

COSENSITIZED ELECTRON TRANSFER PHOTO-OXYGENATION: THE PHOTOCHEMICAL PREPARATION OF 1,2,4-TRIOXOLANES, 1,2-DIOXOLANES AND 1,2,4-DIOXAZOLIDINES[†]

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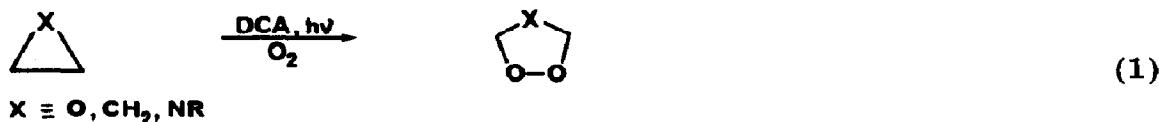
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Summary

9,10-dicyanoanthracene (DCA) sensitizes the electron transfer photo-oxygenation of epoxides, cyclopropanes and aziridines to yield 1,2,4-trioxolanes (ozonides), 1,2-dioxolanes and 1,2,4-dioxazolidines respectively. The addition of biphenyl (BP) as a cosensitizer can provide significantly enhanced rates of reaction of various substrates. An investigation of the stereochemistry of the photo-oxygenation of epoxides and aziridines has given support to a mechanism involving the addition of singlet oxygen as a dipolarophile to intermediate carbonyl and azomethine ylides. A mechanism for DCA-BP cosensitization is presented.

1. Introduction

Cyano-substituted aromatic hydrocarbons such as 9,10-dicyanoanthracene (DCA) have been used to photo-oxidize olefins, acetylenes and sulfides [1]. More recently, it has been demonstrated that cyclopropanes [2 - 4], epoxides [5 - 10] and aziridines [11] can be photochemically converted with DCA to 1,2-dioxolanes, 1,2,4-trioxolanes and 1,2,4-dioxazolidines respectively:



These reactions are of particular interest because the substrates are unreactive toward singlet-oxygen-mediated photo-oxygenation.

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A key step in DCA-sensitized photo-oxygenations is the fluorescence quenching in polar solvents of singlet excited DCA by the substrate S to generate the radical anion DCA^- and the substrate radical cation S^\ddagger . The free-energy change ΔG involved in this electron transfer process is given by the Weller [12] equation:

$$\Delta G = 23.06 \left\{ E(\text{S}|\text{S}^\ddagger) - E(\text{DCA}^-|\text{DCA}) - \frac{e_0^2}{a\epsilon} - \Delta E_{0,0} \right\}$$

where $E(\text{S}|\text{S}^\ddagger)$ is the oxidation potential of the substrate, $E(\text{DCA}^-|\text{DCA})$ is the reduction potential of the sensitizer, $e_0^2/a\epsilon$ is the energy gained by bringing the two radical ions to an encounter distance a in the solvent of dielectric constant ϵ (about 0.06 eV in MeCN (Me \equiv methyl)) and $\Delta E_{0,0}$ is the electronic excitation energy of DCA. For DCA where $E(\text{DCA}^-|\text{DCA}) = -0.98$ V with respect to a saturated calomel electrode (SCE) in MeCN and $\Delta E_{0,0} = 2.89$ eV, Eriksen and Foote [13] have calculated that electron transfer quenching of $^1\text{DCA}^*$ should be exothermic for substrates with oxidation potentials less than 2 V relative to the SCE. Subsequent steps in the mechanism for electron transfer photo-oxygenation are (1) transfer of an electron from DCA^- to oxygen to generate O_2^- and (2) reaction of O_2^- with S^\ddagger to yield the peroxidic products.

It is evident that only easily oxidized substrates capable of quenching the fluorescence of DCA can be photo-oxygenated by the above process. However, we have recently developed a method for the electron transfer photo-oxygenation of compounds that have oxidation potentials greater than 2 V and that consequently do not quench singlet excited DCA [5 - 8]. To effect the photo-oxygenation of such compounds, a non-light-absorbing aromatic hydrocarbon (biphenyl (BP)) is added to the reaction solution as a catalyst or cosensitizer. For example, various epoxides that are unreactive under standard DCA-sensitized conditions can be efficiently converted to the corresponding ozonides in the presence of DCA and BP [5 - 8]. We have now begun to examine the scope of DCA-BP cosensitized photo-oxygenations and have found that this method can be used to provide enhanced rates of photo-oxygenation for a variety of substrates.

2. Experimental section

2.1. General

Proton nuclear magnetic resonance (^1H NMR) spectra were taken on a Nicolet 300 MHz instrument. Chemical shifts are reported in parts per million downfield from tetramethylsilane. High pressure liquid chromatography (HPLC) analyses were carried out on a Varian 5000 instrument interfaced with a Vista 401 data station. An AU TECH C-18 reverse phase column (25 cm \times 4.6 mm; 5 μm) eluted with a gradient of 30% - 100% MeCN in water was used for HPLC.

