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Dicyanoanthracene and Biphenyl Co-sensitized Photooxygenation of 1,1-Diphenyl-2-vinylcyclopropane

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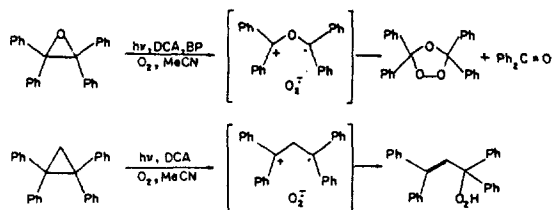
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Co-sensitized photooxygenation of 1,1-diphenyl-2-vinylcyclopropane (VCP-DPh) with 9,10-dicyanoanthracene and biphenyl in oxygen-saturated acetonitrile solution produced 3,3-diphenyl-5-vinyl-1,2-dioxolane as the major product. The same photoproduct was obtained by acetone sensitized photooxygenation in oxygen-saturated acetone solution. However, VCP-DPh remained intact when directly irradiated with DCA or irradiated with Rose Bengal to generate singlet oxygen. A mechanism involving a cosensitizer radical cation and sensitizer radical anion is proposed.

Introduction

Photooxygenation of olefins sensitized by cyano-substituted aromatic hydrocarbons such as 9,10-dicyanoanthracene(DCA) has been shown to proceed by an electron-transfer mechanisms by initial formation of the radical anion of the sensitizer and radical cation of the olefins even though singlet oxygen is definitely involved in certain olefins.¹ Subsequent reaction of O_2 with the radical cation affords the oxygenated product. Recently, Schaap and co-workers showed that the photooxygenation of epoxides to yield the corresponding ozonides could be co-sensitized by the non-light-absorbing, chemically unreactive aromatic hydrocarbon, biphenyl (BP), in conjunction with DCA.² They reported that a dramatic enhancement of the rate of photooxygenation of epoxides was observed in the presence of biphenyl. The photooxygenation of aryl-substituted cyclopropanes in the presence of DCA and acetonitrile also gives rise to the hydroperoxide and dioxolanes.³



Vinylcyclopropane compounds which exhibit bifunctionality show much enhanced chemical reactivities compared to simple cyclopropanes itself, and show extended conjugation of the unsaturated double bond and cyclopropane ring. By introduction of polar substituents to the cyclopropane ring, the vinylcyclopropanes undergo various addition reactions more readily with facile opening of the cyclopropane ring.⁴ In contrast with the extensive studies of photochemical and theoretical aspects of cyclopropane chemistry, the electron-transfer photooxygenation of cyclopropane compounds are only known in limited cases. Our interest has been around electron-transfer photooxygenation of substituted vinylcyclopropanes by cyanoaromatic-sensitization in oxygen saturated polar solvents.

Experimental

Instruments. UV-VIS absorption spectra were recorded on a Cary 17 spectrophotometer. Proton and carbon-13 magnetic resonance spectra were recorded with a Varian FT-80A spectrometer in chloroform-d. Infrared spectra were recorded on a Perkin-Elmer 283B spectrophotometer using potassium bromide pellets or a sodium chloride cell. Mass spectra were determined with a Hewlett Packard 5985A GC/MS system. Fluorescence spectra were recorded on a Aminco-Bowman spectrofluorometer with an Aminco-XY

recorder. Elemental analyses were carried out on F&M Scientific Cooperation C H N Analyzer Model 180. HPLC analyses were performed with a μ -Porasil column eluted with n-hexane and ethyl acetate (17/1, v/v) at a flow rate of 1.5 ml/min. on a Waters Associates Model 244 chromatograph with UV detector.

