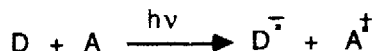


PHOTOXYGENATION OF STRAINED EPOXIDES

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Summary: Photooxygenation of strained epoxides, type 1, in the presence of DCA or TCA afforded ozonide 2 in different ratios. A mechanism involving trapping of a radical cation by $^3\text{O}_2$ is proposed. Trapping of an ylide intermediate by $^1\text{O}_2$ is also considered in the DCA-sensitized photooxygenation.

Organic reactions mediated by electron-transfer interactions between an electronically excited sensitizer and a ground state quencher have been the subject of considerable interest². The photosensitized electron-transfer reaction is based on the principle that a molecule in an excited state is both a better oxidizing and reducing agent than the same molecule in its ground state. The feasibility of photochemical electron transfer between the donor D and the acceptor A in polar solvents,



can be calculated by the use of the Weller equation,³ which predicts the free energy change (ΔG) for the reaction from redox potentials of D and A and the excitation energy of the sensitizer.

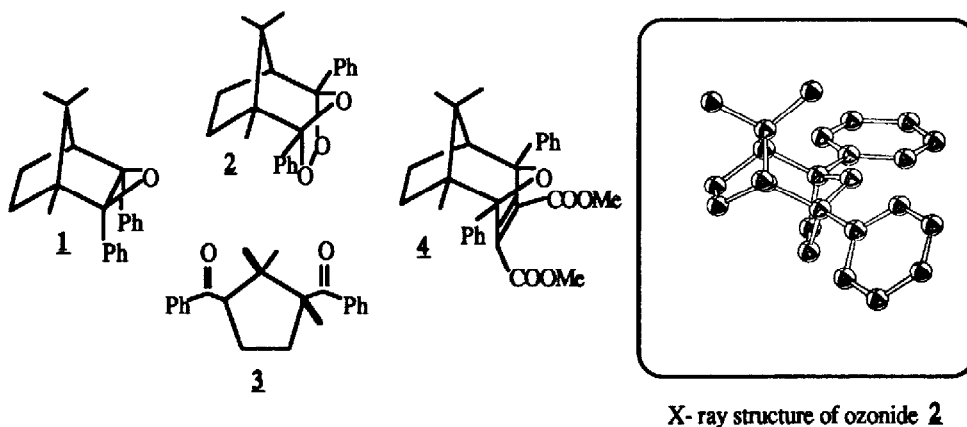
Photooxygenation of epoxides sensitized by cyanoaromatic compounds has been proposed to proceed through different mechanisms. For epoxides with oxidation potentials higher than 2 V and low fluorescence quenching constants, no reaction takes place under standard conditions. With the aid of a cosensitizer, it has been demonstrated that these oxiranes can be efficiently photooxygenated.⁴ The mechanism advanced for this type of reactions involves superoxide and an epoxide radical cation, formed by secondary electron-transfer with the cosensitizer. Formation of singlet oxygen and a stabilized epoxy ylide precedes a concerted cycloaddition to produce ozonides. On the other hand, for electron-rich epoxides, possessing electron-donor substituents, low oxidation potentials (less than 2V), and diffusion-control quenching constants, the photooxygenation proceeds through a radical-chain mechanism, for which diradical intermediates have been invoked.⁵

It is conceptually possible to lower the oxidation potential of the oxiranes through strain and steric hindrance in the system without the use of electron-donating substituents. The advantages of this

approximation are, 1) the possible avoidance of radical-chain processes in the photooxygenation, which can be favored by the electron-donating moieties, 2) the elimination of cosensitizers, and 3) the stabilization of possible intermediate carbonyl ylides by relief of strain and steric hindrance exclusively. To explore the concept of strain in photooxygenations sensitized by some cyanoaromatic compounds and to study the role of such intermediates as superoxide, ylides, radicals, etc., several 2,3 diaryl epoxides bearing a bornane and norbornane skeleton have been prepared. The results obtained with (+)-(1R, 2S, 3R, 4S)-2-endo, 3-endo-diphenyl-2, 3-epoxy bornane, **1**, constitute the subject of this paper.

When oxygen saturated solutions ($1 \times 10^{-2} M$) of epoxide **1** (reported previously in this issue) and 9, 10-dicyanoanthracene, DCA, ($1 \times 10^{-4} M$) in dry acetonitrile were irradiated with a 1000W medium pressure mercury lamp surrounded by a $CuSO_4$ filter solution (bandpass= 400-450 nm) for 40 min, complete conversion into ozonide **2** and diketone **3** was observed (Fig 1). After removal of the solvent, analysis of the samples by 1H -NMR revealed 85% of ozonide **2** and 15% of diketone **3**. Isolation of ozonide **2** in 65% yield was achieved by low temperature (-10 to $-20^\circ C$) medium pressure column chromatography on silica gel and recrystallization from n-pentane.⁶ The structure of ozonide **2** was unambiguously assigned by X-ray analysis (Fig 1). No other product besides ozonide **2** and diketone **3** was detected by 1H -NMR or HPLC of the crude reaction mixture.

