoxyphenyl)trioxolane (2f) almost quantitatively. Other ozonides were also obtained in excellent yields from the corresponding electron-rich epoxides such as *trans*-2-(4-methoxyphenyl)-3-phenyloxirane (1d), *trans*-2-(4-methoxy-



Scheme 1.



- a; R<sup>1</sup> = R<sup>2</sup> = Ph, R<sup>3</sup> = R<sup>4</sup> = H  
 b; R<sup>1</sup> = R<sup>2</sup> = Ph, R<sup>3</sup> = R<sup>4</sup> = Me  
 c; R<sup>1</sup> = R<sup>2</sup> = *p*-MeC<sub>6</sub>H<sub>4</sub>, R<sup>3</sup> = R<sup>4</sup> = H  
 d; R<sup>1</sup> = *p*-MeOC<sub>6</sub>H<sub>4</sub>, R<sup>2</sup> = Ph, R<sup>3</sup> = R<sup>4</sup> = H  
 e; R<sup>1</sup> = *p*-MeOC<sub>6</sub>H<sub>4</sub>, R<sup>3</sup> = Ph, R<sup>2</sup> = R<sup>4</sup> = H  
 f; R<sup>1</sup> = R<sup>2</sup> = *p*-MeOC<sub>6</sub>H<sub>4</sub>, R<sup>3</sup> = R<sup>4</sup> = H  
 g; R<sup>1</sup> = *p*-MeOC<sub>6</sub>H<sub>4</sub>, R<sup>2</sup> = *p*-MeC<sub>6</sub>H<sub>4</sub>, R<sup>3</sup> = R<sup>4</sup> = H  
 h; R<sup>1</sup> = R<sup>2</sup> = *p*-MeOC<sub>6</sub>H<sub>4</sub>, R<sup>3</sup> = R<sup>4</sup> = Et  
 i; R<sup>1</sup> = R<sup>2</sup> = R<sup>3</sup> = R<sup>4</sup> = Ph

Reagents: i, *hν*, DCA, O<sub>2</sub>, MeCN

phenyl)-3-(4-methylphenyl)oxirane (1g), and *trans*-2,3-bis(4-methoxyphenyl)-2,3-diethyloxirane (1h); however no ozonide was obtained from the DCA-sensitized photo-oxidation of *trans*-2,3-diphenyloxirane (1a), *trans*-2,3-diphenyl-2,3-dimethyloxirane (1b), and tetraphenyloxirane (1i), even after prolonged irradiation (see Table 1). Reduction of the product with triphenylphosphine afforded the corresponding carbonyl compounds and triphenylphosphine oxide in stoichiometric yields, supporting the proposed ozonide structure for (2).

DCA was recovered quantitatively and control experiments showed that its presence was essential for ozonide formation.

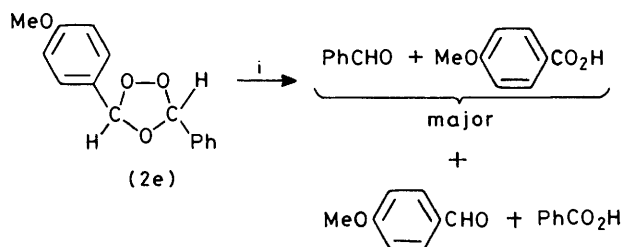
Irradiation of the ozonide (2e) (10<sup>-2</sup>M) in the presence of DCA (10<sup>-4</sup>M) for 2 h led to complete consumption of (2e) and gave benzaldehyde and *p*-anisic acid as the major products along with small amounts of *p*-anisaldehyde and benzoic acid.

An unusual substituent effect observed in the reaction

**Table 1.** DCA-sensitized photo-oxidation reaction of stilbene oxides (1)

Epoxide	Irrad. time (h)	Yield of ozonide (2) (%) <sup>a</sup>
(1a)	18	<i>b</i>
(1b)	23	<i>b</i>
(1c)	19	<i>b</i>
(1d)	1	100
(1e)	6	<i>c</i>
(1f)	3	100
(1g)	2	90
(1h)	1	88
(1i)	24	<i>b</i>

<sup>a</sup> Based on the initial concentration of (1). <sup>b</sup> Compound (1) does not react and is recovered quantitatively. <sup>c</sup> Benzaldehyde and *p*-anisic acid were obtained as the major products, with no ozonide.

