could not be conveniently separated by chromatography or GLC. Partial hydrolysis of the mixture gave an inseparable mixture of **3h** and **6h**. The presence of **3h** was inferred from the NMR spectrum (3.92, d, J = 17; 3.20, d, J = 17) and the IR absorption at 5.61. Pure **4h** was obtained by heating the mixture at 135 °C for 10 h, leaving an oily residue: NMR ($CDCl_3$) δ 8.01 (d with fine splitting, J = 9, 2 H), 6.94 (d with fine splitting, J = 9, 2 H), 3.90 (s, 3 H), 3.80 (s, 2 H), 2.23 (q, J = 8, 2 H), 2.03 (q, J = 8, 2 H), 0.95 (t, J = 8, 6 H), 0.96 (s, 9 H), 0.13 (s, 6 H); IR (film) 5.91, 6.20, 7.93, 8.52, 12.02, 12.85; FDMS, m/e 362. Anal. Calcd for $C_{21}H_{34}O_3Si$: C, 69.56; H, 9.45. Found: C, 69.45; H, 9.53.

Preparation of 4c. A mixture of 1.0 g of **1b** (3.72 mmol) and 0.78 g (4.02 mmol) of **2a** was refluxed with 5 g of CCl_4 for 20 h. Chromatography afforded 1.82 g (>100%) of an oil, pure by NMR except for traces of solvent. Crystals of **4c** were obtained when the product was stored in methanol at -20 °C overnight, mp 69.5-70.5 °C: NMR ($CDCl_3$) δ 7.9-7.1 (m, 14 H), 3.82 (s, 2 H), 0.70 (s, 9 H), -0.15 (s, 6 H); IR (KBr) 5.94, 6.17, 6.30, 7.98, 8.18, 9.88, 10.15, 12.02, 14.30; FDMS, m/e 462. Anal. Calcd for $C_{28}H_{31}ClO_2Si$: C, 72.62; H, 6.75. Found: C, 72.79; H, 6.69.

Hydrolysis of **4c** with acetone-water-HCl yielded the diketone **6c**, which exhibited appropriate spectral and analytical data.

Preparation of 4e. A mixture of 1.0 g of **2a** (5.15 mmol), 1.2 g of **1c** (5.15 mmol), and 2 g of CCl_4 was allowed to react for 3 days at room temperature. Chromatography afforded 1.74 g (79%) of an oil which crystallized on standing. Recrystallization from methanol afforded compact white crystals of **4e**, mp 77-78 °C: NMR ($CDCl_3$) δ 8.0-7.2 (m, 15 H), 3.91 (s, 2 H), 0.74 (s, 9 H), -0.12 (s, 6 H); IR (KBr) 5.93, 6.12, 8.02, 8.10, 9.96, 10.22, 11.93, 12.07, 12.83, 13.21, 14.26; λ_{max} (CH_3OH) 245 nm (ϵ 23 290); FDMS, m/e 428. Anal. Calcd for $C_{28}H_{32}O_3Si$: C, 78.45; H, 7.53. Found: C, 78.37; H, 7.33.

Hydrolysis of **4e** in acetone-water-HCl gave the diketone **6e**, mp 125-126 °C (lit.[17] mp 127 °C).

Preparation of 4g. After chromatography, diphenylketene (1.0 g, 5.15 mmol) and **1d** (1.36 g 5.15 mmol) yielded 2.27 g (96%) of **4g**, pure by NMR. Recrystallization from CH_3OH and then from heptane yielded crystals, mp 76-78 °C: NMR ($CDCl_3$) δ 7.93 (d, 1 H), 7.36 (s, 5 H), 7.30 (s, 5 H), 6.9 (d, 1 H); IR (KBr) 5.95, 6.25, 7.98, 8.15, 8.52, 10.17, 12.04, 12.79, 14.25; λ_{max} (CH_3OH) 268 nm (ϵ 25 320); FDMS, m/e 458. Anal. Calcd for $C_{29}H_{34}O_3Si$: C, 75.94; H, 7.47. Found: C, 76.06; H, 7.46.

Hydrolysis of **4g** in acetone-water-HCl gave the diketone, **6g**, mp 107-108 °C (lit.[17] mp 108 °C).

Measurement of the Relative Amounts of 4d and 3d Produced in the Reaction of 1b with 2b. A mixture of 0.24 g (0.9 mmol) of **1b** and 0.28 g (2.9 mmol) of **2b** was heated at 96 °C for 4 h. The ratio of **4d**:**3d** as well as the conversion (assuming that all **1b** was converted to **4d** and **3d**) was calculated from the integrated NMR spectrum. Within experimental error, there was no difference in **4d**:**3d** from 15% to 85% conversion, and a value **4d**:**3d** = 0.25 ± 0.05 represents the average of four measurements.

Pyrolysis of 5 in 1a. A mixture of 19.4 mg of **5**, 8.8 mg of *n*-octadecane, and 480 mg of **1a** was heated at 138 °C for 4 h. GLC analysis indicated that **4i** had been formed in 22% yield.

Competitive Reaction of 1a and 1b with 2b. A mixture of 0.18 g (1.14 mmol) of **1a**, 0.50 g (1.86 mmol) of **1b**, and 0.05 g (0.51 mmol) of **2b** was heated at 99 °C for 4 h, causing the disappearance of most of the yellow color of diethylketene. The integrated NMR spectrum showed **3d**, **4d**, and **3b** in the molar ratio of 4:1:12. Assuming pseudo-first-order kinetics, **1a** then reacts about 4 times faster with **2b** than does **1b**. Any deviation from the pseudo-first-order approximation will increase this rate difference. The rate difference was not determined with any greater precision because of the inability to measure **3d** by a method other than NMR spectroscopy.