Materials. 9,10-Dicyanoanthracene (Eastman) was recrystallized twice from pyridine. Biphenyl (Aldrich) was purified by vacuum sublimation. Rose Bengal (Aldrich) was used without further purification. Acetonitrile (UV grade, Burdick & Jackson Lab.) was successively refluxed over and distilled from phosphorus pentoxide and calcium hydride under nitrogen. Acetone (Merck), n-hexane (Merck) and other reagents were used as received. Kiesel-gel 60 GF₂₅₄ and Kieselgel 60 (Merck) were used for thin-layer chromatography and flash column chromatography, respectively.

Preparation of 1,1-Diphenyl-2-vinylcyclopropane (VCP-DPh). 1,1-Diphenyl-2-vinylcyclopropane was prepared by thermal decomposition of diphenyldiazomethane in butadiene⁵: H-NMR (CDCl₃) δ 7.33-6.97 (m, 10H), 5.2-4.7 (m, 3H), 2.20 (m, 1H), 1.63-1.35 (m, 2H); IR (NaCl cell) 3060 cm⁻¹ (s), 3020 cm⁻¹ (s), 2910 cm⁻¹ (sh), 2000-1700 cm⁻¹ (monosubstituted phenyl), 1635 cm⁻¹ (m), 1015 cm⁻¹ (w); n_D²⁰ 1.019 g/cc.

Photooxygenation Procedure. Solutions placed in a Pyrex glass reaction vessel were saturated with oxygen by bubbling oxygen for 30 min at 0°C. The solution was then irradiated at 10°C under oxygen sparging with a Hanovia 450W medium-pressure mercury arc lamp.⁶ The products were isolated from sensitizer by dry-packed silica gel column chromatography and analyzed by thin-layer chromatography with ethyl acetate in hexane (1/15, v/v). This procedure was used in all photooxygenations unless otherwise indicated.

Acetone Sensitized Photooxygenation of VCP-DPh. VCP-DPh (0.22g, 1 × 10⁻³M) in 100 ml of acetone was irradiated under oxygen with a Pyrex glass filter sleeve. The reaction was monitored by HPLC and was completed in 12 hours. The solvent was removed on a rotary evaporator, and the residue was subjected to column chromatography on silica gel (10 in. × 1 in.) using successively 500 ml of acetone, and 300 ml of methanol. The ethyl acetate and acetone fractions were evaporated and subjected to preparative thin-layer chromatography to yield an endoperoxide (**2**) as the major product and benzophenone (**3**) as a side product. Recrystallization of **2** from ethyl acetate yielded colorless needle: 3,3-diphenyl-5-vinyl-1,2-dioxolane (**2**), 226 mg 89.7% yield, ¹H-NMR (CDCl₃) δ 7.65-7.30 (m, 10H), 6.15-5.70 (m, 1H), 5.50-5.20 (m, 2H), 4.91 (q, J = 7.5 Hz, 1H), 3.59 (dd, J = 12 Hz, J = 7.5 Hz, 1H), 3.16 (dd, J = 12 Hz, J = 7.5 Hz, 1H); ¹³C-NMR (CDCl₃) δ 142.69, 142.40, 134.94, 128.25, 127.50, 126.46, 126.21, 119.08, 90.60, 82.80, 53.30; IR (KBr) 2000-1700 cm⁻¹ (monosubstituted phenyl), 1605 cm⁻¹ (m, vinyl C=C stretching), 1060 cm⁻¹, 1035 cm⁻¹ (m, asymmetric C-O stretching); mass spectrum, m/e (relative intensity), 252 [M⁺] (0.9%), 218 [M-H₂O]⁺ (26.7%), 142 [C₆H₅C₂H₂]⁺ (24.1%), 129 [C₆H₅C₄H₄]⁺ (39.6%), 105 [C₆H₅C₂H₄]⁺ (55.9%), 77 [C₆H₅]⁺ (100%); mp 92-92.5°C; elemental analysis (C₁₇H₁₆O₂), calc. 'd. C 80.91% H 6.30%, found C 80.92% H 6.30%.

