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Electron-Transfer Photooxygenation. 5. Oxidation of Phenyl-Substituted Alkenes Sensitized by Cyanoanthracenes[1]

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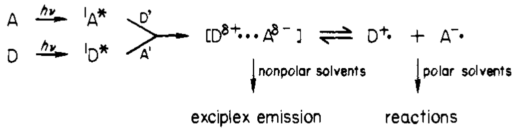
Abstract: The electron-deficient sensitizers 9,10-dicyanoanthracene (DCA) and 9-cyanoanthracene (CNA) sensitize the photooxidation of 1,1-diphenylethylene (**1**), *trans*- and *cis*-stilbene (**12** and **14**), and tetraphenylethylene (**18**) in oxygen-saturated polar solvents. The photoproducts in MeCN include the cleavage products Ph_2CO and PhCHO, the epoxides, and, in the case of the stilbenes, cis–trans isomerized olefin. Quantum yields for disappearance of the alkenes are 0.8, 0.5, 0.2, and 0.15 for **1**, **12**, **14**, and **18**, respectively. No photooxygenation takes place in nonpolar solvents. The reactions in MeCN are accompanied by quenching of the DCA and CNA fluorescence. The measured quenching rate constants closely resemble values calculated for an electron-transfer process and agree, within experimental error, with those determined from the acceptor concentration dependence of product formation. The photooxygenations are quenched by the addition of small amounts of compounds of lower oxidation potential than that of the alkenes, whereas compounds of higher oxidation potential have little effect. All results are consistent with an electron-transfer mechanism involving a donor radical cation and sensitizer radical anion which subsequently reduces oxygen to superoxide. The data are not compatible with a singlet oxygen mechanism.

Introduction

Since the pioneering work of Weller[2] and Cohen[3] and their co-workers, photosensitized electron-transfer reactions have received much attention during the last decade among photochemists and photophysicists.[4] Most work has been centered around electron transfer to or from the excited singlet state of a light-absorbing molecule in the presence of electron-rich (D′) or electron-poor (A′) substrates. The reaction (1) is accompanied by quenching of the sensitizer fluorescence.[2]



(1)

In nonpolar solvents, highly polar exciplexes[5] are often formed, and emission from these has been detected in several cases.[6–9] In polar solvents, however, the ion pairs often diffuse apart to give solvent-separated radical ions, which can react further. Arnold and co-workers[10] have shown the reaction to be synthetically useful. They used electron-deficient sensitizers to add alcoholic solvents and other nucleophiles to electron-rich olefins in an anti-Markovnikov fashion, as exemplified by the addition of MeOH to 1,1-diphenylethylene (**1**) (see eq 2).

$$\underset{\mathbf{1}}{Ph_2C{=}CH_2} \xrightarrow[\text{MeOH, }N_2]{\text{sens, }h\nu} \underset{\mathbf{2}}{Ph_2CH{-}CH_2{-}OCH_3} \qquad (2)$$

Scheme I

$$\text{sens} \xrightarrow{h\nu} {}^1\text{sens}^* \xrightarrow{D} [\text{sens}^{-}\cdot + D^{+}\cdot] \xrightarrow{{}^3O_2} \text{sens} + D^{+}\cdot + O_2^{-}\cdot \;\text{—}\; DO_2$$

Chemical reactions of olefins via photosensitized electron transfer have been demonstrated in several laboratories by Evans, Farid, and Roth, and their co-workers.[9,11,12] The electron-transfer mechanism was supported by quenching of the sensitizer fluorescence and, in some cases, by the observation of nuclear polarization effects[12] and ESR signals.[10c,13] Spada and Foote recently reported detection of radical ions both by flash photolysis and ESR.[14]

Most work in this field has been done in deaerated solutions. Our own interest, however, has been centered around possible electron-transfer photooxygenations sensitized by electron-deficient sensitizers in oxygen-saturated polar solvents. We have proposed[15] the following mechanism involving a donor radical cation and sensitizer radical anion which subsequently reduces O_2. The resulting superoxide radical anion is then believed to react in some way with the donor radical cation (Scheme I).