2.2. Materials

Fisher Scientific HPLC grade MeCN was successively refluxed over and distilled from phosphorus pentoxide and calcium hydride under argon. This doubly distilled MeCN was stored over molecular sieves in an argon atmosphere. DCA (Eastman Kodak) was recrystallized from boiling MeCN. BP (reagent grade, MC and B) was used as received. The synthesis of the epoxides and the characterization of the ozonides have been described previously [8]. The aziridines and the cyclopropanes have been prepared using literature procedures. A complete description of the characterization of the 1,2-dioxolanes and 1,2,4-dioxazolidines will be provided in a subsequent publication.

2.3. General procedure for cosensitized photo-oxygenation

Photo-oxygenations were carried out with a 450 W medium pressure mercury lamp surrounded by a CuSO_4 filter solution which transmits (greater than 50%) between 400 and 450 nm. The filter solution was prepared from 27 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 30 g of NaNO_2 and 50 ml of concentrated NH_4OH diluted with water to 1 l. Dry oxygen was further dried by passing through a bed of Drierite before bubbling through the solution in the photolyzing tube.

A photolyzing tube containing the appropriate substrate (1×10^{-2} M), BP (1×10^{-2} M) and DCA (6×10^{-4} M) in dry MeCN was fitted with a gas inlet tube and placed in a water bath at 10°C . Dry oxygen was bubbled through the solution at a slow rate for a few minutes. An aliquot of the mixture was taken out prior to irradiation for analysis by HPLC. The remaining solution was irradiated while the flow of oxygen was maintained. Small aliquots were taken out at predetermined intervals and analyzed by HPLC. Typical irradiation periods varied from 10 min to 3 h. On completion of the reaction, the MeCN was removed *in vacuo* at 0°C and the mixture was analyzed by 300 MHz ^1H NMR. For isolation of the products, the solid residue was rapidly chromatographed by medium pressure liquid chromatography over silica gel at 0°C or by thin layer chromatography (TLC). For the photo-oxygenation of the aziridines, BP was not included in the reaction solution.

2.4. Stern-Volmer quenching studies


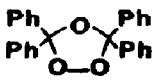

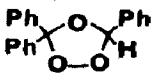
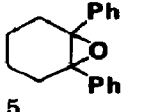
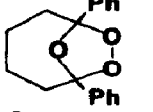
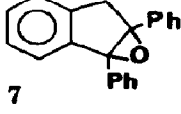
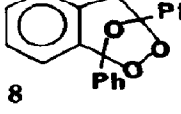

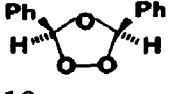

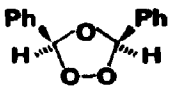
A Spex Fluorolog spectrophotofluorometer was used to measure the relative fluorescence intensities of DCA at 422 nm as a function of the quencher concentration. Typically solutions of DCA (1.85×10^{-5} M) and quencher at five separate concentrations in 1 cm cuvettes were deoxygenated by bubbling oxygen-free nitrogen through the solutions at 0°C for at least 10 min. The emission spectrum of DCA both in the absence and in the presence of a quencher was obtained at room temperature. The slope $k_q\tau$ was determined by plotting the ratio I_0/I of fluorescence intensities against the quencher concentrations [Q] using the equation $I_0/I = 1 + k_q\tau[\text{Q}]$. The lifetime τ for the singlet excited state of DCA is 15.2 ns in MeCN [13].

3. Results

3.1. Conversion of epoxides to ozonides

With the exception of 2,3-diphenylindene oxide (7), the epoxides listed in Table 1 do not measurably quench the fluorescence of DCA in MeCN. It is therefore not unexpected that they are not significantly photo-oxygenated by DCA in oxygenated MeCN. However, in the presence of both BP (1×10^{-2} M) and DCA (6×10^{-4} M), the epoxides are converted to the corresponding ozonides (1,2,4-trioxolanes) in high yields. In all but one case the ozonides have been reported in the literature and authentic samples were prepared by ozonation of the corresponding olefin. An attempt to prepare

TABLE 1
Cosensitized electron transfer photo-oxygenation of epoxides

Epoxide ^a	Ozonide	Yield ^b (%)	Melting point (°C)
 1	 2	93	168 - 169
 3	 4	90	95 - 96
 5	 6	88	105 - 106
 7	 8	85	124 - 125
 9a	 10a	65	98 - 100
 9b	 10a	65	98 - 100

^aThe epoxides are inert to 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. 7 quenches DCA fluorescence as efficiently as BP (k_q for epoxide 7, $3.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$).