Registry No. **1a**, 66031-93-4; **1b**, 90720-21-1; **1c**, 66324-10-5; **1d**, 80676-78-4; **1e**, 84850-50-0; **2a**, 525-06-4; **2b**, 24264-08-2; **3a**, 90720-22-2; **3b**, 90720-23-3; **3c**, 90720-24-4; **3d**, 90720-25-5; **3e**, 90720-26-6; **3f**, 90720-27-7; **3g**, 90720-28-8; **3h**, 90720-29-9; **3i**, 90720-30-2; **4a**, 90720-31-3; **4b**, 90720-32-4; **4c**, 90720-33-5; **4d**, 90720-34-6; **4e**, 90720-35-7; **4f**, 90720-36-8; **4g**, 90720-37-9; **4h**, 90720-38-0; **4i**, 90720-39-1; **5**, 90720-40-4; **6c**, 90720-41-5; **6e**, 16877-30-8; **6f**, 90720-42-6; **6g**, 16877-31-9; **6h**, 90720-43-7; **6i**, 90720-44-8.

Chemistry of Singlet Oxygen. 47. 9,10-Dicyanoanthracene-Sensitized Photooxygenation of Alkyl-Substituted Olefins

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Abstract: 9,10-Dicyanoanthracene (DCA) sensitizes the photooxygenation of 1-methylcyclohexene (**1**), 1,2-dimethylcyclohexene (**2**), and cholesterol (**3**) in acetonitrile and benzene. For all three olefins, the products are the same as those formed by reaction with singlet oxygen. The quantum yields for product formation and the solvent deuterium isotope effects for this reaction in acetonitrile and benzene are in good agreement with the values calculated assuming a singlet oxygen mechanism. These results indicate that singlet oxygen is the reactive intermediate rather than radical ions.

Previously we have shown 9,10-dicyanoanthracene (DCA)-sensitized photooxyygenation of phenyl-substituted olefins occurs exclusively by an electron-transfer pathway (Scheme I).[1] These compounds are essentially unreactive to singlet oxygen. In a later study of a singlet-oxygen-reactive olefin, 1,1-diphenyl-2-methoxyethylene, Steichen and Foote found tentative evidence that both singlet oxygen and electron-transfer mechanisms were operating.[2] Santamaria has provided chemical evidence for the production of singlet oxygen from DCA.[3] More recently, we have demonstrated directly by laser spectroscopy that DCA can sensitize the formation of $^1O_2$ in substantial yield by several mechanisms.[4,5] DCA-sensitized photooxygenation can therefore occur by two distinct pathways: electron transfer (Scheme I) and $^1O_2$. This complication led us to determine the mechanism by which several

(1) Eriksen, J.; Foote, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 6083-6088 and references cited therein.
(2) Steichen, D. S.; Foote, C. S. *J. Am. Chem. Soc.* **1981**, *103*, 1855-1857.
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(4) Manring, L. E.; Gu, C.-L.; Foote, C. S. *J. Phys. Chem.* **1983**, *87*, 40-44.
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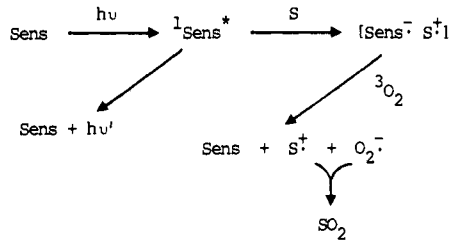
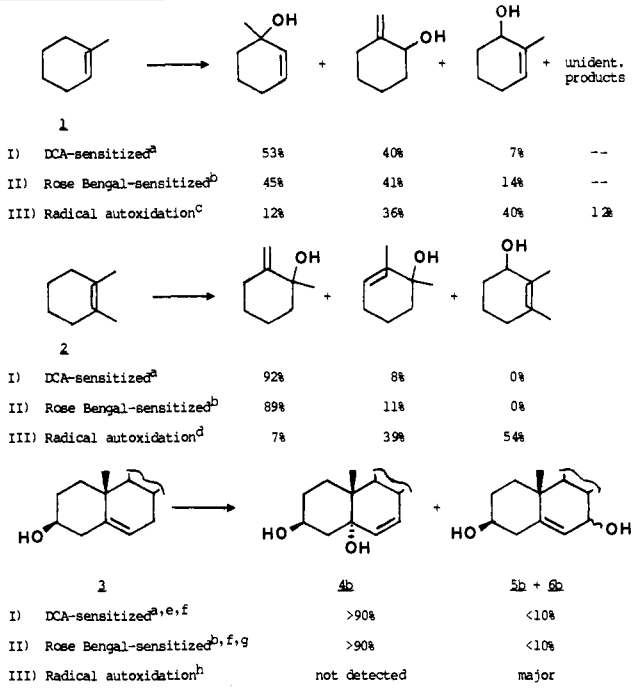
Scheme I



where: Sens = electron-deficient sensitizer

S = olefinic substrate

Table I. Products of Reaction of **1**, **2**, and **3** with Oxygen under Three Sets of Conditions: DCA Sensitization (I), Rose Bengal Sensitization (II), and Radical Autoxidation (III)



[a] This study: (1) [DCA] = 10^{-4} M/$h\nu$ (>400 nm)/O_2 saturated CH_3CN; (2) excess Ph_3P. [b] This study: (1) [Rose Bengal] = 10^{-5} M/$h\nu$ (>500 nm)/O_2 saturated CH_3CN; (2) excess Ph_3P. [c] Neat **1** was refluxed with 1% di-*tert*-butyl peroxide under air for 30 min.[30] The product mixture was reduced with sodium borohydride in methanol. [d] References 29 and 30. [e] 10-min irradiation; ~5% conversion. [f] Percentage of identified products. [g] 10-min irradiation; ~2% conversion. [h] References 19 and 20; the detection limit in these studies was approximately 2%.

typical olefinic substrates for singlet oxygen undergo DCA-sensitized photooxygenation.

