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Photooxygenation of 1,1-Diphenyl-2-vinylcyclopropane

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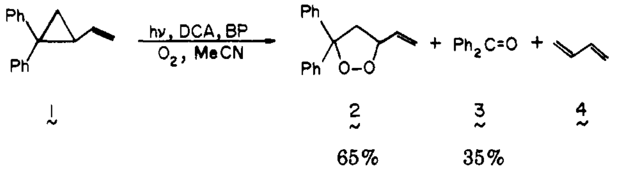
Photooxygenation of olefins sensitized by cyano-substituted aromatic hydrocarbons such as 9,10-dicyanoanthracene (DCA) is known to proceed by electron transfer involving initial formation of the sensitizer radical anion and the olefin radical cation of the olefins.[1] Electron transfer from the sensitizer radical anion to O_2 forms the oxygen radical anion $O_2^{-\bullet}$, which reacts with the olefin radical cation to give the oxygenated product. Recently, Schaap and co-workers have shown that aryl-substituted cyclopropanes and epoxides yield the corresponding ozonides when their photooxygenation is cosensitized by DCA and biphenyl (BP).[2,3] We report here on the similarly cosensitized photooxygenation of 2,2-diphenyl-2-vinylcyclopropane (VCP-DPh, 1).

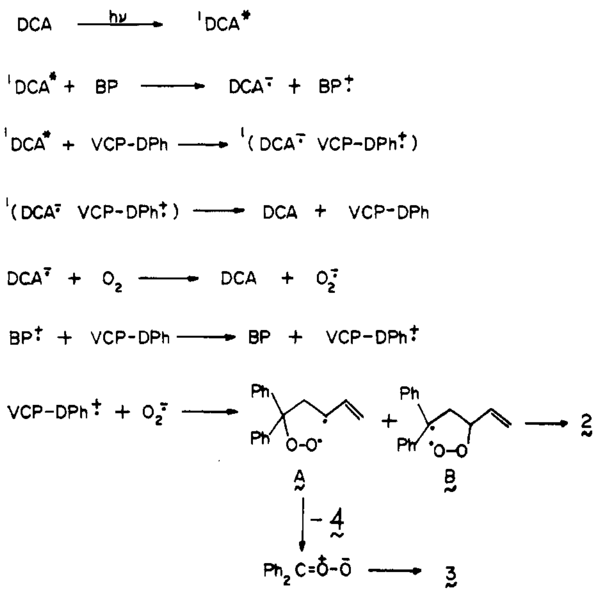
Irradiation ($\lambda > 400$ nm) of an oxygen-saturated acetonitrile solution of 1 (1×10^{-2} M), BP (1×10^{-2} M), and DCA (1×10^{-4} M) yields 3,3-diphenyl-5-vinyl-1,2-dioxolane (2) and benzophenone (3) as the major products. The dioxolane 2 was shown to be stable under our reaction conditions, indicating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



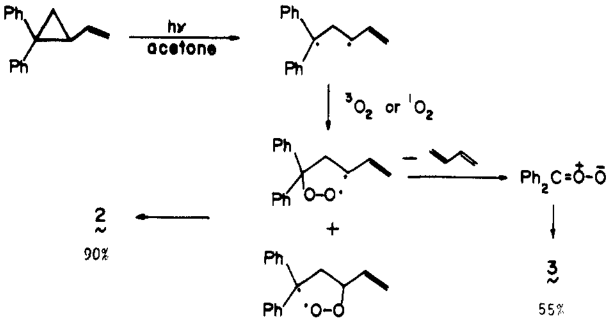
No oxidation was observed when an acetonitrile solution of 1 and DCA was irradiated, although the strong fluorescence of DCA was efficiently quenched by 1 with a rate constant k_q of 7.1×10^9 M^{-1} s^{-1}. BP also quenched the fluorescence of DCA with $k_q = 3.1 \times 10^9$ M^{-1} s^{-1}. No exciplex emission was observed in acetonitrile with both quenchers.

Quenching of ^{1}DCA* by 1 probably forms a primary geminate radical ion pair of singlet multiplicity. In a polar medium, diffusion can lead to solvent-separated radical ions. However, back electron transfer can compete with this diffusion process to return the reactants to the ground state. According to Stern–Volmer analysis, 1 quenches the fluorescence of DCA more efficiently than BP, but the probable radical ion pair formed in the solvent cage is deactivated efficiently by back electron transfer without giving any photoproducts. The escape of BP$^{+\bullet}$ from the solvent cage is more efficient than that of the radical cation of 1, as shown by the longer lifetime of BP$^{+\bullet}$.

Scheme I



Scheme II



We propose that $O_2^{-\bullet}$ generated from DCA$^{-\bullet}$ is involved in the formation of 2 under our reaction conditions. The alternative, involvement of singlet oxygen, was eliminated by our finding that 1 is stable to singlet oxygen generated by irradiation of Rose Bengal, which is known to generate singlet oxygen.