^bYields reported are isolated yields except for 10a and 6 which are NMR and HPLC yields respectively.

the previously unknown ozonide **6** by ozonation of 1,2-diphenylcyclohexene gave a complex mixture of products with **6** as a minor component.

Photo-oxygenation of the epoxides produces in addition to the ozonides varying amounts of carbonyl cleavage products: Ph₂CO (Ph ≡ phenyl) from **1** and **3**, PhCHO from **3** and **9**, 1,4-dibenzoylbutane from **5** and *o*-benzoyl-desoxybenzoin from **7**. The ozonides were shown to be stable to the reaction conditions indicating that the carbonyl products are not derived by subsequent photosensitized decomposition of the ozonides. Preliminary experiments suggest that small amounts of water in the solvent can result in the formation of carbonyl products, possibly through reaction of the intermediate radical cations with water, as noted in a related case by Albini and Arnold [14].

HPLC analysis indicated that BP was not appreciably consumed during these photo-oxygenations. Control experiments have shown that no oxidation occurs in the presence of BP without DCA. Further, epoxides **1** and **9** were not oxidized on irradiation for periods of 30 h with a 400 W high pressure sodium lamp in oxygenated MeCN containing Rose Bengal, indicating that the epoxides do not react with singlet oxygen directly.

Of special interest is the observation that only the *cis* ozonide is formed from the cosensitized photo-oxygenation of *cis*-2,3-diphenyloxirane (**9a**) or *trans*-2,3-diphenyloxirane (**9b**) [7]. The mechanistic implications of these stereochemical results are discussed below.

3.2. Conversion of cyclopropanes to 1,2-dioxolanes

We previously reported that 1,1,2,2-tetraphenylcyclopropane (**11**) undergoes photo-oxygenation in MeCN with DCA alone to yield hydroperoxide **13** and benzophenone as the major products (Table 2). Also produced in this reaction as a minor product was 3,3,5,5-tetraphenyl-1,2-dioxolane (**12**) [2]. We have now observed that addition of BP as a co-sensitizer decreases the time required for complete conversion of **11** by a factor of 10. In addition, dioxolane **12** is a major product under these conditions.

Photo-oxygenations of **11** and the other aryl-substituted cyclopropanes listed in Table 2 were carried out in oxygenated MeCN with 1×10^{-2} M BP, 6×10^{-4} M DCA and 1×10^{-2} M substrate. The reactions were monitored by HPLC and after removal of the solvent at 0 °C under vacuum were analyzed by 300 MHz ¹H NMR. The products were isolated by flash chromatography over silica gel at 0 °C. Hydroperoxide **13** was characterized by its reduction with Ph₃P to the corresponding allylic alcohol. The spectral and physical properties of dioxolane **12** are in accord with literature data [15]. Although **12** was found to be stable under the conditions of the reaction, **13** undergoes photosensitized oxidation to benzophenone. BP is not significantly consumed during the photo-oxygenation of **11**.


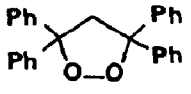
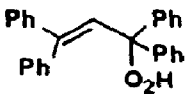

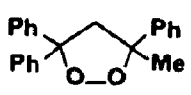

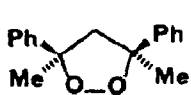





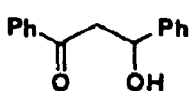
The cosensitized photo-oxygenation of cyclopropane **14** produced the known 3-methyl-3,5,5-triphenyl-1,2-dioxolane (**15**) in 70% yield [15]. The photo-oxygenation of a mixture of the isomeric 1,2-diphenylcyclopropanes

18, however, led to the formation of ketoalcohol 19 in 80% yield. This result is in agreement with the observations of Mizuno *et al.* [3]. It is possible that 19 arises by decomposition of an intermediate 1,2-dioxolane.

Irradiation of 16a or 16b under cosensitized conditions for 45 min gave a mixture of isomeric dioxolanes 17a and 17b in a ratio of 35:65 (74% combined yield) and acetophenone (20%). 17a and 17b were identified by comparison of the NMR spectra with published data [16]. Examination of the NMR spectra of the crude reaction mixture gave no evidence for a hydroperoxide similar to 13. The ratio of the dioxolanes remained unchanged during irradiation. When 16a or 16b was photo-oxygenated in the presence of DCA alone, complete reaction of the cyclopropane required longer irradiation times (more than 25 h) and a complex mixture of products re-

TABLE 2

Cosensitized electron transfer photo-oxygenation of cyclopropanes

Cyclopropane	E_p^{ox} ^a (V)	k_q ^b ($M^{-1} s^{-1}$)	Products ^c	
 11	1.48	1.1×10^{10}	 12 (yield, 35%)	 13 (yield, 59%)
 14	1.70	7.9×10^9	 15 (yield, 70%)	
 16a	1.90	9.4×10^9	 17a (yield, 28%)	 17b (yield, 46%)
 16b	1.85	9.7×10^9	 17a (yield, 27%)	 17b (yield, 47%)
 18	—	—	 19 (yield, 80%)	

^aPeak potentials for the irreversible oxidation of the cyclopropanes were obtained by cyclic voltammetry in MeCN with respect to the SCE; platinum electrode; 0.1 M tetraethylammonium perchlorate; scan rate, 900 mV s⁻¹.