We chose for study three simple alkyl-substituted olefins which are typical singlet-oxygen substrates: 1-methylcyclohexene (**1**), 1,2-dimethylcyclohexene (**2**), and cholesterol (**3**). The reaction of these three substrates with $^1O_2$ yields characteristic products or product distributions.[6] Formation of such products, especially the 5α-hydroperoxide of cholesterol, has been used as an important diagnostic test for the presence of $^1O_2$ in both chemical and biological systems.[7-9] Preliminary study of **1**, **2**, and **3** revealed that the same products are formed by DCA-sensitized photooxygenation (Table I). If any fraction of these products was arising by the electron-transfer pathway (Scheme I), then the diagnostic utility of alkyl-substituted olefins as $^1O_2$ probes would be diminished. For this reason, we undertook a detailed mechanistic investigation of the reaction pathway of the DCA-sensitized photooxygenation of these olefins and report here that the results are consistent with exclusive reaction of these substrates with $^1O_2$.

Table II. Electron-Transfer Quenching of DCA Fluorescence (Experimental Fluorescence Quenching Constants (k_q), Irreversible Oxidation Potentials (E(ox)), and Calculated Free Energies (ΔG) for Electron Transfer)

quencher	solvent	k_q ($M^{-1}s^{-1}$)	E(ox)[a] (V vs. SCE)	ΔG[b] (kcal/mol)
1	CH_3CN	$(8.8 \pm 0.7) \times 10^9$	1.82[c]	-3.4
1	C_6H_6	$(1.8 \pm 0.7) \times 10^7$		
2	CH_3CN	$(1.3 \pm 0.1) \times 10^{10}$	1.49[c]	-11.1
2	C_6H_6	$(3.9 \pm 0.1) \times 10^9$		
3	CH_3CN	$(4.2 \pm 0.2) \times 10^9$	1.75	-5.1
3	C_6H_6	2×10^8[d]		

[a] Scan rate is 250 mV/s. Measured half-wave potentials are expressed relative to SCE with use of the conversion, E(ox) vs. SCE = E(ox) vs. Ag/Ag^+ + 0.337 V.[31] [b] The values calculated from eq 1 are only approximate since the oxidation potentials are irreversible. Such approximations have been shown to agree quite well with experiment.[1] [c] These values are in fair agreement with reported oxidation potentials: 1.70 V for **1**[32] and 1.40 V for **2**.[33] [d] No quenching was observed; this value corresponds to the minimum detectable quenching.

Table III. Physical Parameters Needed for Calculation of the Quantum Yield of Product Formation (Φ_p)

parameter	in CH_3CN	in CD_3CN	in C_6H_6	in C_6D_6
k_2	$0.021k_q$[a]		$0.021k_q$[a]	
k_q	see Table II		see Table II	
$k_3[O_2]$ ($\times 10^{-7}$ s^{-1})	5.45[b]		3.5 ± 0.1[c]	
k_4 (s^{-1})	$0.017/\tau$[a]		$0.017/\tau$[a]	
τ (ns)	15.3 ± 1.3[d-f]	15.2 ± 1.9[d]	12.4[f]	
$1/k_8$ (μs)	65 ± 2[g]	600 ± 33[h]	30 ± 2[g]	550 ± 11[h]
$k_9(1)$ ($\times 10^{-5}$ M^{-1} s^{-1})	2.6[i,j]		2.6[i,j]	
$k_9(2)$ ($\times 10^{-7}$ M^{-1} s^{-1})	1.0[i,k]		1.0[i,k]	
$k_9(3)$ ($\times 10^{-4}$ M^{-1} s^{-1})	7.0[i,l]		7.0[i,l]	

[a] Measured for 2-methyl-2-pentene in acetonitrile;[4] assumed to be the same in benzene and for other olefins. [b] In oxygen-saturated acetonitrile; ref 5. [c] In oxygen-saturated benzene. [d] This study; fluorescence lifetimes from raw data fitted to a single exponential by a nonlinear least-squares analysis; [DCA] = 10^{-4} M. Errors are χ^2 values. [e] Reference 22. [f] Reference 34. [g] Reference 5. [h] Reference 35. [i] Variation of k_9 with solvent has been neglected. [j] In benzene; ref 36. [k] In methanol; ref 36. [l] Calculated from the β value[36] for **3** in pyridine and the lifetime of $^1O_2$ in pyridine.[37]

Experimental Section

^1H NMR spectra were recorded on a Brucker WP-200 spectrometer and infrared spectra on a Perkin-Elmer 137 spectrophotometer. Mass spectra were recorded by Dr. K. Fang on an AEI MS-9 spectrometer. Fluorescence quenching experiments were carried out on a Spex Fluorolog instrument equipped with a photon-counting detector. Oxidation half-wave potentials were measured on a Bioanalytical Systems CV-1A cyclic voltamograph at a platinum disk electrode vs. a silver/silver nitrate electrode in acetonitrile at 25 °C. Tetraethylammonium perchlorate (0.1 M) was the supporting electrolyte. The instrument was calibrated with ferrocene ($E_{1/2}$(ox) = +0.378 V vs. SCE).[10] Unless otherwise indicated,

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(7) Foote, C. S.; Abakerli, R. B.; Clough, R. L.; Shook, F. C. In "Biological and Clinical Aspects of Superoxide and Superoxide Dismutase"; Bannister, W. H., Bannister, J. V., Eds.; Elsevier: New York, 1980; pp 222-230.
(8) Foote, C. S.; Abakerli, R. B.; Clough, R. L.; Lehrer, R. I. In "Bioluminescence and Chemiluminescence"; DeLuca, M. A., McElroy, W. D., Eds.; Academic Press: New York, 1981; pp 81-88.
(9) Teng, J. I.; Smith, L. L. *J. Am. Chem. Soc.* **1973**, *95*, 4060-4061.