Results and Discussion

Fluorescence Quenching and Electrochemical Considerations. As fluorescent, electron-deficient sensitizers, we chose 9,10-dicyanoanthracene (DCA) and 9-cyanoanthracene (CNA). These compounds absorb at >400 nm and exhibit strong, blue fluorescence in both polar and nonpolar solvents. We have already reported[6,15] that electron-rich substrates quench the fluorescence of DCA and CNA in N_2-saturated MeCN according to the Stern–Volmer equation, and the singlet lifetimes, transition energies, and reduction potentials of sensitizers and donors were reported.[6]

The free-energy change (ΔG) involved in an electron-transfer process is given by eq 3,[2] where $E(D/D^+)$ and $E(A^-/A)$ are the

$$\Delta G \text{ (kcal/mol)} = 23.06[E(D/D^+) - E(A^-/A) - e_0^2/a\epsilon - \Delta E_{0,0}] \qquad (3)$$

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[1] Paper 4: see ref 35.

[2] H. Leonhardt and A. Weller, *Ber. Bunsenges. Phys. Chem.*, 67, 791 (1963); D. Rehm and A. Weller, *Isr. J. Chem.*, 8, 259 (1970), and references therein.

[3] J. B. Guttenplan and S. G. Cohen, *J. Am. Chem. Soc.*, **94**, 4040 (1972).

[4] M. Koizumi, S. Kato, N. Mataga, T. Matsuura, and Y. Usui, "Photosensitized Reactions", Kagakudojin Publishing Co., Inc., Kyoto, Japan, 1978, Chapters 5 and 11.

[5] M. S. Gordon and W. R. Ware, Eds., "The Exciplex", Academic Press, New York, 1975.

[6] J. Eriksen and C. S. Foote, *J. Phys. Chem.*, **82**, 2659 (1978).

[7] H. Beens, H. Knibbe, and A. Weller, *J. Chem. Phys.*, **47**, 1183 (1967).

[8] (a) G. N. Taylor, *Chem. Phys. Lett.*, **10**, 355 (1971); (b) W. R. Ware, D. Watt, and J. D. Holmes, *J. Am. Chem. Soc.*, **96**, 7853 (1974); (c) W. R. Ware, J. D. Holmes, and D. R. Arnold, *ibid.*, **96**, 7861 (1974); (d) R. A. Caldwell and L. Smith, *ibid.*, **96**, 2995 (1974); (e) R. A. Caldwell, N. I. Ghali, C.-K. Chien, D. DeMarco, and L. Smith, *ibid.*, **100**, 2857 (1978); (f) F. D. Lewis and T.-I. Ho, *ibid.*, **99**, 7991 (1977); (h) N. C. Yang, D. M. Shold, and J. K. McVey. *ibid.*, **97**, 5004 (1975).

[9] K. A. Brown-Wensley, S. L. Mattes, and S. Farid, *J. Am. Chem. Soc.*, **100**, 4162 (1978).

[10] (a) A. J. Maroulis, Y. Shigemitsu, and D. R. Arnold, *J. Am. Chem. Soc.*, **100**, 535 (1978); (b) Y. Shigemitsu and D. R. Arnold, *J. Chem. Soc., Chem. Commun.*, 407 (1975); (c) R. A. Neunteufel and D. R. Arnold, *J. Am. Chem. Soc.*, **95**, 4080 (1973).

[11] (a) T. R. Evans, R. W. Wake, and O. Jaenicke, *Exciplex Proc. Meet.*, 345 (1975); (b) S. Farid, S. E. Hartman, and T. R. Evans, *ibid.*, 327 (1975).

[12] H. D. Roth and M. L. Manion. "Abstracts, The 7th International Conference on Photochemistry", U2, Aug 1975.

[13] A. P. Schaap, K. A. Zaklika, B. Kaskar, and L. W.-M. Fung, *J. Am. Chem. Soc.*, **102**, 389 (1980).

