$d_\pi$ density near the iron nucleus. The higher $\nu_{CO}$ values for **1** and Fe(Pc)(CO)$_2$ suggest greater competition between axial and equatorial ligands for the iron $d_\pi$ electrons, which may well result in more diffuse distributions of the $\pi$ density.

Of the three macrocycles, OMBP appears to be the most effective "electron sink" in the sense that it is best able to accommodate the $\pi$-bonding demands of the axial CO ligands.

**Registry No.** **1**, 66746-95-0; **2**, 86261-22-5; Fe, 7439-89-6.

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# Stereoselective Formation of *cis*-Stilbene Ozonide from the Cosensitized Electron-Transfer Photooxygenation of *cis*- and *trans*-2,3-Diphenyloxiranes

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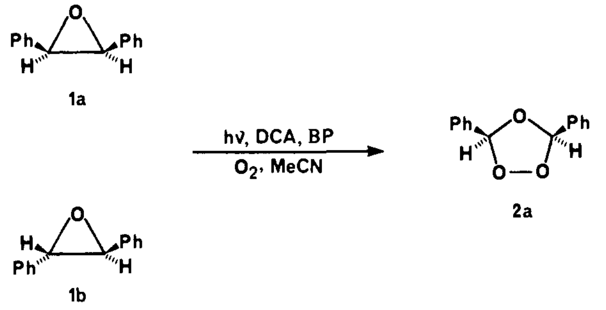
Cyano-substituted aromatic hydrocarbons such as 9,10-dicyanoanthracene (DCA) sensitize the photooxygenation of olefins, acetylenes, and sulfides.[1] A key step in this reaction is the electron-transfer quenching of singlet excited DCA by the substrate to generate DCA$^{-}\cdot$ and the substrate radical cation.[2] Subsequent reaction of $O_2^{-}\cdot$ with the radical cation affords the peroxidic product. We have, however, recently developed a method by which a compound that does not quench DCA may nevertheless be rapidly oxidized under electron-transfer photooxygenation conditions.[3] It was found that the photooxygenation of tetraphenyloxirane to yield the corresponding ozonide could be cosensitized by a non-light-absorbing, chemically unreactive aromatic hydrocarbon (biphenyl, BP) in conjunction with DCA. In the absence of BP, this epoxide is relatively unreactive.[4]

The stereochemistry of this reaction has now been examined by an investigation of the DCA/BP-cosensitized photooxygenation of *cis*-2,3-diphenyloxirane (**1a**) and *trans*-2,3-diphenyloxirane (**1b**). We have observed that a *single isomer of the ozonide is formed from both epoxides.* Photooxygenation of **1a** and **1b** gives rise exlusively to *cis*-3,5-diphenyl-1,2,4-trioxolane (**2a**). This striking stereochemical result is consistent with a novel mechanism involving concerted 4 + 2 cycloaddition of singlet oxygen to an intermediate carbonyl ylide.



Photooxygenations of **1a** and **1b** were carried out in dry acetonitrile[6] with $1 \times 10^{-2}$ M epoxide, $1 \times 10^{-2}$ M BP, and $6 \times 10^{-4}$ M DCA. The solutions were irradiated for 2 h at 10 °C under oxygen with a 450-W medium-pressure mercury lamp by using a CuSO$_4$-filter solution[7] and monitored by HPLC.[8] Yields of products were determined by removal of the solvent at 0 °C under vacuum and analysis in CDCl$_3$ by 300-MHz $^1$H NMR. The spectra obtained from photooxygenations of **1a** and **1b** exhibited absorptions at $\delta$ 6.331 for the ring proton of *cis*-ozonide **2a** (65–70%) and at $\delta$ 10.015 for the aldehydic proton of benzaldehyde (**3**).[9] Within the limits of detection (2%) no absorption for *trans*-3,5-diphenyl-1,2,4-trioxolane (**2b**) was observed. Authentic samples of the isomeric ozonides were prepared by ozonation of stilbene. Treatment of *cis*- and *trans*-stilbene with ozone at low temperature in pentane gave a 60:40 mixture of *trans*-ozonide **2b** and *cis*-ozonide **2a**, respectively.[10] The $^1$H NMR spectrum of the mixture in CDCl$_3$ exhibited ring proton absorptions at $\delta$ 6.360 for **2b** and 6.331 for **2a**.[11] Criegee and Korber[10b] report absorptions in CCl$_4$ at $\delta$ 6.22 and 6.18 for **2b** and **2a**, respectively. Additional evidence for the structure of *cis*-ozonide **2a** was obtained by preparative TLC of the photooxygenation products over silica gel with 10% ethyl acetate in hexane. Recrystallization of the chromatographed material from petroleum ether yielded colorless needles of **2a**, mp 98–100 °C (lit.[10b] mp 100 °C). As expected, **2a** was converted to benzaldehyde by reaction with Ph$_3$P.