Fig 1

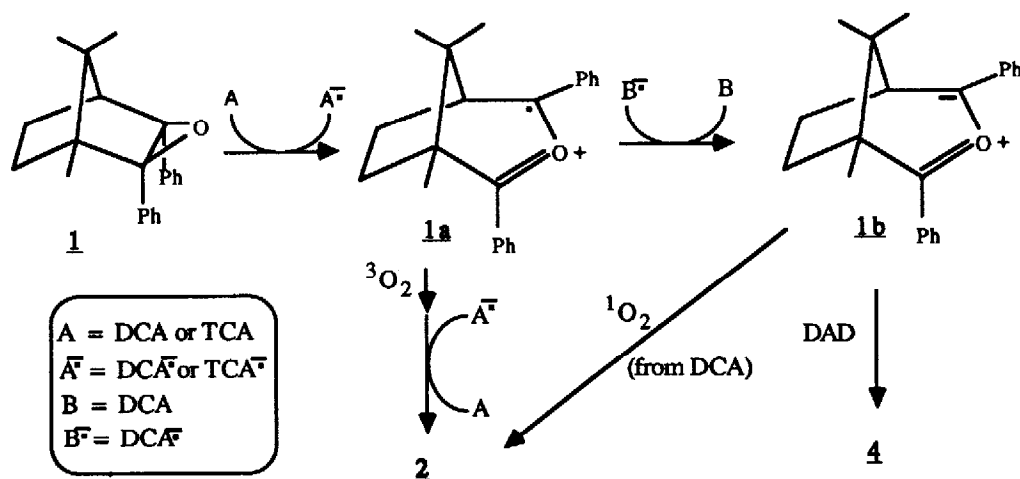


It has been suggested that, given the proper energetics, triplet oxygen can react very rapidly with the radical anion of DCA with the formation of superoxide.⁷ To test the possible involvement of the latter in this reaction, several runs were performed in the presence of benzoquinone, a superoxide trap.⁸ No change in reaction time or product ratio was observed. When the photooxygenation reaction was performed in the presence of 2,6,9,10-tetra cyanoanthracene, TCA⁹, 30% of ozonide **2** and 70% of diketone **3** were

obtained. This last result suggests that superoxide is not involved in the latter reaction since the reduction potential of TCA is lower than the reduction value of oxygen, therefore its formation is energetically unfavorable. It also reveals, indirectly, that although superoxide can be formed in the presence of DCA, peroxydic products can also be generated efficiently by the trapping of radical cation intermediates with triplet oxygen.

[4+2] Cycloadditions to ylides, derived photochemically from epoxides, is well documented.¹⁰ To test the involvement of such an intermediate in the photooxygenation of **1**, several trapping experiments were performed in the presence of dimethyl acetylene dicarboxylate (DAD). Irradiation of **1** ($1 \times 10^{-2} \text{M}$) for 20 min. in a nitrogen-saturated acetonitrile solution of DCA (10^{-4}M) and DAD ($1 \times 10^{-2} \text{M}$) afforded a single compound, adduct **4**¹¹ (Fig. 1). The structure of **4** was deduced by comparison of its ¹H-NMR values with related products. Irradiation of **1** in the presence of TCA and DAD in a nitrogen-saturated acetonitrile solution produced no adduct after prolonged exposure. Limiting quantum yields for photooxygenation and phototrapping correlated quite closely ($\Phi \cong 0.27$), suggesting a common intermediate in both cases.

Fig 2



Formation of ozonide **2** can occur through two possible intermediates, radical cation **1a** and ylide **1b** (Fig. 2), the latter being formed from **1a** by back electron transfer reaction with the radical anion of DCA but not TCA. Trapping of this ylide intermediate can only be attained by ¹O₂, which in turn can be produced by DCA and ³O₂ or from superoxide.⁴ The participation of superoxide is ruled out based on irradiation experiments involving benzoquinone; on the other hand, formation of ¹O₂ by DCA has been documented for DCA-sensitized photooxygenations of some alkenes¹² and, given the fact that an ylide

intermediate is demonstrated by trapping experiments, the involvement of $^1\text{O}_2$ is a mechanistic possibility in the DCA-sensitized photooxygenation (Fig 2). In conclusion, these observations suggest that ozonide **2** can derive from the reaction of $^3\text{O}_2$ with the radical cation **1a** in the TCA- and DCA-sensitized reactions, and also from the trapping of ylide **1b** by $^1\text{O}_2$ in the DCA-sensitized photooxygenation (Fig 2).

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6. (+)-(1R, 2S, 3R, 4S)-2-endo, 3-endo-Diphenyl bornane-2,3-ozonide, **2**, is a white crystalline solid stable in the solid state at room temperature, decomposes readily in the presence of water or by reduction with Ph_3P giving diketone **3** as the only product. Ozonide **2** has mp = 114-117 °C., $^1\text{H-NMR}(\text{CDCl}_3)$ δ = 0.64 (s, CH₃), 0.92 (s, CH₃), 1.41 (s, CH₃), 1.4(m,1H), 1.8(m,1H), 2.4(m,1H), 2.6(m,1H), 2.64 (d,H), 7.0-8.5 (m,10H). $\text{C}_{22}\text{H}_{24}\text{O}_3$ calculated: C 78.54, H 7.19. Found: C 78.27, H 6.99 $[\alpha]_{\text{D}}^{22}$ = (+) 56.0 (c = 0.1 in pentane).
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11. Glassy adduct **4** has $^1\text{H-NMR}(\text{CDCl}_3)$ δ = 0.726 (s, CH₃), 0.911 (s, CH₃), 1.308 (s, CH₃), 1.70 (m,2H), 2.0 (m,1H), 2.6 (m,1H), 2.8(d,1H, J=5.5 Hz), 3.52 (s, CH₃), 3.69 (s, CH₃) 7.0-8.0 (m,10H). $\text{C}_{28}\text{H}_{30}\text{O}_5$ calculated: C 75.33, H 6.72. Found: C 75.50, H 7.00.
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