^bRate constants for the quenching of DCA fluorescence in nitrogen-saturated MeCN.

^cYields were determined by ¹H NMR using phthalide as an internal standard.

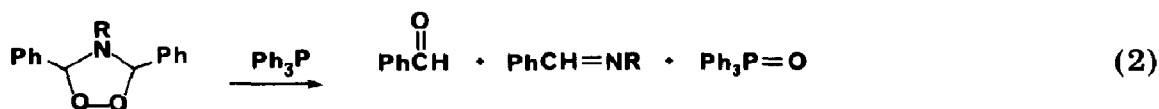
sulted. We have shown by HPLC and NMR that cyclopropanes **16** do not isomerize significantly during conversion to dioxolanes **17**. However, irradiation of **16a** in the presence of DCA-BP under argon led to a mixture of **16b** and **16a** in the ratio 76:24. In the absence of BP, no appreciable isomerization of either **16a** or **16b** is observed for irradiation periods up to 9 h.

The oxidation potentials of the aryl-substituted cyclopropanes were determined by cyclic voltammetry. As the oxidations are irreversible, only peak potentials can be obtained. Rate constants for quenching of DCA fluorescence were found by Stern-Volmer studies (Table 2). Although the cyclopropanes quench $^1\text{DCA}^*$ at diffusion-controlled rates, photo-oxygenation of these substrates in the absence of BP proceeded very slowly compared with the cosensitized reactions.

3.3. Conversion of aziridines to 1,2,4-dioxazolidines

Our results on the photochemical synthesis of ozonides from epoxides have led us to investigate the DCA-sensitized reaction of other heterocycles. We recently provided the first report of the electron transfer photo-oxygenation of an aziridine and isolation of the resulting 1,2,4-dioxazolidine [11]. Described below are additional results on the photochemical preparation of these novel heterocycles.

Photo-oxygenations of the aziridines shown in Table 3 were carried out in oxygenated MeCN with 1×10^{-2} M substrate and 6×10^{-4} M DCA. Reactions were complete in 1.5 - 3 h as determined by reverse phase HPLC. BP was not used for these oxygenations as the aziridines have oxidation potentials similar to BP and efficiently quench the fluorescence of DCA (Table 3). The products were analyzed by removal of the solvent at 0°C under vacuum and acquiring NMR spectra in CDCl_3 . The dioxazolidines were further characterized by reduction with Ph_3P to yield benzaldehyde and the corresponding imines which were compared with authentic samples:



In addition to the dioxazolidines, benzaldehyde and *N*-alkyl-substituted benzamides are products in the photo-oxygenations [11]. The mechanism for the formation of these cleavage products has not been established. However, we have shown that in most cases the dioxazolidines are stable to the reaction conditions. A mixture of **22d** and **23d** was isolated in 25% yield by preparative TLC over silica gel. The chromatography must be carried out rapidly as decomposition occurs on silica gel. The material was shown to be a peroxide by its positive test with acidic potassium iodide and ferrous ammonium thiocyanate.

In our previous report we indicated that photo-oxygenation of the *n*-butyl-substituted aziridine **20d** gave an 87:13 mixture of stereoisomers [11].

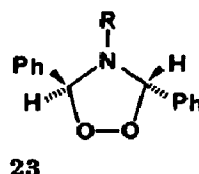
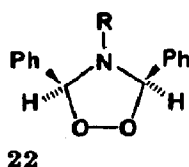
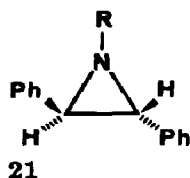
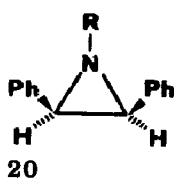
By analogy with the corresponding phenyl-substituted ozonides [7, 8], the major product 22d with the higher field ^1H NMR absorption for the ring protons was tentatively assigned the *cis* phenyl configuration. We have recently expanded our study to include various substituted aziridines and are now able to confirm our original stereochemical assignment.