As control experiments we have shown that authentic samples of ozonides **2a** and **2b** are stable under the photooxygenation conditions. No *trans*-ozonide **2b** is observed at partial conversion of **1a** or **1b** nor is any isomerization of the starting epoxides **1** found. In the absence of BP, only 7% benzaldehyde and no ozonide was obtained after 20-h irradiation. Additionally, BP is not appreciably consumed during photooxygenation.

We[3] have proposed that BP acts as a cosensitizer in photooxygenations by a process analogous to homogeneous redox catalysis for electrode reactions.[12] Epoxides **1** do not measurably quench the fluorescence of DCA in MeCN as is expected for compounds with oxidation potentials greater that 2 V vs. SCE[2] (*trans*-2,3-diphenyloxirane (**1b**), $E^{ox}$ = 1.89 V vs. Ag/AgNO$_3$ in MeCN;[13] ~2.2 V vs. SCE in MeCN). However, BP is more easily oxidized ($E_p^{ox}$ = 1.85 V vs. SCE in MeCN[14]) than epoxides **1** and consequently quenches $^1$DCA* more efficiently ($k_q$ (for BP) =

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(2) Foote has calculated that electron-transfer fluorescence quenching of DCA should be possible for substrates with oxidation potentials less than ~2 V vs. SCE.[1b]

(3) (a) Presented at the IXth IUPAC Symposium on Photochemistry, Pau, France, July 26, 1982; Abstr, ST 15. (b) Schaap, A. P.; Lopez, L.; Gagnon, S. D. *J. Am. Chem. Soc.* **1983**, *105*, 663.

(4) Ohta and co-workers have recently reported that tetraphenyloxirane does not react under their conditions with DCA alone.[5] Ozonides have, however, been obtained from more easily oxidized epoxides bearing electron-donating groups.

(5) Futamura, S.; Kusunose, S.; Ohta, H.; Kaniya, Y. *J. Chem. Soc., Chem. Commun.* **1982**, 1223.

(6) Distilled from P$_2$O$_5$ and then from CaH$_2$.

(7) The 1-cm path-length filter solution was prepared from 27 g of CuSO$_4$·5H$_2$O, 30 g of NaNO$_2$, and 50 mL of concentrated NH$_4$OH diluted with water to 1000 mL.

(8) Using a C-18 reverse-phase column and elutions with a gradient of 30–100% acetonitrile in water.

(9) The mechanism for the formation of **3** has not yet been established. Control experiments have shown that **3** is not produced photochemically from **2a** under reaction conditions.

(10) (a) Criegee, R.; Kerckov, A.; Zinke, H. *Chem. Ber.* **1955**, *88*, 1878. (b) Criegee, R.; Korber, H. *Chem. Ber.* **1971**, *104*, 1807. (c) Bishop, C. E.; Denson, D. D.; Story, P. R. *Tetrahedron Lett.* **1968**, 5739. (d) Murray, R. W.; Suzui, A. *J. Am. Chem. Soc.* **1973**, *95*, 3343.

(11) Recrystallization (6x) of the mixture of ozonides from methanol gave authentic *cis*-ozonide **2a**, mp 97–99 °C (lit.[10b] mp 100 °C), with a $^1$H NMR absorption at $\delta$ 6.331. The reported melting point of the *trans*-ozonide **2b** is 94 °C.[10b]

(12) For leading references, see: (a) Andrieux, C. P.; Blocman, C.; Dumas-Bouchiat, J. M.; M'Halla, F.; Saveant, J. M. *J. Electroanal. Chem. Interfacial Electrochem.* **1980**, *113*, 19. (b) Saveant, J. M. *Acc. Chem. Res.* **1980**, *13*, 323. (c) Evans, E. H.; Naixian, X. *J. Electroanal. Chem. Interfacial Electrochem.* **1982**, *133*, 367. (d) Sease, J. W.; Reed, R. C. *Tetrahedron Lett.* **1975**, 393. (e) Lund, H.; Simonet, J. *J. Electroanal. Chem. Interfacial Electrochem.* **1975**, *65*, 205. (f) Boujlel, K.; Simonet, *Electrochim Acta* **1979**, *24*, 481. (g) Britton, W. E.; Fry, A. *J. Anal. Chem. USSR (Engl. Transl.)* **1975**, *47*, 95.

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(14) Osa, T.; Yildiz, A.; Kuwana, T. *J. Am. Chem. Soc.* **1969**, *91*, 3994.

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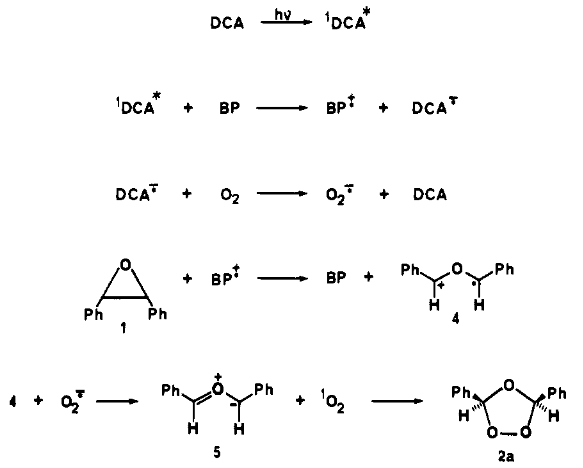
Scheme I



$3.1 \times 10^9$ M$^{-1}$ s$^{-1}$) to generate DCA$^{-}\cdot$ and BP$^{+}\cdot$. Although energetically unfavorable, a reversible electron transfer from epoxide **1** to BP$^{+}\cdot$ could generate the unopened epoxide radical cation. This step would be driven by the subsequent opening to **4** and irreversible formation of the ozonide (Scheme I).