**Scheme 2.** Reagents: *i*, *hν*, DCA, O<sub>2</sub>, MeCN, 2 h

prompted us to investigate the interaction between <sup>1</sup>DCA\* and compounds (1). As Table 2 shows, the epoxides (1d), (1f), (1g), and (1h) quenched the fluorescence of <sup>1</sup>DCA\* at a diffusion-controlled rate, while no quenching occurred with unreactive epoxides such as (1a), (1b), and (1i). The Rehm-Weller equation<sup>15</sup> predicts that an electron transfer proceeds exothermically from (1f) or (1h) to <sup>1</sup>DCA\*, but much less exothermically from (1a) or (1i) to <sup>1</sup>DCA\* (see Table 2). Addition of 0.1 equiv. (10<sup>-3</sup>M) of methoxybenzenes quenched the DCA-sensitized photo-oxygenation of (1h), and a correlation was observed between Δ*G* for the electron transfer from the methoxybenzenes to an epoxide radical cation (1g)<sup>+</sup> and the observed quenching efficiencies (see Table 3).

All these facts indicate that the DCA-sensitized photo-oxidation reaction of (1) is initiated by an electron transfer from (1) to <sup>1</sup>DCA\*, as shown in equation (4) (Scheme 3).

Although the quenching rate constant for (1c) is larger than 10<sup>10</sup> mol<sup>-1</sup> l s<sup>-1</sup> no ozonide is produced. The lack of reactivity of (1c) could be ascribed to back electron transfer from DCA<sup>-•</sup> to (1c)<sup>+•</sup>.†

Under the reaction conditions, singlet oxygen can be generated by the transfer of energy from <sup>3</sup>DCA\* to O<sub>2</sub> [equation (3)] or by the back electron transfer from O<sub>2</sub><sup>-•</sup> to (1)<sup>+•</sup> [equation (6)]. Thus, singlet oxygenation of (1h) was carried out, using Rose Bengal, Methylene Blue, or Ru(bpy)<sub>3</sub>-Cl<sub>2</sub> as a triplet sensitizer. Even after prolonged irradiation (>20 h), no ozonide was obtained, and (1h) was recovered quantitatively in each case. From these findings, <sup>1</sup>O<sub>2</sub> can be ruled out as the active oxygen species in the production of the ozonides [*i.e.* equation (11) can be neglected].

† Since ISC in DCA is extremely inefficient, little <sup>3</sup>DCA should be produced in this process [equation (2)]. However, exciplex formation may prompt triplet formation and therefore the possibility of <sup>1</sup>O<sub>2</sub> formation still remains. We thank a referee for reminding us of this point.

**Table 2.** Quenching of DCA fluorescence by stilbene oxides (1)

Compound	<i>k<sub>q</sub></i> (mol <sup>-1</sup> l s <sup>-1</sup> ) <sup>a</sup>	<i>E</i> <sub>1/2</sub> <sup>OX</sup> (V vs. SCE) <sup>b</sup>	Δ <i>G</i> <sub>ET</sub> (kcal mol <sup>-1</sup> ) <sup>c</sup>
(1a)		1.98 <sup>c</sup>	-0.2
(1b)			
(1c)	1.09 × 10 <sup>10</sup>		
(1d)	2.95		
(1e)	1.00		
(1f)	2.00	1.30 <sup>d</sup>	-15.5
(1g)	1.71		
(1h)	1.64	1.21 <sup>d</sup>	-18.7
(1i)		1.98 <sup>c</sup>	-0.2

<sup>a</sup> Rate constant for quenching of DCA fluorescence from Stern-Volmer plot. τ<sub>DCA</sub> 8.0 ns. See ref. 1a. <sup>b</sup> Oxidation potential. <sup>c</sup> See ref. 14. <sup>d</sup> Measured in MeCN, concentration of (1) (10<sup>-3</sup>M), tetrabutylammonium perchlorate (10<sup>-4</sup>M) as supporting electrolyte, ferrocene (10<sup>-3</sup>M) as internal standard. <sup>e</sup> Free energy change for an electron transfer from (1) or (2d) to <sup>1</sup>DCA\*, and given by Δ*G*<sub>ET</sub> = 23.06 [*E*<sub>1/2</sub><sup>OX</sup>(D<sup>+•</sup>/D) - *E*<sub>1/2</sub><sup>RED</sup>(DCA<sup>-•</sup>/DCA) - *e*<sup>2</sup>/ε*a* - Δ*E*<sub>0,0</sub>(DCA)]. See ref. 18. *E*<sub>1/2</sub><sup>RED</sup>(DCA<sup>+•</sup>/DCA) - 0.98 V, Δ*E*<sub>0,0</sub>(DCA) 2.89 eV (see ref. 19), *e*<sup>2</sup>/ε*a* = 0.06 in MeCN.