Consistent with the proposed mechanism for this reaction [11], we find that the ratio of isomers is a function of the substituent on nitrogen. Only the *cis* isomer is formed from the unsubstituted aziridines 20a and 21a. However, with increasing steric bulk of the group more of the *trans* isomer is formed. The benzyl-substituted aziridine 20e was particularly useful in establishing the stereochemistry of the dioxazolidines. Photo-oxygenation of *cis*-1-benzyl-2,3-diphenylaziridine (20e) in MeCN for 30 min gave a combined yield of 40% for the peroxides with an isomeric ratio of 40:60. The minor isomer (22e) exhibited two singlets (2 H each) at $\delta = 5.673$ ppm and $\delta = 4.102$ ppm while the major isomer (23e) exhibited a singlet (2 H) at

TABLE 3

Electron transfer photo-oxygenation of aziridines

Aziridine	E_p^{ox} ^a (V)	k_q ^b ($\text{M}^{-1}\text{s}^{-1}$)	Ratio of 1,2,4-dioxazolidine isomers (22:23) ^c	Combined yield of both isomers ^c (%)	^1H NMR for ring protons, δ (ppm)	
					Cis	Trans
20a, R = H	1.64	7.8×10^9	100:<1	39	5.937	—
20b, R = ethyl	1.66	7.4×10^9	87:13	40	5.563	5.884
20c, R = methyl	1.55	8.7×10^9	85:15	40	5.379	5.808
20d, R = <i>n</i> -butyl	1.70	8.2×10^9	87:13	83	5.543	5.879
20e, R = PhCH ₂	1.65	8.6×10^9	40:60	40	5.673	5.886
20f, R = <i>tert</i> -butyl	1.73	8.5×10^9	<1:100	48	—	5.918
21a, R = H	1.50	1.1×10^{10}	100:<1	36		
21b, R = ethyl	1.73	—	86:14	39		



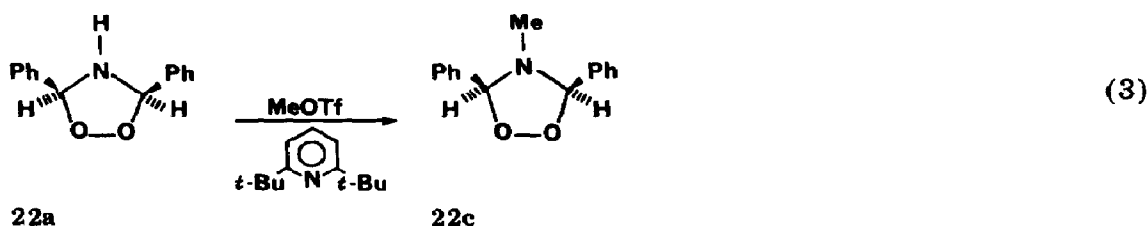
^aPeak potentials for the irreversible oxidation of the aziridines were obtained with respect to the SCE as described in Table 2.

^bRate constants for quenching of DCA fluorescence in nitrogen-saturated MeCN.

^cYields were determined by 300 MHz ^1H NMR using an internal standard.

$\delta = 5.886$ ppm and an AB quartet (2 H) for the diastereotopic *N*-benzyl protons centered at $\delta = 3.737$ ppm ($J = 13.2$ Hz).

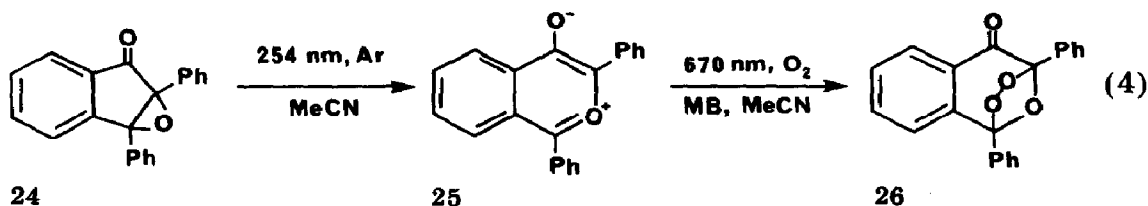
As only one isomer was observed from the photo-oxygenation of the *N*-unsubstituted aziridines **20a** and **21a**, the chemical shift of the ring protons could not be used to provide an unambiguous assignment of the configuration of this peroxide. However, treatment with 1.2 equivalents of methyl triflate (MeOTf) in the presence of 2,6-di-*tert*-butylpyridine afforded in 80% yield the *cis* isomer **22c** of the *N*-methyl dioxazolidine:



We have shown that the aziridines do not isomerize during the photo-oxygenations. In addition, aziridine **20d** was not oxidized on irradiation for 4 h with a 400 W high pressure sodium lamp in oxygenated MeCN containing Rose Bengal, indicating that **20d** does not react directly with singlet oxygen.