[14] L. T. Spada and C. S. Foote, *J. Am. Chem. Soc.*, **102**, 391 (1980).

[15] J. Eriksen, C. S. Foote, and T. L. Parker, *J. Am. Chem. Soc.*, **99**, 6455 (1977).

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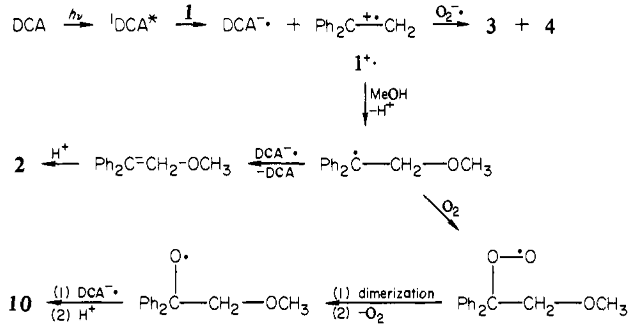
Scheme II



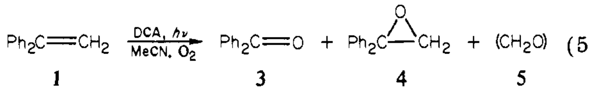
oxidation potential of the donor (D) and the reduction potential of the acceptor (A), respectively, and $e_0^2/a\epsilon$ is the energy (~0.06 eV in MeCN[2]) gained by bringing the two radical ions to the encounter distance (a) in a solvent of dielectric constant ϵ. From the oxidation potential of each quencher and eq 3, ΔG could be estimated for electron transfer from quencher to fluorescer, and a plot[6] of k_q vs. ΔG gave a very good correlation with the theoretical line calculated by Rehm and Weller[2] for an electron-transfer process. This correlation strongly supports the electron-transfer mechanism for the quenching of the fluorescence of DCA and CNA. Exciplex emission was observed only in nonpolar solvents, but not in CH_3CN, suggesting that dissociation of the ion pairs occurs in the most polar solvents.[6]

The proposed mechanism in Scheme I requires a second-electron transfer from sens$^-\cdot$ to $^3O_2$. The free-energy change of this process is given by eq 4, which contains the reduction potentials of the

$$\Delta G\ (\text{kcal/mol}) = 23.06[E_{1/2}(\text{sens}^-/\text{sens}) - E_{1/2}(O_2^-/O_2)] \quad (4)$$

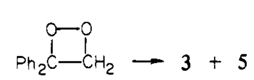
sensitizer (DCA = −0.97 V or CNA = −1.47 V) and of O_2 (−0.94 V), all vs. SCE in CH_3CN.[16] The second-electron transfer is thus calculated to be exothermic by 0.7 kcal/mol for DCA and 12.2 kcal/mol for CNA.

Sensitized Photoreactions. 1,1-Diphenylethylene (1). Irradiation (>400 nm) of an oxygen-saturated solution of **1** (2×10^{-2} M) and DCA (10^{-4} M) in MeCN gave benzophenone (**3**) and 2,2-diphenyloxirane (**4**) in a ratio of 3:1 (see eq 5). The products were separated by column chromatography and identified from their spectral properties and by comparison with authentic samples.[17]



(5)

Presumably, formaldehyde (**5**) is also formed. Compound **3** (and **5**) is most likely derived from 3,3-diphenyl-1,2-dioxetane (**6**) (see eq 6) which under the reaction conditions would be expected to decompose by direct or sensitized photolysis (see discussion in the stilbene case).