(10) The discrepancy between this value and the reported oxidation potential of ferrocene in acetonitrile, 0.331 V vs. SCE (Morris, M. D.; Kok, G. L. In "Encyclopedia of Electrochemistry of the Elements"; Bard, A. J., Lund, H., Eds.; Marcel Dekker: New York, 1979; Vol. 13, p 4), is probably due to differences in experimental details.

reported errors are 95% confidence intervals.

Materials. Olefins **1** and **2** (Albany International) were passed through a column containing basic aluminum oxide (Merck). Cholesterol (**3**) (MCB) was purified by the bromination–debromination method[11] and then recrystallized from methanol. (4-[^{14}C])-Cholesterol (New England Nuclear) was purified by TLC as detailed below. Cholesterol oxidation products **4b**, **5b**, and **6b** were prepared as previously described.[12,13] DCA (Eastman Organic Chemicals) was recrystallized from hot toluene, mp 324–326 °C. Acetonitrile and benzene were distilled from P_2O_5. Acetonitrile-d_3 and benzene-d_6 (Cambridge Isotope Laboratories) and Rose Bengal (Eastman Certfied; 82%) were used as received.

Fluorescence lifetimes were measured by single photon counting with a modified Ortec 9200 nanosecond spectrometer.[14,15] Corning filters were used to isolate excitation (filter 3-71) and emission (filter 3-68) bands. Raw fluorescence lifetime data were fitted to a single exponential decay by using a weighted nonlinear least-squares method.[16] Goodness of fit was estimated from the reduced χ^2.[16] As a check on the raw values, the method of moments was used for deconvolution of the observed fluorescence decays fitted to a sum of two exponentials. The second-order mean deconvoluted lifetimes were within 0.5 ns of the raw lifetimes reported in Table III.

Photolysis Equipment. DCA-sensitized reactions were irradiated at >400 nm with a 1200-W Hanovia medium-pressure mercury lamp filtered through a 1 cm path length, 3% aqueous solution of sodium nitrite.[17] Rose Bengal sensitized reactions were irradiated with a 650-W DWY Sylvania tungsten–halogen incandescent lamp operated at 70 V. The lamp was filtered through a 0.5-cm solution of 2% potassium dichromate in water which cut off light below 500 nm.[18]

Irradiation Procedure. All solutions for analytical photolysis were placed in Bausch and Lomb Spectronic 20 test tubes. Each tube was stoppered with a serum cap, and oxygen was bubbled through the solution for 3 min prior to irradiation. During photolysis, the tubes rotated around the light source on a merry-go-round.

Analysis Procedures. For cyclohexenes **1** and **2**, each reaction mixture was treated with excess triphenylphosphine followed by addition of *p*-dimethoxybenzene as an internal standard. Gas chromatographic analysis was carried out on a Hewlett-Packard 5880 instrument equipped with a flame ionization detector with a 20 × 0.25 in. column packed with 2% OV-101 on 100/120 mesh Chromosorb W-HP (Hewlett Packard). For **3**, 0.1 μCi of (4-[^{14}C])-cholesterol was added to each reaction mixture. Following photolysis, excess triphenylphosphine was added and the product mixture applied to a 0.25 mm × 20 cm × 20 cm silica gel TLC plate (Merck) along with unlabeled standards (**3**, **4b**, **5b**, and **6b**). The plates were irrigated twice with toluene/ethyl acetate (17:8) and the standards visualized with 50% H_2SO_4–methanol.[19] Radioactive products were visualized by exposing Kodak SB 54 film to the plate for 1 week at −70 °C. Dupont Cronex Quantum 2 intensifying screens were used to enhance the image. Each chromatogram was divided according to the positions of the various products, and the bands were scraped from the plate and assayed for ^{14}C activity by liquid scintillation counting. Observed activities were corrected for quenching by the internal standard method.

Product Isolation. The products from the DCA-sensitized photooxygenation of **1** and **2** were isolated by preparative GC with a Varian Aerograph A90-P3 chromatograph equipped with a thermal conductivity detector. The column was 60 × 0.25 in. packed with 20% DC-200 on 60/80 mesh Chromosorb W. Products were identified by comparing ^{1}H NMR and IR spectra with those of authentic samples. The product mixture from **3** was separated by medium-pressure liquid chromatography on a 9 × 1000 mm silica gel column (40–60-μm particle size) using toluene/ethyl acetate (17:8) at a flow rate of 2 mL/min. The separated products were identified by comparison of ^{1}H NMR and mass spectra with those of authentic samples.

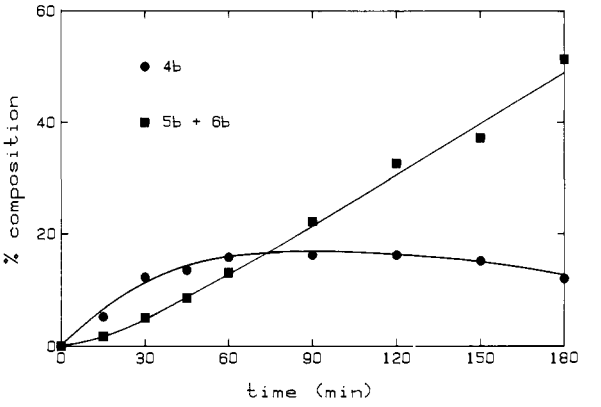


Figure 1. Plot of product composition vs. time for the DCA-sensitized photooxygenation of cholesterol (**3**). See the Experimental Section and Table I for details.