Benzophenone (**3**) (10 mg, 5.5% yield) was identified from its spectral properties and by comparison with an authentic sample. The evolved gases were trapped with 200 ml of Br₂/CHCl₃ (1/1, v/v) at -40°C and the resulting reddish-brown

solution was stirred for 15 hours at room temperature. After evaporation of excess bromine and solvent, the dark liquid crystallized on standing. The products were filtered, washed with cold ethanol and recrystallized from ethanol to obtain colorless crystal (17.6 mg). The product was identified as 1,2,3,4-tetrabromobutane from its spectral properties and by comparison with an authentic sample. The gaseous product is thus proven to be 1,3-butadiene.

Co-sensitized Photooxygenation of VCP-DPh with DCA and BP. Co-sensitized photooxygenation was carried out in dry acetonitrile solution with 1 × 10⁻²M VCP-DPh, 1 × 10⁻²M BP, and 1 × 10⁻⁴M DCA. The solution was irradiated at 10°C under oxygen sparging and through a CuSO₄-filter solution.⁶ The reaction was completed in 8 hours. The products were isolated by preparative silica gel thin-layer chromatography to obtain 64.8% of 3,3-diphenyl-5-vinyl-1,2-dioxolane (**2**) and 35.2% of benzophenone (**3**). 1,3-Butadiene was detected as described.

Results and Discussion

Fluorescence Quenching of DCA by BP and DCA.

9,10-Dicyanoanthracene absorbs the light of $\lambda > 400$ nm and exhibits strong, blue fluorescence in both polar and nonpolar solvents. In degassed acetonitrile solution, a Stern-Volmer analysis of the fluorescence quenching of DCA by VCP-DPh gives a slope of 108 M⁻¹ (Figure 1). The lifetime of 'DCA*' in this solvent is reported as 15.2 ns⁷, thus the rate of quenching of the fluorescence of DCA by VCP-DPh is 7.1 × 10⁹ M⁻¹s⁻¹. BP also quenches the fluorescence of DCA with the rate constant of 3.1 × 10⁹ M⁻¹s⁻¹ (Figure 2). However, no exciplex emission was observed in this solvent with both quenchers.

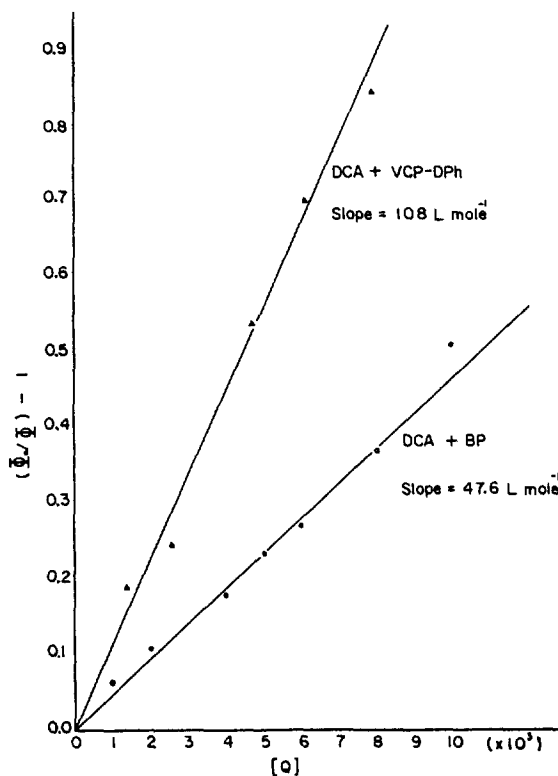
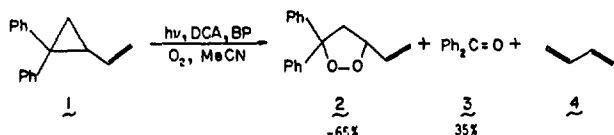


Figure 1. A Stern-Volmer plot for the fluorescence quenching of DCA by BP and VCP-DPh.