**Table 3.** Quenching of the DCA-sensitized photo-oxygenation of *trans*-2,3-bis(4-methoxyphenyl)oxirane (1h) by methoxybenzenes<sup>a</sup>

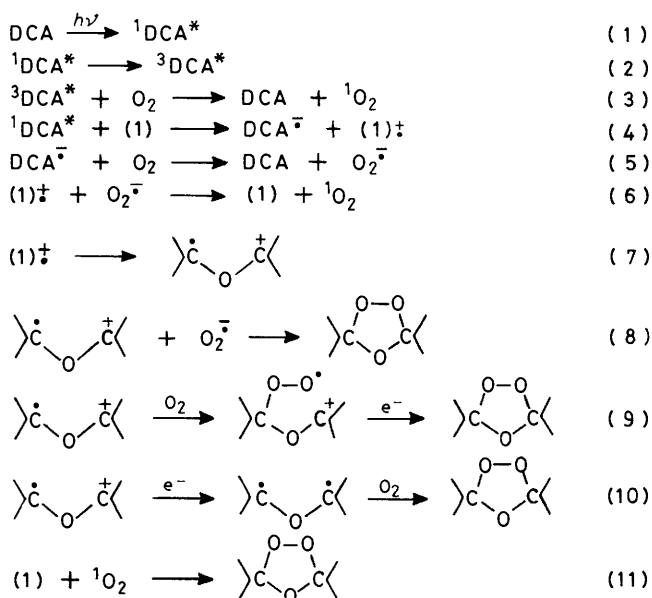
Quencher <sup>b</sup>	<i>E</i> <sub>1/2</sub> <sup>OX</sup> (V vs. SCE) <sup>c</sup>	Observed quenching (%)	Δ <i>G</i> <sub>ET</sub> (kcal mol <sup>-1</sup> ) <sup>d</sup>
TMB	1.12	97	-3.5
<i>p</i> -DMB	1.34	63	+1.6
<i>m</i> -DMB	1.49	39	+5.1

<sup>a</sup> Oxygen bubbling in MeCN at room temperature. <sup>b</sup> [Quencher] = 10<sup>-3</sup>M. <sup>c</sup> Oxidation potential of quencher. See ref. 8c. <sup>d</sup> Free energy change for the following one electron transfer process: Quencher + (1)<sup>+•</sup> → Quencher<sup>+•</sup> + (1). Δ*G*<sub>ET</sub> is given by Δ*G*<sub>ET</sub> = 23.06 [*E*<sub>1/2</sub><sup>OX</sup>(Q<sup>+•</sup>/Q) - *E*<sub>1/2</sub><sup>OX</sup>[(1h)<sup>+•</sup>/(1h)] - 0.06]. *E*<sub>1/2</sub><sup>OX</sup>[(1h)<sup>+•</sup>/(1h)] = 1.21 V vs. SCE. See Table 2. TMB = 1,2,4-Trimethoxybenzene, *p*- and *m*-DMB = *p*- and *m*-dimethoxybenzene.

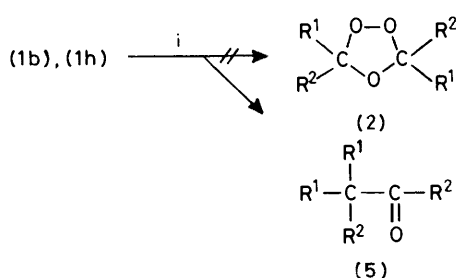
Miller *et al.* have reported that tetraphenylethylene oxide radical cation, formed by anodic oxidation, is cleaved at the C-C bond to afford benzophenone as a final product,<sup>14</sup> and more recently, Baumann and MacLeod have shown that 2-oxapropyl radical cation is the most stable of the isomers of ethylene oxide radical cation, with the aid of *ab initio* calculations.<sup>17</sup> These experimental and theoretical studies suggested, by analogy, that the C-C bond cleavage of the stilbene oxide radical cation (1)<sup>+•</sup> would occur rapidly to afford the 2-oxapropyl radical cation in an aprotic solvent such as acetonitrile under the reaction conditions. This species could then undergo various reactions, such as (i) coupling with superoxide [equation (8)], (ii) coupling with O<sub>2</sub> followed by reductive cyclization [equation (9)], and (iii) reduction followed by coupling with O<sub>2</sub> [equation (10)].<sup>18</sup>