Of present interest are the mechanistic implications of the exclusive formation of *cis*-ozonide **2a** from both epoxides **1a** and **1b**. These results are not consistent with a mechanism involving attack of $O_2^{-}\cdot$ on epoxide radical cation **4** to give long-lived biradical or zwitterion intermediates.[15] Such mechanisms would predict the formation of a mixture of isomeric ozonides. A plausible mechanism that is consistent with the stereoselective formation of ozonide **2a** involves (1) formation of the most stable *E,E* conformation of epoxide radical cation **4** from either **1a** or **1b**, (2) subsequent reduction of **4** by $O_2^{-}\cdot$ (or DCA$^{-}\cdot$) to yield the *E,E* isomer of carbonyl ylide **5**, and (3) 4 + 2 cycloaddition with $^1O_2$ acting as a dipolarophile. Santamaria[16] and Foote[17] have shown that $^1O_2$ can be formed in DCA-sensitized photooxygenations 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 $O_2^{-}\cdot$ to **4**.

The proposed intermediacy of carbonyl ylide **5** and its reaction with $^1O_2$ to form *cis*-ozonide **2a** is in accord with observations of several groups on the trapping of photogenerated carbonyl ylides.[13,18] For example, Griffin[18a] has recently shown that direct photolysis or thermolysis of 2,3-diaryloxiranes such as **1a** and **1b** generates carbonyl ylides that can be trapped by dipolarophiles to afford substituted tetrahydrofurans. As in the present study, the major products arise from a 4 + 2 cycloaddition of the dipolarophiles to the thermodynamically more stable *E,E* carbonyl ylides. In related work, Arnold[13] has utilized 1,4-dicyanonaphthalene as an electron-transfer sensitizer with epoxides **1** in the presence of dipolarophiles to yield substituted tetrahydrofurans in which the major products have a *cis*-diphenyl relationship. The proposed mechanism involves formation of the epoxide radical cation followed by back electron transfer from the sensitizer radical anion to give the carbonyl ylide.[19] Trozzolo and Griffin have used spectroscopic methods to characterize carbonyl ylides produced by the photochemical cleavage of epoxides.[20]

Experiments are continuing on the mechanism of the cosensitized electron-transfer photooxygenation of epoxides and other substrates. We have extended our investigations to the photooxygenation of substituted aziridines and have recently been able to isolate the first photochemically prepared 1,2,4-dioxazolidine.[21] The possibility that this reaction may involve azomethine ylides as intermediates is under study.

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**Registry No. 1a**, 1689-71-0; **1b**, 1439-07-2; **2a**, 21072-45-7; DCA, 1217-45-4; BP, 92-52-4.

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## Syn and Anti Stereochemistry in Elimination Reactions Producing Acyclic Conjugated Thioesters

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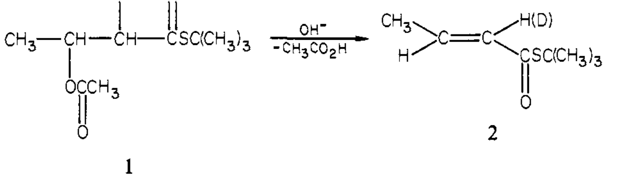
Although base-catalyzed addition–elimination reactions that involve the C=C—C=O moiety are important in organic chemistry, almost nothing has been reported on their innate stereochemistry. We now report the first stereochemical studies of a base-catalyzed 1,2-elimination reaction producing an alkene conjugated to a carbonyl group. Preliminary results show that syn and anti elimination pathways have comparable rates.

The dominant anti stereochemistry in 1,2-elimination reactions of acyclic compounds seemed secure until the work of Sicher and his colleagues on the syn–anti dichotomy.[1] The general importance of syn elimination pathways is accepted now, and factors that favor them have summarized.[2,3] Nevertheless, it was surprising when enzyme-catalyzed syn eliminations were observed.[4] Each of these involves a conjugated thioester or ketone product. No advantage for enzymic syn eliminations is apparent in the context of natural selection, other than the possible mechanistic efficiency due to the presence of relatively acidic protons $\alpha$ to the carbonyl group of each substrate. ElcB-like transition states may favor syn stereochemistry.[5]

Our substrate, (*R,R*)- and (*S,S*)-*S*-*tert*-butyl 3-acetoxy[2-$^2H_1$]butanethioate (**1**), was chosen because it provides an ap-



(1)

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