Neither the expected photoene reaction nor cycloaddition of $^1O_2$ to the vinyl group was observed. The two phenyl groups attached to the cyclopropane ring of 1 are not conjugated with the vinyl group because the cyclopropane ring does not transmit conjugation.[4] Presumably the photoene reaction does not occur because the allylic hydrogen is sterically shielded from singlet oxygen by the two phenyl groups. In addition, the vinyl group of 1 is not sufficiently electron rich to undergo 1,2 cycloaddition with singlet oxygen.[5]

Arnold[6] and Roth[7] 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 cosensitizer in photooxygenations by a process analogous to homogeneous redox catalysts of electrode reactions.[8]

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[1] (a) Barton, D. H. R.; Leclerc, G.; Magnus, P. D.; Menzies, I. D. *J. Chem. Soc., Chem. Commun.* **1972**, 447. (b) Eriksen, J.; Foote, C. S.; Parker, T. L. *J. Am. Chem. Soc.* **1977**, *99*, 6455. (c) Haynes, R. K. *Aust. J. Chem.* **1978**, *31*, 121. (d) Brown-Wensley, K. A.; Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* **1978**, *100*, 4162. (e) Saito, I.; Tamoto, K.; Matsuura, T. *Tetrahedron Lett.* **1979**, 2889. (f) Berenjian, N.; deMayo, P.; Phoenix, F. H.; Weedon, A. C. *Ibid.* **1979**, 4179. (g) Ando, W.; Nagashima, T.; Saito, K.; Kohmoto, S. *J. Chem. Soc., Chem. Commun.* **1979**, *154*. (h) Mattes, S. L.; Farid, S. *Ibid.* **1980**, 126. (i) Eriksen, J.; Foote, C. S. *J. Am. Soc.* **1980**, *102*, 6083. (j) Spada, L. T.; Foote, C. S. *Ibid.* **1980**, *102*, 391. (k) Schaap, A. P.; Zaklika, K. A.; Kaskar, B.; Fung, L. W.-M. *Ibid.* **1980**, *102*, 389. (l) Mattes, S. L.; Farid, S. *Ibid.* **1982**, *104*, 1454.

[2] (a) Schaap, A. P.; Lopez, L.; Gagnon, S. D. *J. Am. Soc.* **1983**, *105*, 663. (b) Schaap, A. P.; Siddigui, S.; Gagnon, S. D.; Lopez, L. *Ibid.* **1983**, *105*, 5149. (c) Schapp, A. P.; Siddigui, S.; Balakrishnan, P.; Lopez, L.; Gagnon, S. D. *Isr. J. Chem.* **1983**, *23*, 415.

[3] Schaap, A. P.; Lopez, L.; Anderson, S. D.; Gagnon, S. D. *Tetrahedron Lett.* **1982**, *23*, 5493.

[4] Shim, S. C.; Suh, S. W. *J. Korean Chem. Soc.* **1979**, *23*, 115.

[5] Shim, S. C.; Song, J. S. *Bull. Korean Chem. Soc.* **1984**, *5*, 265.

[6] Arnold, D. R.; Humphreys, R. W. R. *J. Am. Chem. Soc.* **1979**, *101*, 2743.

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We propose a similar mechanism involving a cosensitizer radical cation and a sensitizer radical anion which subsequently reduces O_2 (Scheme I). The cosensitizer radical cation ($BP^{+\cdot}$) then oxidizes the substrate VCP-DPh. The radical cation VCP-DPh$^{+\cdot}$ is generated in an open form that reacts with superoxide to form the biradicals A or B.[9] These biradical intermediates close to give the cyclic peroxide **2** as the major product. However, if biradical A cleaves before it closes, it can give the carbonyl oxide that yields benzophenone and 1,3-butadiene. The latter was isolated as its tetrabromide.

The same photoproducts **2** and **3** were obtained by acetone-sensitized photooxygenation of **1**, for which we propose the mechanism of Scheme II.

Direct irradiation of **1** at 253.7 nm in the absence of oxygen produces 1,1-diphenylethylene as the major product. A small amount of 4,4-diphenylcyclopentene was also formed, probably via the biradical intermediate from the initial cyclopropane ring opening.[4]

Experimental Section

Instruments. UV–vis absorption spectra were recorded on a Cary 17 spectrophotometer. ^1H and ^{13}C NMR spectra were recorded with a Varian FT-80A spectrometer in chloroform-*d*. Infrared spectra were recorded on a Perkin-Elmer 283B spectrophotometer using the KBr pellets of 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 a 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 chromatography 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 GF_{254} and Kiesel-gel 60 (Merck) were used for TLC and flash chromatography, respectively.