Quenching of $^1\text{DCA}^*$ by VCP-DPh 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. From the Stern-Volmer analysis, VCP-DPh quenches the fluorescence of DCA more efficiently than BP but the probable radical ion pair is deactivated very efficiently by a back electron transfer without giving any photoproducts.

Photooxygenation of VCP-DPh(1). Irradiation ($\lambda > 400$ nm) of an oxygen-saturated acetonitrile solution of **1** ($1 \times 10^{-2}\text{M}$), BP ($1 \times 10^{-2}\text{M}$), and DCA ($1 \times 10^{-4}\text{M}$) yielded 3,3-diphenyl-5-vinyl-1,2-dioxolane (**2**) and benzophenone (**3**) as the major products. The oxolane (**2**) was shown to be stable in the reaction conditions indicating that benzophenone (**3**) is not derived by subsequent photosensitized decomposition of the oxolane. Additionally, BP is not appreciably consumed during the cosensitized photooxygenation.



Control experiment showed that no oxidation occurs in the presence of DCA alone. Furthermore, VCP-DPh is stable to singlet oxygen since the compound remained intact when irradiated with Rose Bengal which is known to generate singlet oxygen.

Arnold⁸ and Roth⁹ have shown that electron-transfer photooxygenations of aryl-substituted cyclopropanes lead to C-C bond cleavage and formation of radical cations. More recently, it has been demonstrated that BP acts as a cosen-

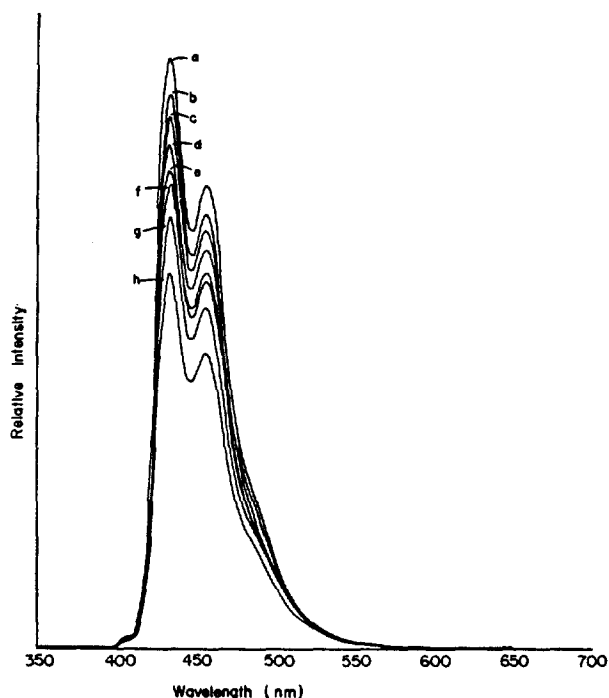
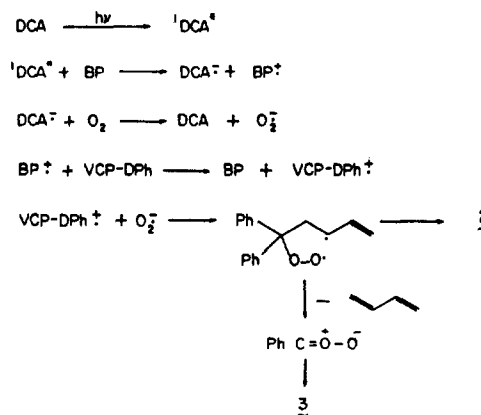


Figure 2. Emission spectra of DCA (1×10^{-5} M) in degassed acetonitrile containing BP at concentrations of 0, 1×10^{-3} , 2×10^{-3} , 4×10^{-3} , 5×10^{-3} , 6×10^{-3} , 8×10^{-3} , and $1 \times 10^{-2}\text{M}$ (a-h, respectively). Excitation wavelength; 410 nm.