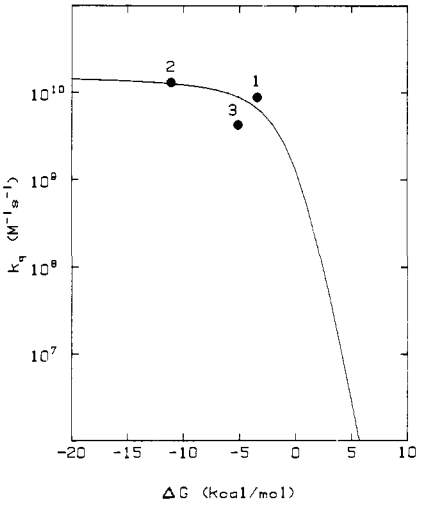
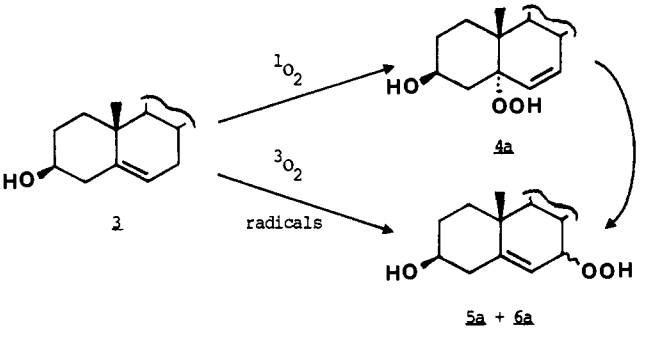


Figure 2. Fit of observed fluorescence quenching constants (dots) to a theoretical curve calculated by Rehm and Weller for an electron-transfer process (solid line).

Scheme II



Results and Discussion

Product Studies. The products of reaction of **1**, **2**, and **3** with oxygen under three sets of conditions are shown in Table I. DCA and Rose Bengal sensitized photooxygenations are shown in entries I and II, respectively, and radical autoxidation is shown in entry III. The initially formed hydroperoxide products were reduced with triphenylphosphine to the corresponding alcohols before analysis. Product mixtures for **1** and **2** were analyzed by GC; product mixtures for **3** were analyzed by reacting [^{14}C]-labeled **3**, separating the product mixture by TLC, and measuring the radioactivity of TLC bands. Approximately 50% of the product mixture from **3** occupied regions of the TLC plate between standards; these unidentified products are presumably formed by radical autoxidation. The product mixtures reported for **3** in Table I and Figure 1 are based on the identified products alone.

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1, **2**, and **3** behave similarly under the three sets of conditions: DCA and Rose Bengal sensitized photooxygenations yield similar product distributions which differ from the product distribution of radical autoxidation. For **1** and **2**, all products are believed to be primary photoproducts—ene products in the case of reaction with $^1O_2$ (entry II) and products derived from intermediate allylic radicals in the case of radical autoxidation (entry III). For **3**, the picture is complicated by the fact that 5-hydroperoxycholest-6-en-3-ol ($3\beta,5\alpha$) (**4a**) rearranges to 7-hydroperoxycholest-5-en-3-ol ($3\beta,7\alpha$) (**5a**) which can in turn epimerize to 7-hydroperoxycholest-5-en-3-ol ($3\beta,7\beta$) (**6a**) (Scheme II).[12,20] In addition, **3** is extremely susceptible to radical autoxidation.[19,20] It has been established that reaction of $^1O_2$ with **3** yields **4a** as the sole primary photoproduct and that **5a** and **6a** form by subsequent rearrangements.[12,20] In contrast, **5a** and **6a** are primary photoproducts of the radical autoxidation of **3** along with approximately 50 other products.[19,20] It was therefore of considerable importance to identify the primary photoproduct(s) from the DCA-sensitized photooxygenation of **3** (Table I, entry I). Product composition was determined at various degrees of starting material conversion (Figure 1). The concentration of **4b** is seen to rise rapidly and then decrease, while the formation of **5b** and **6b** initially lags and then exceeds that of **4b**. This behavior is consistent with formation of **5a** and **6a** at the expense of **4a**. It is likely that these products are arising by both rearrangement of **4a** and radical autoxidation initiated by radicals derived from **4a**.

In a related experiment, [^{14}C]-**4a** was prepared by Rose Bengal sensitized photooxygenation of [^{14}C]-cholesterol and isolated by preparative TLC (along with impurities which included **5a** and **6a**). This mixture was subjected to DCA-sensitized photooxygenation; TLC analysis revealed that **4a** was rapidly destroyed under the reaction conditions.

Fluorescence Quenching and Oxidation Potentials. Electron-transfer reaction between ^{1}DCA* and an olefin (Scheme I) results in quenching of DCA fluorescence. This quenching follows the Stern–Volmer equation[21] and has been observed for a large number of electron-rich molecules.[22] For a photochemically induced electron-transfer reaction, Rehm and Weller have proposed a relationship between the electrochemical properties of the donor and acceptor and ΔG of the electron-transfer step:[23]

$$\Delta G = (23.06 \text{ kcal mol}^{-1}\text{ V}^{-1}) \times [E(D^+/D) - E(DCA/DCA^-) - e^2/a\epsilon - \Delta E_{0,0}] \quad (1)$$

where $E(D^+/D)$ is the oxidation potential of the donor (D), $E(DCA/DCA^-)$ is the reduction potential of DCA, $e^2/a\epsilon$ is the energy gained by bringing two radical ions to the encounter distance (a) in a solvent of dielectric two constant ϵ, and $\Delta E_{0,0}$ is the electronic excitation energy of DCA. $e^2/a\epsilon$ has an average value of approximately 0.06 eV for a large number of donors in acetonitrile;[23] for DCA, $E(DCA/DCA^-) = -0.98$ V and $\Delta E_{0,0} = 2.89$ eV.[22] Table II lists experimental quenching constants, irreversible oxidation potentials, and calculated ΔG values for the electron-transfer step for **1**, **2**, and **3** in acetonitrile. The experimentally determined k_q values are fit, within the experimental error, by the curve calculated from the equation of Rehm and Weller for an electron-transfer process (Figure 2).