3.4. Formation of an ozonide by the addition of singlet oxygen to a carbonyl ylide

The striking stereochemical results of the cosensitized electron transfer photo-oxygenation of *cis*- and *trans*-2,3-diphenyloxirane have led us to propose a mechanism for this reaction involving the addition of singlet oxygen as a dipolarophile to an intermediate carbonyl ylide [7]. We have therefore recently investigated the addition of singlet oxygen to the stabilized ylide **25** formed by photolysis of 2,3-diphenylindenone oxide (**24**) (MB \equiv methylene blue):



Several years ago Ullman and Henderson [17] demonstrated that epoxide **24** and ylide **25** are photochemically interconvertible. Irradiation of **24** with UV light results in a deep red solution of pyrylium oxide **25**. Subsequent exposure to visible light regenerates **24**. Ullman and Henderson [18] also found that photolysis of **24** in the presence of oxygen yielded products that could be explained in terms of the decomposition of an intermediate ozonide (see also ref. 19). We have re-examined this reaction and now provide the first direct evidence for the formation of an ozonide from a

dipolar cycloaddition of singlet oxygen to a carbonyl ylide. Ground state oxygen also reacts with 25 to give 26 but at a significantly slower rate.

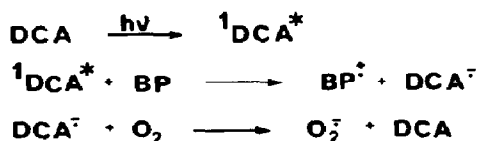
Solutions of epoxide 24 (7×10^{-5} M) in MeCN were deoxygenated with argon. Irradiation in a quartz cuvette with a low pressure mercury lamp for 1 min afforded intense red solutions of ylide 25 (λ_{\max} in MeCN, 535 nm). After generation of the ylide, a solution of methylene blue (MB) in MeCN was added (λ_{\max} of MB, 655 nm; final optical density, 1.8). The resulting solution was simultaneously bubbled with oxygen and irradiated at 670 nm using a 150 W Varian EIMAC illuminator and monochromator for 1 min. The absorption spectrum of the solution after the photo-oxygenation showed no residual ylide. 1,3,5-tri-*tert*-butylbenzene was added to the solution as an internal standard. Reverse phase HPLC indicated that 72% of epoxide 24 had been consumed with the formation of ozonide 26 in greater than 95% yield (based on reacted 24). The ozonide was characterized by comparison with an authentic sample prepared by ozonation of diphenylindeneone [20] and by its reduction with Ph_3P . MB was chosen as the singlet oxygen sensitizer for these experiments because it could be selectively excited at 670 nm in the presence of the ylide. A control experiment in which oxygen was bubbled through a solution of 25 in the dark was carried out. After 1 min the absorption spectrum indicated that 60% of the original concentration of the ylide 25 still remained. After 20 min ylide 25 had completely reacted with ground state oxygen. HPLC analysis showed that only 3% of 26 had been formed (on the basis of reacted 24). The major product in the reaction of ylide 25 with ground state oxygen is the mixed anhydride of benzoic and *o*-benzoylbenzoic acids [18, 19]. Additional studies of this system are in progress. However, these preliminary results demonstrate that singlet oxygen is highly reactive toward carbonyl ylides.

4. Discussion

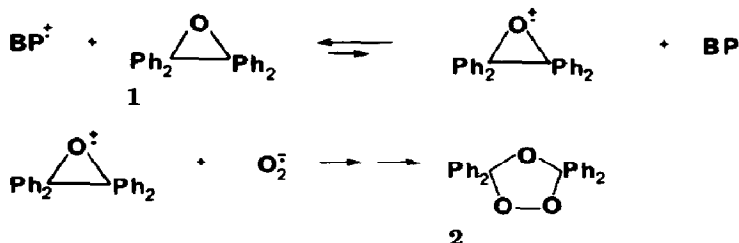
4.1. Mechanisms of 9,10-dicyanoanthracene-biphenyl cosensitization

We have observed that the addition of BP to DCA-sensitized photo-oxygenations can, in some cases, provide dramatic rate enhancements. Cosensitization by BP can be utilized for the photo-oxygenation of substrates that have high oxidation potentials and do not quench the fluorescence of DCA as well as for substrates that are more easily oxidized and quench $^1\text{DCA}^*$ efficiently (Fig. 1).