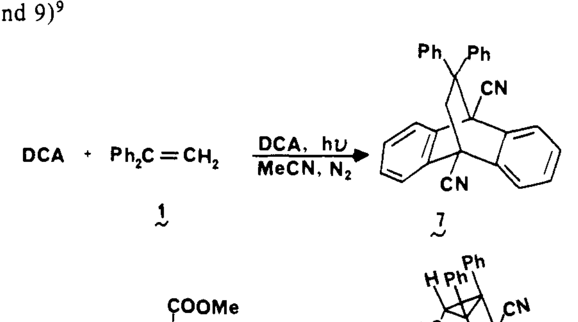
$\rightarrow$ **3** + **5** (6)

6

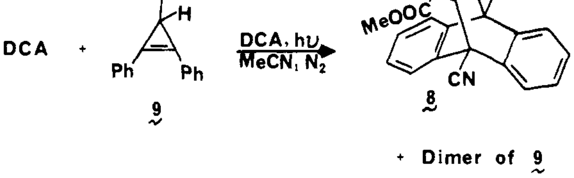
Epoxide **4** could be formed by a mechanism (eq 7) analogous to that suggested by Bartlett and Landis,[19] although other mechanisms are conceivable. This mechanism would predict nonstereospecific formation of the epoxide (see below under *cis*-stilbene).

$$\mathrm{Ph_2C\overset{+\cdot}{-}2 + O_2^{-}\cdot \rightarrow Ph_2\dot{C}{-}CH_2{-}O{-}O\cdot \rightarrow Ph_2\dot{C}{-}CH_2{-}O{-}O{-}O{-}O{-}CH_2{-}\dot{C}Ph_2 \xrightarrow{-O_2} Ph_2\dot{C}{-}CH_2{-}\dot{O} \rightarrow \mathbf{4}} \quad (7)$$

Similar irradiation of **1** and DCA in N_2-saturated MeCN led to rapid consumption of DCA, as determined by UV analysis. Formation of an adduct (**7**) is a likely cause of the observed decrease in DCA concentration, since the adduct (**8**) has been reported to be formed from the photolysis of DCA and **9** (eq 8 and 9)[9]



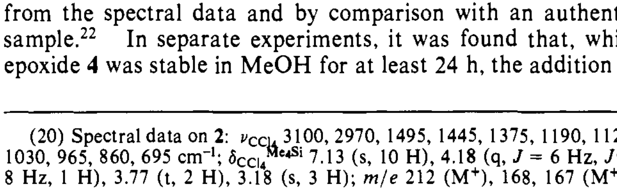
(8)



(9)

The product of the reaction is unstable and apparently regenerates DCA and **1**, as demonstrated by the reappearance of the DCA absorption spectrum upon standing, especially upon exposure to room light. Thus, an attempt to isolate **7** failed and its structure must be regarded as tentative.

Irradiation of an oxygen-saturated MeOH solution of **1** and DCA led to several oxidation products. After separation on a chromatographic column, these products were identified from their spectral properties and by comparison with authentic samples[20,21] as **2**, **3**, **4**, and **10**, as in eq 10, where the relative yields are given.



(10)

During and after the photolysis, **4** was unstable and a new product, **11**, was readily formed at the expense of **4**. This reaction could be stopped by the addition of small amounts of base. Compound **11** was identified as 2-methoxy-2,2-diphenylethanol from the spectral data and by comparison with an authentic sample.[22] In separate experiments, it was found that, while epoxide **4** was stable in MeOH for at least 24 h, the addition of

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[16] (a) P. Allen and C. S. Foote, unpublished results. (b) H. C. Wang, G. Levin, and M. Szwarc, *J. Am. Chem. Soc.*, **99**, 2642 (1977); C. K. Chien, H. C. Wang, M. Szwarc, A. J. Bard, and K. Itaya, *ibid.*, **102**, 3100 (1980).

[17] Spectroscopic data on **4**: ν_{CCl_4} 3100, 2950, 1490, 1440, 1335, 1290, 1010, 930, 900, 830, 690 cm^{-1}; $\delta_{CCl_4}^{Me_4Si}$ 3.07 (s, 2 H), 7.22 (s, 10 H). These data were identical with those obtained on authentic 2,2-diphenyloxirane synthesized from phenacyl chloride and phenylmagnesium bromide followed by treatment with base.[18]

[18] H. E. Zaugg and R. J. Michaels, *J. Am. Chem. Soc.*, **80**, 2770 (1958).