Kinetics of DCA-Sensitized Formation of Singlet Oxygen. Since the product studies suggested a singlet-oxygen pathway and the fluorescence quenching results implied an electron-transfer process, three additional experiments were carried out to assist in distinguishing between the two mechanisms: (1) the effect of changes in solvent polarity, (2) the solvent isotope effect, and (3) the quantum yield of product formation. Before discussing the results of these experiments, it is worth anticipating the behavior expected from each mechanism. DCA-sensitized electron-transfer photooxygenation is only understood in sufficient detail to allow qualitative predictions of kinetic behavior. In contrast, the role of DCA as a singlet-oxygen sensitizer is understood well enough to allow one to predict kinetic behavior quantitatively. Scheme III shows reaction and decay routes for ^{1}DCA* and derived species in the presence of $^3O_2$ and substrate (S). Three potential sources of $^1O_2$ have been identified: (1) direct intersystem crossing (ISC) of ^{1}DCA* to yield ^{3}DCA* (k_4),[4] (2) substrate-induced ISC (k_2),[4] and (3) spin-allowed energy transfer from ^{1}DCA* to $^3O_2$ (k_3).[5] Once formed, ^{3}DCA* is very efficiently trapped by $^3O_2$ to yield $^1O_2$.[24] Note that spin-allowed energy transfer from ^{1}DCA* to $^3O_2$ yields two molecules of $^1O_2$ for every ^{1}DCA* trapped.

Scheme III

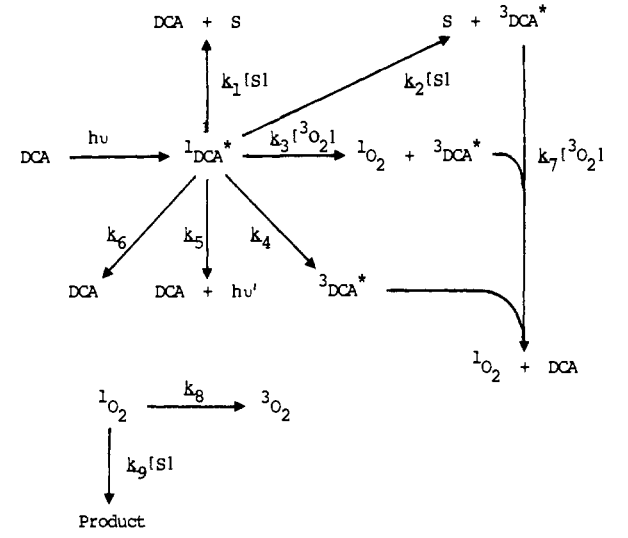

Table IV. Relative Rates of DCA-Sensitized Photooxygenation of **1**, **2**, and **3** in Benzene and Acetonitrile

olefin	concn, M	$\Phi_p(CH_3CN)/\Phi_p(C_6H_6)$ obsd[a]	calcd[b]
1	0.0634	0.43 ± 0.06[c] (3)	0.46
1	0.0211	1.59 ± 0.06[c] (2)	1.13
2	0.0560	0.22 ± 0.02[c] (3)	0.67
2	0.0423	0.24 ± 0.03[c] (2)	0.72
3	0.00100	4.2 ± 0.3 (6)	>3.1

[a] The number of determinations is shown in parentheses. [b] Calculated from eq 2 and Table III (see footnote *a*, Table III). [c] Errors are standard deviations.

From Scheme III, one can derive the following expression for the quantum yield of product formation

$$\Phi_p = \Phi_{^1O_2}F = \left(\frac{k_2[S] + 2k_3[^3O_2] + k_4}{k_q[S] + k_3[^3O_2] + 1/\tau}\right)\left(\frac{[S]}{\beta + [S]}\right) \quad (2)$$

where $\Phi_{^1O_2}$ = quantum yield of $^1O_2$ formation, F = the fraction of $^1O_2$ trapped by substrate, $k_q = k_1 + k_2$, $1/\tau = k_4 + k_5 + k_6$, and $\beta = k_8 / k_9$. The experimentally determined values of the physical parameters needed to evaluate eq 2 are all available from various sources and are listed in Table III.

Effect of Changes in Solvent Polarity. The DCA-sensitized electron-transfer photooxygenation of phenyl-substituted olefins takes place only in polar solvents such as acetonitrile and methanol.[2] This behavior is that expected for a process proceeding via an intermediate ion pair, since such a pair would be too poorly solvated to diffuse apart in a nonpolar solvent. Singlet-oxygen reactions, in contrast, show only very small effects of changes in solvent polarity.[25] As detailed in Table IV, **1**, **2**, and **3** all show considerable reactivity in benzene, a strong indication that reaction does not proceed via intermediate ions for these olefins.