The first case is illustrated by the DCA-BP-cosensitized photo-oxygenation of epoxides. Tetraphenylloxirane (1) exhibits an oxidation potential greater than 2 V (SCE) and therefore does not measurably quench the fluorescence of DCA in MeCN. BP is oxidized at a lower potential ($E_{\text{p}}^{\text{ox}} = 1.90$ V (SCE) in MeCN) and quenches $^1\text{DCA}^*$ ($k_{\text{q}} = 3.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) to generate DCA^- and BP^+ . Although secondary electron transfer from 1 to BP^+ is endothermic, this process is favored by the longer lifetime of BP^+ compared with $^1\text{DCA}^*$. Mattes and Farid [21] have advanced a similar argument



ENDOTHERMIC SECONDARY ELECTRON TRANSFER



EXOTHERMIC SECONDARY ELECTRON TRANSFER

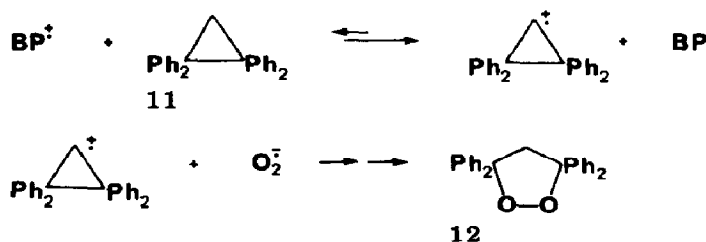


Fig. 1.

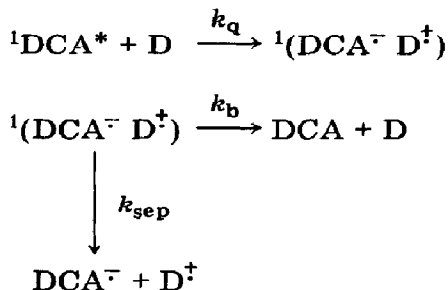
for the cosensitization by phenanthrene and 9-cyanoanthracene of the electron transfer dimerization of phenyl vinyl ether.

We have suggested that additional insight into the mechanism of DCA-BP cosensitized photo-oxygenation of epoxides may be obtained by considering the analogous process in homogeneous redox catalysis of electrochemical reactions [7]. 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 the unstable RX^- and regenerates the hydrocarbon. Although this reversible step is energetically unfavorable, it is driven by the irreversible cleavage of RX^- . A similar mechanism may obtain in the present case. Although energetically unfavorable, a reversible electron transfer from epoxide 1 to BP^\cdot would generate the unopened epoxide radical cation. This step would be driven by the subsequent generation of a ring-opened radical cation and trapping by superoxide to form the ozonide.

Cosensitization by BP may also provide rate enhancements for photo-oxygenations of substrates that are in fact better quenchers of ${}^1\text{DCA}^*$ than BP. As an example, 1,1,2,2-tetraphenylcyclopropane (11) is more easily oxidized ($E_p^{\text{ox}} = 1.48 \text{ V}$) than BP and therefore quenches ${}^1\text{DCA}^*$ at a faster rate ($k_q = 1.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$). Nevertheless, the rate of photo-oxygenation

of 11 can be increased by more than a factor of 10 by the addition of an equimolar concentration of BP [2]. We have proposed that this catalysis by BP results from a higher efficiency for the formation of cage-escaped BP^\ddagger compared with the radical cation of 11. Secondary electron transfer from 11 to BP^\ddagger is exothermic by about 0.5 eV and is expected to occur at a diffusion-controlled rate (Fig. 1).

An explanation for this second case of cosensitization by BP is suggested by the recent reports of Mattes and Farid [22] and Masuhara and Mataga [23] which showed that the quantum yield for solvent-separated radical ions in electron transfer fluorescence quenching is a function of the exothermicity of the back electron transfer from the electron acceptor radical anion to the donor radical cation:



($\Delta G_b = E_{\text{DCA}}^{\text{red}} - E_{\text{D}}^{\text{ox}}$). With ${}^1\text{DCA}^*$ in MeCN, the quantum yield for the formation of separated radical ions increases from 0.03 to 0.3 as the exothermicity for back electron transfer increases from 2.1 to 2.8 eV [22]. Quenching of ${}^1\text{DCA}^*$ by an electron donor D forms a primary geminate radical ion pair of singlet multiplicity. In a polar medium, diffusion can lead to solvent-separated radical ions. Competing with this diffusion process is back electron transfer to give the reactants in the ground state. The rate constant k_b for this singlet recombination is thought to decrease as the exothermicity increases. These results have been explained in terms of the gap theory for radiationless decay and the Marcus "inverted region" of electron transfer [22].

The above considerations suggest that the most effective cosensitizers for DCA will be those with oxidation potentials of 1.8 - 2 V. In this range the material will not only be able to quench ${}^1\text{DCA}^*$ but will also have a sufficiently high oxidation potential to maximize cage escape efficiency and to facilitate secondary electron transfer. We are currently evaluating various aromatic hydrocarbons as possible cosensitizers for DCA.