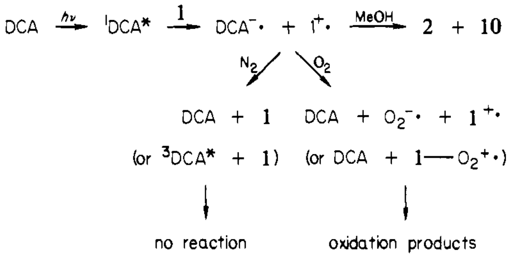
[19] P. D. Bartlett and M. E. Landis, *J. Am. Chem. Soc.*, **99**, 3033 (1977).

[20] Spectral data on **2**: ν_{CCl_4} 3100, 2970, 1495, 1445, 1375, 1190, 1120, 1030, 965, 860, 695 cm^{-1}; $\delta_{CCl_4}^{Me_4Si}$ 7.13 (s, 10 H), 4.18 (q, J = 6 Hz, J' = 8 Hz, 1 H), 3.77 (t, 2 H), 3.18 (s, 3 H); *m/e* 212 (M$^+$), 168, 167 (M$^+$ − CH_2OCH_3), 166, 165, 152, 45, 44, 40. These data are consistent with the structure of **2**, and the NMR data are identical with those reported for **2**: W. A. Bonner and F. D. Mango, *J. Org. Chem.*, **29**, 430 (1964).

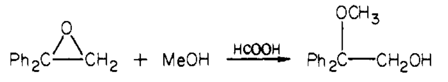
[21] Spectral data on **10**: ν_{CCl_4} 3600, 3100, 2950, 1600, 1480, 1440, 1370, 1325, 1255, 1190, 1170, 1120, 1100, 1060, 1020, 930, 906, 860, 692 cm^{-1}; $\delta_{CCl_4}^{Me_4Si}$ 3.23 (s, 1 H), 3.34 (s, 3 H), 3.78 (s, 2 H), 7.1–7.4 (m, 10 H); *m/e* 228 (M$^+$), 211, 210 (M$^+$ − H_2O), 195 (M$^+$ − H_2O, Me), 183 (100% M$^+$ − CH_2OCH_3), 180, 179, 167, 166, 165, 152, 105, 77. These data were identical with those obtained on authentic samples of **10** obtained from the late Professor Saul Winstein and from Mr. Dale S. Steichen, who prepared **10** by the addition of MeOH to epoxide **4** under basic conditions.

[22] Spectral data on **11**: ν_{CCl_4} 3500, 3100, 2960, 1600, 1490, 1440, 1100, 1065, 1030, 940, 905, 694 cm^{-1}; $\delta_{CCl_4}^{Me_4Si}$ 1.27 (br s, 1 H), 3.11 (s, 3 H), 4.11 (br s, 2 H), 7.27 (s, 10 H); *m/e* no M$^+$, 198, 197 (100%, M$^+$ − OMe), 167, 165, 152, 105, 89, 77. These data and the GLPC retention time were essentially identical with those of an authentic sample of **11** obtained from the late Professor Saul Winstein.

Scheme III



minute amounts of HCOOH led to rapid addition of MeOH to **4**, resulting in the formation of **11** (eq 11).



4 **11** (11)

It is very likely that HCOOH could be formed under the photooxygenation conditions by oxidation of H_2CO, an expected product. The mechanism (Scheme II) of formation of **2** and **10** most likely involves initial attack on $\mathbf{1}^{+}\cdot$ by MeOH followed by reaction with O_2 or by back-transfer of the electron from $DCA^{-}\cdot$.