sitizer in photooxygenations by a process analogous to homogeneous redox catalysis for electrode reactions.¹⁰ Therefore, a mechanism involving a cosensitizer radical cation and sensitizer radical anion which subsequently reduces O_2 is proposed as shown in scheme I. The cosensitizer radical cation ($\text{BP}^{\cdot+}$) then oxidizes the substrate (VCP-DPh). The radical cation of VCP-DPh ($\text{VCP-DPh}^{\cdot+}$) is generated in an open form, which reacts with superoxide by a stepwise process to form the biradicals **A** or **B**.¹¹ These biradical intermediates close to give rise to the cyclic peroxide product (**2**) as the major product, and if the biradical **A** cleaves before it closes, it can give the carbonyl oxide which will subsequently yield benzophenone (**3**) and 1,3-butadiene (**4**) as detected in brominated form. The major product is formed from the closure of the biradicals to give an endoperoxide (**2**).

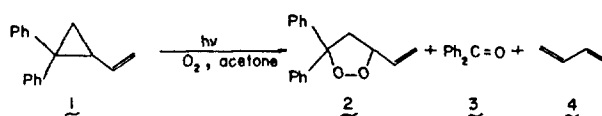


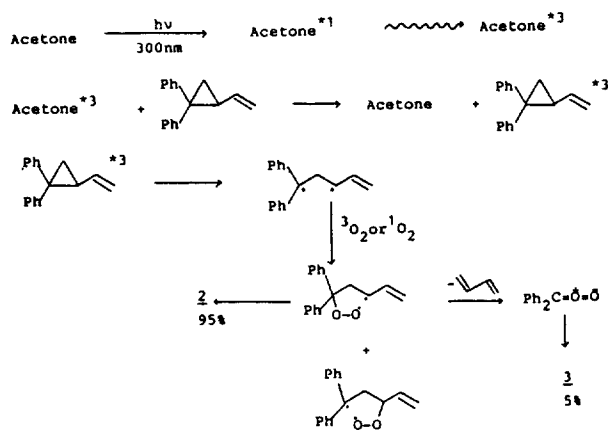
Scheme 1.

Although VCP-DPh quenches $^1\text{DCA}^*$ at a faster rate, it is not photooxygenated by DCA in oxygenated acetonitrile. These results suggest that the radical ion pair formed between $^1\text{DCA}^*$ and VCP-DPh is deactivated very efficiently by a back electron transfer process and the formation of cage-escaped $\text{BP}^{\cdot+}$ has a higher efficiency compared with the formation of radical cation of **1** by electron transfer to $^1\text{DCA}^*$.

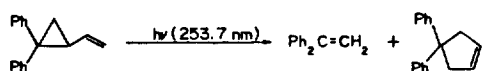
Reaction of VCP-DPh with singlet oxygen was carried out but the expected photo-ene or cycloaddition of $^1\text{O}_2$ to vinyl group was not observed. In VCP-DPh, two phenyl groups attached to cyclopropane ring are not conjugated with the vinyl group and cyclopropane ring does not transmit the conjugation.¹² The allylic hydrogen is sterically restricted by the two phenyl groups. Therefore, the vinyl group of VCP-DPh is not electron-rich enough to undergo 1,2-cycloaddition with singlet oxygen to produce 1,2-dioxetanes or ene-reaction.

The same photoproducts, **2** and **3**, were obtained by acetone sensitized photooxygenation in oxygen-saturated acetone solution. The following mechanism for the photooxygenation reaction is proposed (Scheme II). Upon direct irradiation of VCP-DPh at 253.7 nm in the absence of oxygen, 1,1-diphenylethylene was formed as a major product along with a small amount of 4,4-diphenylcyclopentene probably via the biradical intermediate formed through the initial cyclopropane ring opening.^{12a}





Scheme 2.



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