These possibilities were investigated by control experiments using trityl tetrafluoroborate and KO<sub>2</sub>.

As shown in Scheme 4, (1b) and (1h) rapidly rearranged to afford the ketone (5) quantitatively in the presence of trityl tetrafluoroborate under air, and no ozonide was obtained. Adding KO<sub>2</sub> before or after trityl tetrafluoroborate gave similar results, (5) being obtained almost quantitatively. In the above reactions, trityl tetrafluoroborate is considered to act as an acid catalyst, as reported by House.<sup>19</sup> The reactivity of (1) contrasts markedly with that of 1,2-diarylcyclopropane, which can be oxidized to 1,2-dioxolane in the presence of



Scheme 3.

Scheme 4. Reagents: *i*, Ph<sub>3</sub>C<sup>+</sup>BF<sub>4</sub><sup>-</sup>, air, MeCN

trityl tetrafluoroborate under air.<sup>20</sup> The difference between the two may be ascribed to the greater basicity of (1) due to an oxygen atom on the three-membered ring.

These unsuccessful results prompted us to measure the quantum yields for ozonide formation from epoxides. As Table 4 shows, the quantum yield decreases in the order (1g) > (1e) > (1f) > (1c), which parallels the electron-donating abilities of compounds (1); the quantum yields for the highly reactive derivatives (1h) and (1f) exceed unity. This fact suggests that some sort of chain reaction is involved in the ozonide formation.\* Moreover, the concentration of (1) affects the quantum yield, as can be observed in the reaction of (1h) to give (2h). These facts lead us to assume that electron transfer from electron-rich epoxides such as (1h) and (1f) to 1,3-radical cations [equation (10)] and 1,5-peroxy radical cations [equation (9)]<sup>21</sup> is favoured, and that the contribution of equations (9) and (10) is greater than that of equation (8) for (1h) and (1f).

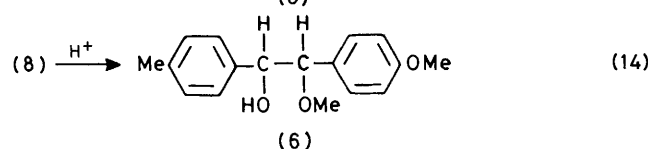
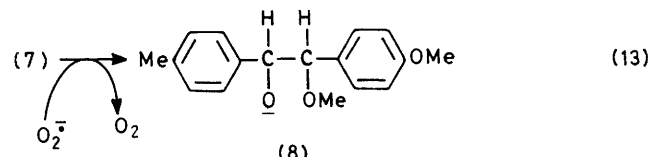
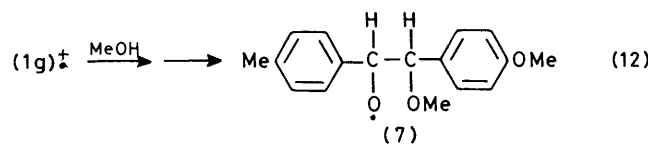
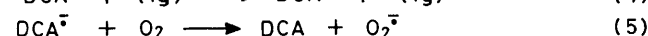
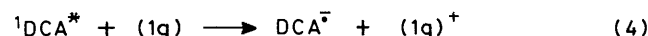
It is well known that radical cations are trapped by alcohol to afford *anti*-Markovnikov adducts;<sup>22</sup> however, (1g) was quantitatively recovered when it was irradiated with DCA in

\* Farid *et al.* have proposed a Barton mechanism for the DCA-sensitized photo-oxidation of 1,2-diphenylcyclopropane derivatives as the quantum yield for its conversion is *ca.* 20 (see ref. 8a). Saito *et al.* explain the DCA-sensitized photo-oxidation reaction of alkylbenzenes in terms of a free-radical chain mechanism. See ref. 10a.