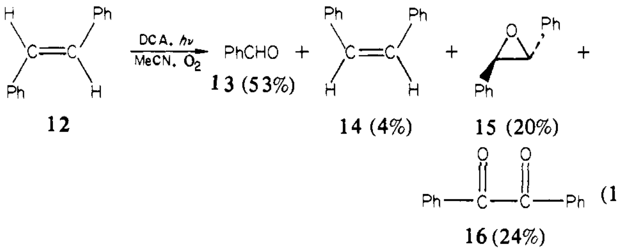
In nitrogen-saturated MeOH, the DCA-sensitized photolysis of **1** led to only one product, **2** (eq 12), in agreement with the report of Arnold et al.[10]

$$\underset{\mathbf{1}}{Ph_2C{=}CH_2} \xrightarrow[\text{MeOH, N}_2]{\text{DCA, }h\nu} \underset{\mathbf{2}}{Ph_2CH{-}CH_2{-}OCH_3} \qquad (12)$$

The disappearance of **1** in the photolysis was considerably slower under N_2 than under air. This suggests that back-transfer of the electron to yield ground-state (or triplet) DCA and **1** is an important deactivation pathway in the former case. In the presence of O_2, however, this back-transfer is largely inhibited, since the quantum yield for disappearance of **1** under these conditions was found to be almost unity (see Scheme III).

No products were observed when the photolysis was carried out in benzene/O_2 or CCl_4/O_2. These solvents apparently are too nonpolar to allow separation of the radical ions, in agreement with the suggested mechanism.

***trans*-Stilbene (12).** DCA-sensitized photolysis of **12** in MeCN/O_2 gave four products[23] which were separated by column chromatography and identified from their spectral properties and by comparison with authentic samples to be benzaldehyde (**13**), *cis*-stilbene (**14**),[24] *trans*-2,3-diphenyloxirane (**15**),[25] and benzil (**16**).[26] The approximate product distribution is shown in eq 13.



(13)

Table I. Quantum Yields of Loss of Alkene (ϕ_{-sm}) for DCA-Sensitized Photooxygenation of Phenyl-Substituted Alkenes[a]

alkene	ϕ_{-sm}
1,1-diphenylethylene (1)	0.8[c]
trans-stilbene (12)	0.5[d]
cis-stilbene (14)	0.2[d]
tetraphenylethylene (18)	0.15[d]

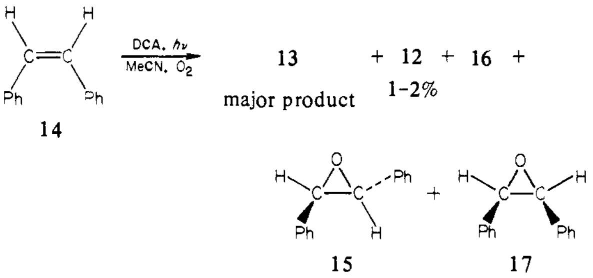
[a] In oxygen-saturated MeCN. [b] Quantum yield at 405 nm for disappearance of the alkene. Values have been extrapolated to 100% quenching of the DCA fluorescence (i.e., infinite-concentration intercept values are used). [c] By ferrioxalate actometry. [d] Determined relative to 1.

Possible mechanisms for the formation of **13** and **15** are analogous to those suggested for corresponding products from 1,1-diphenylethylene. In this case, an intermediate dioxetane was carefully searched for by HPLC and NMR but not found. However, a known sample of the dioxetane added to the reaction mixture was very rapidly destroyed.[16] The isomerization product **14** is *not* formed by direct light absorption of **12** or by energy transfer from ^{3}DCA* to **12** since if this were the case, **14** would have been produced under photolysis in MeCN/N_2, which was *not* observed (see below). Several mechanisms can account for the formation of **14**.

NMR and HPLC studies show that *cis*-stilbene (**14**) is a *primary* photoproduct. It is formed from the outset of the reaction and thus is not photosensitized by products such as benzil. It is presumably formed directly from $\mathbf{12}^{+}\cdot$ by bond rotation and back-transfer.[16] (This is somewhat surprising in light of the observation that $\mathbf{12}^{-}\cdot$ is exclusively trans.[16a]) The lack of formation of **14** under N_2 may reflect the shorter lifetime of $\mathbf{12}^{+}\cdot$ under N_2, where electron back-transfer from $DCA^{-}\cdot$ can occur, than under O_2, as observed in flash photolysis.[14] The mechanism for the formation of **16** is as yet unknown.