If reaction of these olefins proceeds via $^1O_2$ as shown in Scheme III, then the relative rates of reaction in acetonitrile and benzene

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Table V. Solvent Deuterium Isotope Effects on the Rate of Sensitized Photooxygenation of **1**, **2**, and **3**

olefin	concn, M	solvent	sensitizer	$\Phi_p(D)/\Phi_p(H)$ obsd[a]	$\Phi_p(D)/\Phi_p(H)$ calcd[b]
1	0.0634	CD_3CN/CH_3CN	DCA	1.5 ± 0.3[c] (4)	1.8
1	0.0211	CD_3CN/CH_3CN	DCA	2.4 ± 0.5[c] (2)	2.9
1	0.0634	C_6D_6/C_6H_6	DCA	2.7 ± 0.7[c] (2)	2.7
1	0.0211	C_6D_6/C_6H_6	DCA	5.1 ± 2.1[c] (2)	5.3
3	0.0010	CD_3CN/CH_3CN	DCA	8 ± 2 (6)	8.9
3	0.0010	CD_3CN/CH_3CN	Rose Bengal	10 ± 3 (6)	8.9

[a] The number of determinations is shown in parentheses. [b] From eq 3 and Table III (see footnote *a*, Table III). [c] Errors are ranges.

should equal the ratio of quantum yields of product formation in the two solvents. The ratios calculated from eq 2 and Table III are shown in Table IV. The observed and calculated ratios agree within a small factor. The differences are believed to be primarily due to the large number of parameters required to evaluate eq 2 and uncertainties in some of the parameters. In particular, slight variation in the value of k_3 or k_9 causes a substantial difference in the calculated relative rates of reaction. In fact, the slight solvent dependence of k_9,[25] which has been neglected in the calculations, could readily account for the difference between the observed and calculated relative rates of reaction. The key distinction is that the ratio of quantum yields of product formation is close to that calculated for a singlet oxygen reaction and not infinitely large, as has been observed for electron-transfer photooxygenations.[2]

Solvent Isotope Effect. It has recently been found that the lifetime of $^1O_2$ is significantly longer in deuterated vs. protiated solvents (Table III). This fact results in large solvent deuterium isotope effects for the rates of $^1O_2$ reactions. In contrast, an electron-transfer mechanism would not be expected to exhibit a solvent isotope effect unless the lifetime of ^{1}DCA* were affected. The lifetime of ^{1}DCA* was measured by single-photon counting and found to be the same in deuterated and protiated acetonitrile (Table III). The lack of a rate enhancement by deuterated acetonitrile for the DCA-sensitized photooxygenation of *trans*-stilbene[26] lends experimental support to the view that electron-transfer reactions should not exhibit a solvent isotope effect.

The solvent isotope effect on the mechanism shown in Scheme III is given by the ratio of quantum yields (eq 2) for deuterated and protiated solvents. Making the reasonable assumption that the lifetime of $^1O_2$ is the only affected parameter, this ratio simplifies to

$$\frac{\Phi_p(D)}{\Phi_p(H)} = \frac{k_8(H) + k_9[S]}{k_8(D) + k_9[S]} \quad (3)$$

Table V lists observed solvent isotope effects on the rate of DCA-sensitized photooxygenation of **1** and **3** as well as the values calculated with eq 3. **2** was not studied because k_9 is large and the small concentration of **2** necessary to observe an isotope effect ($k_8 > k_9[S]$) would be too low for accurate measurement by GC. The observed isotope effects are in remarkably good agreement with those expected for a singlet-oxygen mechanism.

Quantum Yield. The quantum yields of product formation for the DCA-sensitized photooxygenations of **1**, **2**, and **3** were determined by using the DCA-sensitized photooxygenation of 1,1-diphenylethylene (DPE) as a chemical actinometer.[27] The experimental quantum yields along with values calculated from eq 2 are shown in Table VI and are again in as good agreement with a singlet-oxygen mechanism as could be expected given the uncertainties mentioned above.

Table VI. Quantum Yields of Product Formation for the DCA-Sensitized Phooxygenation of **1**, **2**, and **3** in Acetonitrile at 25 °C

olefin	concn, M	Φ_p obsd	Φ_p calcd[a]
1	0.025	0.054	0.10
2	0.025	0.19	0.25
3	0.00091	0.0023	0.0037

[a] From eq 2 and Table III (see footnote *a*, Table III).

Summary

The results reported here show that the products of DCA-sensitized photooxygenation of **1** and **2** are the same as those formed by reaction with $^1O_2$ (Table I). The major product from the photooxygenation of **3** is also the same. **1**, **2**, and **3** all react at appreciable rates in benzene as well as in acetonitrile (Table IV). As discussed above, this behavior is inconsistent with an electron-transfer mechanism. **1** and **3** exhibit solvent isotope effects which are in close agreement with those expected for a singlet-oxygen mechanism (Table V). Finally, the quantum yields for product formation for **1**, **2**, and **3** are close to the values expected for a singlet-oxygen reaction (Table VI).

In view of the above, it is curious that the kinetics of DCA fluorescence quenching are consistent with an electron-transfer interaction (Figure 2). There are several possible explanations for the apparent lack of radical ion chemistry in the system. The most likely is that electron transfer between the olefin and ^{1}DCA* is immediately followed by back electron transfer. From the previous discussion, it is clear that electron-transfer quenching of ^{1}DCA* is not leading to substantial amounts of product. Rather, ^{1}DCA* quenching is a nonproductive process which serves only to effectively shorten the lifetime of ^{1}DCA*. The shortened lifetime reduces the fraction of ^{1}DCA* trapped by oxygen and correspondingly the amount of $^1O_2$ formed. Since quenching of ^{1}DCA* by **1** is so much more efficient (500-fold) in acetonitrile than benzene, the lifetime of ^{1}DCA* is shortened to a greater extent in acetonitrile. For this reason, the ratio of quantum yields (acetonitrile/benzene) decreases as the concentration of **1** increases. Alternatively, the ^{1}DCA* fluorescence quenching constant for **2** is only 3 times greater in acetonitrile than in benzene (Table II). In this case, the lifetime of ^{1}DCA* is being shortened by roughly the same amount in both solvents, and an increase in the concentration of **2** has only a nominal effect on the ratio of quantum yields (Table IV). These results support the suggestion of olefin quenching of ^{1}DCA* followed by rapid back electron transfer.