Table 4. Quantum yields and relative rates for ozonide formation from stilbene oxides (1)<sup>a</sup>

Epoxide	Concn. (M)	Φ	<i>k</i> <sub>rel.</sub>
(1d)	10 <sup>-2</sup>	0.5	0.25
(1f)	10 <sup>-2</sup>	2.1	1.0
(1g)	10 <sup>-2</sup>	1.1	0.51
(1h)	10 <sup>-2</sup>	2.4 ± 0.4	1.1
	5 × 10 <sup>-2</sup>	2.7	1.3
	10 <sup>-3</sup>	0.3	0.12

<sup>a</sup> Potassium ferrioxalate actinometry, λ<sub>irrad.</sub> 405 nm.



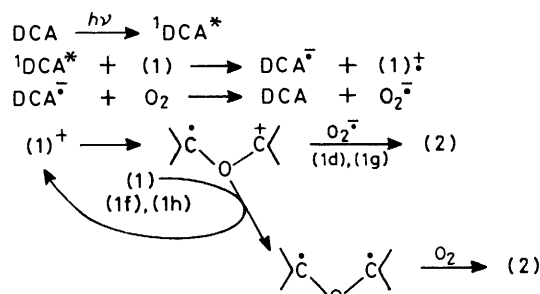
Scheme 5.

MeOH under nitrogen for 20 h. On the other hand, an adduct of MeOH and (1g), (6), was obtained in modest yield with no ozonide formation when oxygen was bubbled through.† These facts imply that oxygen acts as an electron carrier [equations (5) and (13) in Scheme 5] and that the possibility of transfer of an electron from DCA<sup>-</sup> or (1g) to the alkoxy radical (7) can be neglected.

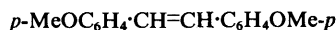
Thus the lower quantum yields for ozonide formation from (1d) and (1g) were confirmed, and the contribution of the possible electron transfer from (1d) or (1g) to 1,3-radical cations [equation (10)] and 1,5-peroxy radical cations [equation (9)] shown to be small or non-existent. Our results reveal that a duplex photo-oxygenation mechanism operates in the DCA-sensitized photo-oxidation reactions of stilbene oxides (1) (see Scheme 6), which is dependent on the substituents on the aromatic rings; thus photo-sensitized electron-transfer oxidation reactions cannot be interpreted in terms of the simple alternatives, oxygenation by superoxide or the Barton mechanism.

The stereochemistry of the ozonide was still uncertain as it was formed *via* a radical ion mechanism. Two experiments were carried out to determine the stereochemistry of (2): DCA-sensitized photo-oxidation of the *cis*-epoxide (1e), and ozonation of the *trans*-bis(4-methoxyphenyl)ethylene (3).

† The reaction is extremely complex and the formation of carbonyl compounds is suggested by i.r. spectroscopy. It is possibly due to the secondary decomposition of ozonide and generation of hydroperoxy radical by deactivation of superoxide in a protic solvent such as methanol.



Scheme 6.



(3) *trans*  
(4) *cis*

Complete consumption of (1e) required irradiation for 6 h [1 h for (1d)] in its DCA-sensitized photo-oxidation, and only the degradation products, benzaldehyde, *p*-anisaldehyde, benzoic acid, and *p*-anisic acid, were obtained.

As Table 5 shows, the  $k_q$  value decreases in the order (1d) > (4d) > (1e). This suggests that (1e) is less reactive than (1d) and that (4d) is degraded to aldehydes and acids by transfer of an electron to  ${}^1\text{DCA}^*$  during the reaction.

Ozonation of (3) in  $\text{CCl}_4$  at  $-20^\circ\text{C}$  gave *p*-anisaldehyde (80%) and small amounts of an ozonide. The methine proton on the trioxolane ring of the latter product appeared at  $\delta$  6.13 ( ${}^1\text{H}$  n.m.r. spectroscopy), identical with that of (2e). N.m.r. spectroscopy also showed two peaks at  $\delta$  6.13 and 6.18 in the reaction mixture from *cis*-bis(4-methoxyphenyl)ethylene (4), suggesting the formation of an isomeric mixture of ozonides. These findings support the proposal that the *trans*-ozonide (2) was the product in the DCA-sensitized photo-oxidation reaction of (1).