1,1-Diphenyl-2-vinylcyclopropane (VCP-DPh). 1,1-Diphenyl-2-vinylcyclopropane was prepared by thermal decomposition of diphenyldiazomethane in butadiene:[10] ^1H NMR ($CDCl_3$) δ 7.33–6.97 (m, 10 H), 5.2–4.7 (m, 3 H), 2.20 (m, 1 H), 1.63–1.35 (m, 2 H); IR (NaCl cell) 3060 (s), 3020 (s), 2910 (sh), 2000–1700 (monosubstituted phenyl), 1635 (m), and 1015 cm^{-1} (w); n^{25} 1.5870; d^{20} 1.019 g/cc.

Acetone-Sensitized Photooxygenation of VCP-DPh. VCP-DPh (0.22 g, 1 mmol) in 100 mL of acetone witth irradiation ($\lambda > 290$ nm) under oxygen with a Hanovia 450-W medium-pressure mercury arc lamp. The reaction was monitored by HPLC and was completed in 12 h. 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 ethyl acetate, 500 mL of acetone, and 300 mL of methanol. The ethyl acetate and acetone fractions were evaporated and subjected to preparative TLC to yield endoperoxide **2** as the major product and benzophenone (**3**) as a side product. Recrystallization of **2** from ethyl acetate yielded colorless needles: 3,3-diphenyl-5-vinyl-1,2-dioxolane (**2**), 226 mg (89.7%): ^1H NMR ($CDCl_3$) δ 7.65–7.30 (m, 10 H), 6.15–5.70 (m, 1 H), 5.50–5.20 (m, 2 H), 4.91 (q, $J = 795$ Hz, 1 H), 3.59 (dd, $J = 12$ and 7.5 Hz, 1 H), 3.16 (dd, $J = 12$ and 7.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$) 142.69, 142.40, 134.94, 128.25, 127.50, 126.46, 126.21, 19.08, 90.60, 82.80, 53.30; IR (KBr) 2000–1700 (monosubstituted phenyl), 1605 (m, vinyl C=C stretching), 1060 and 1035 cm^{-1} (m, asymmetric C–O stretching); mass spectrum, *m/e* (rel intensity), 252 [M^+] (0.9), 218 [$M - H_2O^+$] (26.7), 142 [$C_6H_5C_5H_5^+$] (24.1), 129 [$C_6H_5C_4H_4^+$] (39.6), 105 [$C_6H_5C_2H_4^+$] (55.9), 77 [$C_6H_5^+$] (100); mp 92–92.5 °C. Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.91; H, 6.30. Found: C, 80.92; H, 6.30.

Benzophenone (10 mg, 5.5%) was identified from its spectral properties and by comparison with an authentic sample. The evolved gases were trapped with 20 mL of $Br_2/CHCl_3$ (1/1, v/v) at −40 °C and the resulting reddish brown solution was stirred for 15 h 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.

Cosensitized Photooxygenation of VCP-DPh with DCA and BP. Cosensitized photooxygenation was carried out in dry acetonitrile with 1×10^{-2} M VCP-DPh, 1×10^{-2} M BP, and 1×10^{-4} M DCA. The solution was irradiated at 10 °C under oxygen sparging and through a $CuSO_4$ filter solution.[11] The reaction was completed in 8 h. The products were isolated by preparative silica gel TLC 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.

Registry No. **1**, 57393-03-0; **2**, 102261-93-8; **3**, 119-61-9; **4**, 106-99-0; DCA, 1217-45-4; BP, 92-52-4; diphenyldiazomethane, 883-40-9; acetone, 67-64-1; 1,2,3,4-tetrabromobutane, 1529-68-6.

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(8) Schaap, A. P.; Siddigui, S.; Prasad, G.; Palomino, E.; Lopez, L. *J. Photochem.* **1984**, *25*, 167 and references cited therein.

(9) Alternatively, ground-state oxygen could add to VCP-DPh$^{+\cdot}$ with subsequent reduction of the peroxy radical cation by $O_2^{-\cdot}$, DCA$^{-\cdot}$, VCP-DPh, or BP.

(10) Cho, I.; Ahn, K. B. *J. Korean Chem. Soc.* **1978**, *22*, 158.

(11) The 1-cm pathlength filter solution was prepared from 27 g of $CuSO_4 \cdot H_2O$, 30 g of $NaNO_2$, and 50 mL of concentrated NH_4OH diluted with water to 1000 mL.

Organic Sonochemistry. New Ultrasonically Accelerated Reactions Involving Lithium

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There is a growing list of successful applications of ultrasonic waves to organic syntheses.[1] To this we wish to add the significant rate enhancements that ultrasound produces when the substrates given in Table I are treated with lithium.[1a,b] All reactions were run at room temperature with 20–50% excess lithium dispersion or powder. In the absence of ultrasonic waves the reaction times were 2–5 times longer.

The reaction of α,α'-dibromo-*o*-xylene with lithium is noteworthy (Scheme I) because it does not lead to *o*-xylylene, the major product obtained when zinc is used.[2] Evidence against *o*-xylylene formation and in favor of an ionic intermediate is the isolation of α,α'-bis(trimethylsilyl)-*o*-xylene when trimethylchlorosilane is present as a trap.

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