While these results demonstrate that DCA acts as a singlet-oxygen sensitizer with the olefins studied, it is necessary to be judicious about extrapolating this conclusion to other alkyl-substituted olefins or other conditions. Mechanistic investigations must be used to distinguish between electron transfer and $^1O_2$

(26) While the reaction is much more complicated than initially anticipated, there is no evidence of a singlet oxygen deuterium isotope effect (Allen, P. M.; Dobrowolski, D. C., unpublished results).

(27) The reported quantum yield for disappearance of DPE caculated for infinite DPE concentration is 0.81.[2] However, quenching of ^{1}DCA* by $^3O_2$ (i.e., $k_3[^3O_2]$ in Scheme III) was neglected in this calculation. Correction for $^3O_2$ quenching yields a value of 0.96.

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pathways for each DCA-sensitized photooxygenation. A number of reported cyanoaromatic-sensitized electron-transfer photooxygenations[28] may prove to be $^1O_2$ reactions upon reinvestigation, using techniques of the sort described here.

Acknowledgment. The authors thank Prof. V. N. Schumaker for use of his single photon counting instrumentation. This work was supported by National Science Foundation Grant CHE80-20140.[38]

Registry No. 1, 591-49-1; **2**, 1674-10-8; **3**, 57-88-5; **4b**, 34310-88-8; **5b,6b**, 16840-37-2; DCA, 1217-45-4; D_2, 7782-39-0; 1-methyl-2-cyclohexenol, 23758-27-2; 2-methylenecyclohexanol, 4065-80-9; 2-methyl-2-cyclohexenol, 20461-30-7; 1-methyl-2-methylenecyclohexanol, 52134-08-4; 1,2-dimethyl-2-cyclohexenol, 51036-24-9; 2,3-dimethyl-2-cyclohexenol, 52134-09-5.

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Asymmetric Induction Arising from σ/π Interactions

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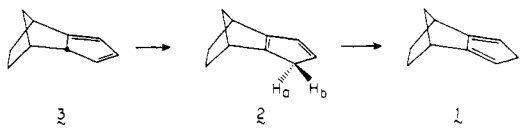
Abstract: Long-range σ/π interactions were unambiguously shown to determine the stereoselectivity of a [1,5]-hydrogen shift. The three isomeric isodicyclopentadienes **1**, **2**, and **3** were prepared, and the cycloadditions and thermal interconversions of these dienes were investigated. A labeling study of the [1,5]-sigmatropic shift transforming **2** to the more stable isomer **1** confirmed the existence of a theoretically predicted interaction of the σ and π orbitals. The preferential migration of the endo hydrogen of **2** by a factor of 6.8 at 125 °C indicated that this effect corresponded to a 1.5-kcal difference in the two diastereotopic transition states.

The transfer of chirality from a chiral center to a reaction site has become an increasing preoccupation of synthetic chemists.[1] For example, significant asymmetric induction can be obtained for the aldol and related condensations by utilization of metal chelates that will permit the manipulation of stereoelectronic factors.[1b] To date these efforts have focused on the exploitation of the diastereotopic transition-state-energy differences arising from differential steric interactions developed along the reaction coordinate. For the most part, efforts to account for stereoselective or stereospecific transformations in terms of electronic influences arising from interaction of the σ and π framework have not been widely pursued.[2,3] We report here examples of asymmetric induction for sigmatropic rearrangements and electrophilic attack arising from molecular orbital interactions.

The classic example for which σ/π interaction has been invoked is the preferential exo attack of electrophiles on norbornene.[2] This explanation has been controversial since two prior explanations had been advanced. Brown suggested that steric hindrance due to the endo C_5 and C_6 hydrogens blocks endo attack.[4] Schleyer invoked the minimization of torsional effects involving the bridgehead C–H bond and the vinylic hydrogen to explain preferential exo attack.[5] The relative importance of these three explanations remains to be convincingly demonstrated.

Fukui originally showed computationally that the exo face of the π bond was asymmetrically extended, thereby providing the means to preferentially stabilize the approach of an electrophile from the exo face.[2c] He attributed this nonequivalent extension of the π system to the mixing of three orbitals: the anti C_7 hydrogen σ bond and/or the methano bridge bonds with the π and σ bonds joining C_2 and C_3 to generate a distorted π orbital, for which an exaggerated representation is shown in Figure 1.[2b] More recently the importance of σ/π mixing for norbornene has been questioned since subsequent computational investigations revealed only slight rehybridization of C_2 and C_3.[6-8] More recently Gleiter has described the σ/π interaction in terms of a hyperconjugative phenomenon entailing minimization of filled shell repulsions, thereby accounting for the disrotatory twisting of the orbitals and slight pyramidization of C_2 and C_3.[7] These findings remain controversial, since Houk has arrived at a similar representation of norbornene by invoking only relief of torsional contributions.[9]

Scheme I



We chose the isodicyclopentadienyl system to evaluate the importance of σ/π electronic interactions to control product stereochemistry. In particular, we focused on the [1,5]-sigmatropic hydrogen migrations that would sequentially convert isodicyclopentadiene **3** via diene **2** to the thermodynamically more stable diene **1** (Scheme I). The critical feature would be whether the chirality of the norbornyl subunit would influence the relative

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