To further extend the applicability of the photo-sensitized electron transfer oxygenation of epoxides, the DCA-sensitized photo-oxidation reaction of (1a) was carried out in the presence of a better electron donor such as biphenyl.<sup>23</sup> Nearly 40% of (1a) had been converted after 3 h, but only benzaldehyde and benzoic acid, which arose from the decomposition of the ozonide, were obtained and no ozonide was detected by  ${}^1\text{H}$  n.m.r. spectroscopy.

In conclusion, we have shown that the DCA-sensitized photo-oxidation of electron-rich stilbene oxides gives ozonides in excellent yields *via* an electron transfer mechanism.

## Experimental

The g.c. analyses were carried out on a Shimadzu GC-6A-FID apparatus equipped with a column of 5% OV 17 on Chromosorb P. The products were analyzed on a Shimadzu liquid chromatograph LC-3A with a column of  $\mu$ -PORASIL (silica gel). The i.r. spectra were taken on a Shimadzu IR-420 Infrared spectrophotometer. The n.m.r. spectra were obtained on a Varian EM 360A NMR spectrometer (60 MHz), using  $\text{Me}_4\text{Si}$  as the internal standard. The u.v. and visible spectra were recorded on a JASCO NEW-UV-210A digital double-beam spectrophotometer. The fluorescence spectra were taken on a Shimadzu RF-502A fluorescence spectrophotometer. The m.p.s were measured by means of a Yazawa hot plate and are uncorrected.

The ozonides (2) obtained were isolated by direct recrystallization from a hexane-chloroform solution of the reaction mixture or by solution chromatography [ $\text{SiO}_2$  Wakogel C-200

Table 5. Rate constant for quenching  ${}^1\text{DCA}^*$  fluorescence

Compound	$k_q$ ( $\text{mol}^{-1} \text{l s}^{-1}$ )
(1d)	$2.95 \times 10^{10}$
(4d)	1.34
(1e)	1.00

in columns and Merck Kieselgel 60 PF<sub>254</sub> in 1.0 mm (p.l.c.) layers, respectively].

DCA (Kodak) was purified by silica gel column chromatography, m.p. 250.0–251.0°C. *p*- and *m*-Dimethoxybenzenes, 1,2,4-trimethoxybenzene, biphenyl,  $\text{KO}_2$ , 18-crown-6, trityl tetrafluoroborate, Rose Bengal, Methylene Blue, acetonitrile, and methanol (reagent special grade) were used without further purification. Tris(2,2'-bipyridyl)ruthenium chloride was prepared by the method described in the literature.<sup>24</sup>

All the epoxides were synthesized by *m*-CPBA oxidation of the corresponding olefins: (1a) and (1i) were refluxed in chloroform for 3 h, while (1b)–(1h) were vigorously stirred with base ( $\text{NaHCO}_3$ ) ( $\text{pH} > 8$ ) in water-dichloromethane at room temperature for 1 day.<sup>25</sup>

*trans*-2,3-Diphenyloxirane (1a) had m.p. 66.2–67.0°C, 3.17 (s, 2 H), 6.92 (s, 10 H);  $\nu_{\text{max}}$  1 070, 850, 747, and 695  $\text{cm}^{-1}$ .

*trans*-2,3-Diphenyl-2,3-dimethyloxirane (1b), liquid,  $\delta$  1.60 (s, 6 H), and 6.57 (m, 10 H);  $\nu_{\text{max}}$  1 600, 1 493, 1 245, 1 055, 1 027, and 770  $\text{cm}^{-1}$ .

*trans*-2,3-Bis(4-methylphenyl)oxirane (1c), m.p. 94.0–94.5°C,  $\delta$  2.38 (s, 6 H), 3.85 (s, 2 H), and 7.32 (s, 8 H);  $\nu_{\text{max}}$  1 512, 1 110, 878, 852, 831, and 808  $\text{cm}^{-1}$ .

*trans*-2-(4-Methoxyphenyl)-3-phenyloxirane (1d), m.p. 76.2–78.0°C,  $\delta$  3.72 (s, 2 H), 3.79 (s, 3 H), 6.73–7.05 (d, 4 H), and 7.57 (s, 5 H);  $\nu_{\text{max}}$  1 617, 1 515, 1 110, 1 030, 830, 773, and 705  $\text{cm}^{-1}$ .