4.2. Stereochemical investigations

Insight into the mechanism of the electron transfer photo-oxygenation of epoxides, aziridines and cyclopropanes has been obtained from investigations of the stereochemistry of these reactions [7, 8, 11]. The exclusive formation of the *cis* ozonide 10a from both epoxides 9a and 9b is not consistent with a mechanism involving attack of O_2^- on the epoxide radical

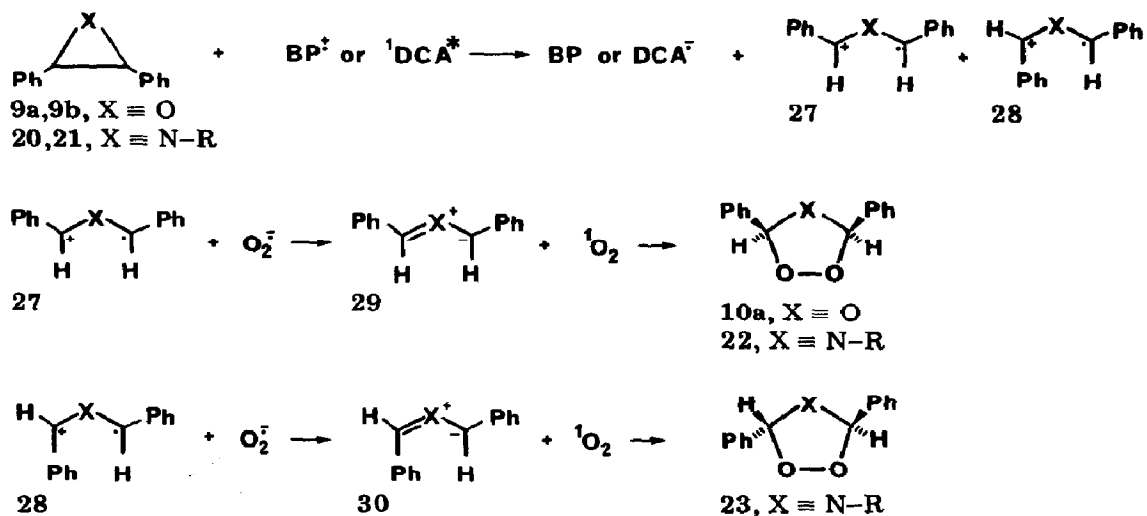


Fig. 2.

cation to give long-lived biradical or zwitterion intermediates. Such intermediates would be expected to lead to the formation of a mixture of isomeric ozonides. We have therefore proposed an alternative mechanism that accounts for the stereoselective formation of ozonide 10a: (1) formation of the most stable *E,E* conformation of epoxide radical cation from either 9a or 9b; (2) subsequent reduction by $\text{O}_2^{\bullet-}$ (or DCA^-) to yield the *E,E* isomer of carbonyl ylide 29 ($\text{X} \equiv \text{O}$); (3) [4 + 2] cycloaddition with singlet oxygen acting as a dipolarophile (Fig. 2). Foote and coworkers [24] have shown that singlet oxygen can be formed in DCA-sensitized photo-oxygenations by energy transfer from singlet and triplet excited DCA to oxygen. Singlet oxygen could also be generated as a result of the electron transfer from $\text{O}_2^{\bullet-}$ to the radical cations [25].

The photo-oxygenations of *N*-unsubstituted aziridines 20a and 21a follow a similar stereochemical course with exclusive formation of the *cis*-1,2,4-dioxazolidine 22a. This result is explained in terms of a mechanism involving trapping of the more stable azomethine ylide 29 ($\text{X} \equiv \text{NH}$) by singlet oxygen. It is expected that sterically bulky groups on nitrogen should destabilize radical cation 27 ($\text{X} \equiv \text{NR}$). Consistent with this idea is the observation that the *cis*-to-*trans* ratio of isomeric 1,2,4-dioxazolidines 22 and 23 is inversely related to the size of the group on nitrogen.

The proposed intermediacy of carbonyl and azomethine ylides in the electron transfer photo-oxygenation of epoxides and aziridines is in accord with the extensive literature on the trapping of photolytically and thermally generated ylides by dipolarophiles [14, 26]. Additional support has been provided by our observation that singlet oxygen adds to a stabilized carbonyl ylide to form an ozonide in high yield.

5. Conclusions

We have proposed above a mechanism for DCA-BP cosensitized photo-oxygenations. We anticipate that cosensitization by various electron-deficient sensitizers and aromatic hydrocarbons will provide a generally useful approach to the photo-oxygenation of normally unreactive substrates. Our method has been utilized for the photochemical conversion of epoxides to ozonides. We have also obtained rate enhancements with BP as a cosensitizer for DCA-sensitized photo-oxygenations of aryl-substituted cyclopropanes. Investigations in our laboratory have also been extended to the photo-oxygenation of substituted aziridines and the isolation of the first photochemically prepared 1,2,4-dioxazolidines.

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