*cis*-2-(4-Methoxyphenyl)-3-phenyloxirane (1e), liquid,  $\delta$  3.14 (s, 2 H), 3.69 (s, 3 H), 6.73–7.02 (d, 4 H), and 7.42 (s, 5 H);  $\nu_{\text{max}}$  1 610, 1 513, 1 025, 830, 745, and 705  $\text{cm}^{-1}$ .

*trans*-2,3-Bis(4-methoxyphenyl)oxirane (1f), m.p. 96.0–97.2°C,  $\delta$  3.03 (s, 2 H), 3.07 (s, 6 H), 6.77 (d, 4 H), and 7.13 (d, 4 H);  $\nu_{\text{max}}$  1 600, 1 500, 1 162, 1 098, 1 023, and 805  $\text{cm}^{-1}$ .

*trans*-2-(4-Methoxyphenyl)-3-(4-methylphenyl)oxirane (1g), m.p. 75.0–76.7°C,  $\delta$  2.30 (s, 3 H), 3.17 (s, 1 H), 3.57 (s, 1 H), 3.80 (s, 3 H), and 6.67–7.30 (m, 8 H);  $\nu_{\text{max}}$  1 610, 1 493, 1 248, 1 177, 1 030, and 807  $\text{cm}^{-1}$ .

*trans*-2,3-Diethyl-2,3-bis(4-methoxyphenyl)oxirane (1h), m.p. 114.5–115.2°C,  $\delta$  0.67 (t, 6 H), 1.57 (m, 4 H), 3.56 (s, 6 H), 6.45 (d, 4 H), and 6.87 (d, 4 H);  $\nu_{\text{max}}$  1 594, 1 282, 1 235, 843, 829, and 814  $\text{cm}^{-1}$ .

Tetraphenyloxirane (1i), m.p. 205.0–206.5°C,  $\delta$  7.10 (s, 20 H);  $\nu_{\text{max}}$  1 180, 1 030, 900, 800, 755, and 703  $\text{cm}^{-1}$ .

*DCA-sensitized Photo-oxidation of the Epoxides (1)*.—A MeCN or MeOH solution of (1) ( $10^{-2}\text{M}$ ) and DCA ( $10^{-4}\text{M}$ ) in the presence or absence of biphenyl ( $5 \times 10^{-3}\text{M}$ ) was irradiated with a 400-W high-pressure mercury arc through an aqueous  $\text{NaNO}_2$  solution ( $\lambda_{\text{irrad.}} \geq 410 \text{ nm}$ ) or with a 200-W super-high-pressure mercury arc through a u.v.-cut off glass filter ( $\lambda_{\text{irrad.}} \geq 430 \text{ nm}$ ) while oxygen was bubbled through. The following products were obtained. 3-(4-Methoxyphenyl)-5-phenyltrioxolane (2d), m.p. 62.0–62.8°C,  $\delta$  3.80 (s, 3 H), 6.33 (s, 1 H), 6.40 (s, 1 H), and 6.90–7.80 (m, 9 H);  $\nu_{\text{max}}$  1 170 and 830  $\text{cm}^{-1}$  (Found: C, 70.0; H, 5.6.  $\text{C}_{15}\text{H}_{14}\text{O}_4$  requires C, 69.76; H, 5.46%).

3,5-Bis(4-methoxyphenyl)trioxolane (2f), m.p. 73.9–74.5°C,  $\delta$  3.73 (s, 6 H), 6.13 (s, 2 H), 6.83 (d, 4 H), and 7.37 (d, 4 H);  $\nu_{\text{max}}$  1 170, 838  $\text{cm}^{-1}$  (Found: C, 66.5; H, 5.5.  $\text{C}_{16}\text{H}_{16}\text{O}_5$  requires C, 66.66; H, 5.59%).

3-(4-Methoxyphenyl)-5-(4-methylphenyl)trioxolane (2g), m.p. 66.2–66.6 °C,  $\delta$  2.30 (s, 3 H), 3.70 (s, 3 H), 6.13 (s, 1 H), 6.18 (s, 1 H), and 6.67–7.50 (m, 8 H);  $\nu_{\text{max}}$  1 175, 818 (Found: C, 70.7; H, 5.9. C<sub>16</sub>H<sub>16</sub>O<sub>4</sub> requires C, 70.58; H, 5.92%).

3,5-Diethyl-3,5-bis(4-methoxyphenyl)trioxolane (2h), m.p. 78.8–79.1 °C,  $\delta$  0.67 (t, 6 H), 1.67 (m, 4 H), 3.53 (s, 6 H), 6.37 (d, 4 H), and 6.87 (d, 4 H);  $\nu_{\text{max}}$  1 180, 850 cm<sup>-1</sup> (Found: C, 69.7; H, 7.1. C<sub>20</sub>H<sub>24</sub>O<sub>5</sub> requires C, 69.75; H, 7.02%).

**Quantum Yields.**—Potassium ferrioxalate actinometry and the procedure described by Murov<sup>26</sup> were used. The light source was a 200-W super-high-pressure mercury arc and the 405 nm line was isolated by a Shimadzu-Bausch-Lomb monochromator. The light intensity was determined twice before the irradiation ( $1.07 \times 10^{-9}$  E/min). No variation in light intensity was detected during the experiment. Irradiations of the epoxide (1h) ( $10^{-2}$ M) and DCA ( $10^{-4}$ M) in oxygen-saturated MeCN solutions in 3-ml cuvettes were carried out to ca. 3% conversion of (1h). The reaction was monitored by g.c. using an internal standard. The photo-oxidation of (1h) was used as an actinometer for the measurements of the quantum yields for the photo-oxidation of (1d), (1f), and (1g), which were irradiated on the merry-go-round.

**Ozonolysis Procedure.**—To determine the stereochemistry of the ozonide (2g), ozonolyses of *trans*- and *cis*-1,2-bis(4-methoxyphenyl)ethylene (3) and (4) were carried out using a Sugiyamagen ozonator. Ozone was supplied at a rate of 0.2 mmol/min. In both experiments, (3) and (4) (150 mg;  $6.3 \times 10^{-2}$ M) were ozonized to completion in CCl<sub>4</sub> at -20 °C. The solvent was evaporated from the reaction mixture and it was analyzed by <sup>1</sup>H n.m.r.

**Singlet Oxygenation of the Epoxides (1).**—Compound (1g) was irradiated in the presence of a triplet sensitizer ( $10^{-4}$ M) such as Rose Bengal ( $\lambda_{\text{irrad.}} > 530$  nm), Methylene Blue ( $\lambda_{\text{irrad.}} \geq 640$  nm) and Ru(bpy)<sub>3</sub>Cl<sub>2</sub> ( $\lambda_{\text{irrad.}} \geq 410$  nm).

**Thermal Oxidation Reactions of the Epoxides (1) using Trityl Tetrafluoroborate and/or KO<sub>2</sub>.**—An acetonitrile solution of trityl tetrafluoroborate ( $2 \times 10^{-2}$ M; 10 ml) and KO<sub>2</sub> ( $2 \times 10^{-2}$ M; 10 ml) with 18-crown-6 ( $2.2 \times 10^{-2}$ M) was added dropwise under anhydrous conditions to the stirred acetonitrile solution of compound (1) in a solid CO<sub>2</sub>-CH<sub>2</sub>Cl<sub>2</sub> bath (temp. < -20 °C). The following were obtained. 3,3-Diphenylbutan-2-one (5b), liquid,  $\delta$  1.77 (s, 3 H), 2.02 (s, 3 H), and 7.27 (s, 10 H);  $\nu_{\text{max}}$  1 705, 1 190, and 1 030 cm<sup>-1</sup>.

4,4-Bis(4-methoxyphenyl)hexan-3-one (5h), liquid,  $\delta$  0.63 (t, 3 H), 0.85 (t, 6 H), 2.27 (m, 4 H), 3.82 (s, 6 H), 6.83 (d, 4 H), and 7.21 (d, 4 H);  $\nu_{\text{max}}$  1 702, 1 183, and 1 035 cm<sup>-1</sup>.

2-(4-Methoxyphenyl)-2-methoxy-1-(4-methylphenyl)ethanol (6), liquid,  $\delta$  2.26 (s, 3 H), 3.24 (s, 3 H), 3.70 (s, 3 H), 4.09 (s, 1 H), 4.56 (s, 1 H), and 6.38–7.40 (m, 9 H);  $\nu_{\text{max}}$  3 450, 2 950, 1 250, 1 097, 1 034, and 975 cm<sup>-1</sup>.

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