Irradiation in MeCN/N_2 gave none of the products **13**–**16**. Instead, rapid consumption of DCA was observed as determined by UV spectroscopy, presumably due to adduct formation analogous to the reaction of DCA and **1** under similar conditions (see above).

***cis*-Stilbene (14).** Irradiation of **14** (eq 14) under conditions similar to that for **12** in MeCN/O_2 gave five products, which were isolated and separated by column chromatography and identified from their spectral properties and by comparison with authentic samples.[25]



(14)

The formation of both **15** and **17** (in a ratio of 5:1) is particularly interesting and shows that the epoxidation reaction is nonstereospecific. The formation of *trans*-epoxide **15** cannot be due to isomerization of *cis*- to *trans*-stilbene, because trans reacts only about twice as fast as cis and only small amounts of *trans*-stilbene are ever formed. Presumably, **15** is formed from $\mathbf{12}^{+}\cdot$ formed from $\mathbf{14}^{+}\cdot$.[14]

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(23) In a preliminary report,[15] only two products, **13** and **14**, were identified.

(24) Spectral data on **14**: ν_{CCl_4} 3010, 1600, 1490, 1440, 1180, 1070, 1020, 920, 855, 695 cm^{-1}; $\delta_{CCl_4}{}^{Me_4Si}$ 6.50 (s, 2 H), 7.12 (s, 10 H). These data were identical with those obtained on an authentic sample (Aldrich).

(25) Spectral data on **15**: ν_{CCl_4} 3090, 3000, 1600, 1490, 1445, 1280, 1240, 1060, 1020, 860, 690 cm^{-1}; $\delta_{CCl_4}{}^{Me_4Si}$ 3.68 (s, 2 H), 7.25 (s, 10 H). These data were identical with those obtained on an authentic sample of **15** prepared from **12** and *m*-chloroperbenzoic acid in $CHCl_3$.

(26) Spectral data on **16**: ν_{CCl_4} 3050, 1670, 1600, 1440, 1200, 1170, 865, 710, 680 cm^{-1}; $\delta_{CCl_4}{}^{Me_4Si}$ 7.3–8.1 (complex m), *m/e* 210 (M$^+$), 106, 105 (Ph-CO$^+$), 78, 77, 51, 44. These data were identical with those obtained on an authentic sample (Aldrich).

(27) Compounds **15** and **16** gave the same spectra as reported in ref 25 and 26, while **12** and **13** were identical with authentic samples (Aldrich and MC and B, respectively). Spectral data on **17**: $\delta_{CCl_4}{}^{Me_4Si}$ 4.17 (s, 2 H), 7.10 (s, 10 H). The NMR spectra of *cis*- (**17**) and *trans*-2,3-diphenyloxirane (**15**) were very similar to those published by Varian.[28] (Unfortunately, Varian[28] has interchanged the two spectra!)

(28) "NMR Spectra Catalog" compiled by N. S. Bhacca, D. P. Hollis, L. F. Johnson, and E. A. Pier of the Instrument Division of Varian Associates, Spectra 625 and 626, 1963.

Scheme IV

$$\text{sens} \xrightarrow{h\nu} {}^1\text{sens}^* \quad \text{absorption}$$

$${}^1\text{sens}^* \xrightarrow{k_f} \text{sens} + h\nu_f \quad \text{fluorescence}$$

$${}^1\text{sens}^* \xrightarrow{k_d} \text{sens} \quad \text{radiationless decay}$$

$${}^1\text{sens}^* \xrightarrow{k_{ST}} \text{sens}^* \quad \text{intersystem crossing}$$

$${}^1\text{sens}^* \xrightarrow[O_2]{k_O} \text{sens} \quad \text{quenching by } {}^3O_2$$

$${}^1\text{sens}^* \xrightarrow[D]{k_D} \text{sens}^{-}\cdot + D^{+}\cdot \quad \text{electron transfer}$$

$$(\text{sens}^{-}\cdot + D^{+}\cdot) \rightarrow \rightarrow DO_2 \quad \text{product formation}$$

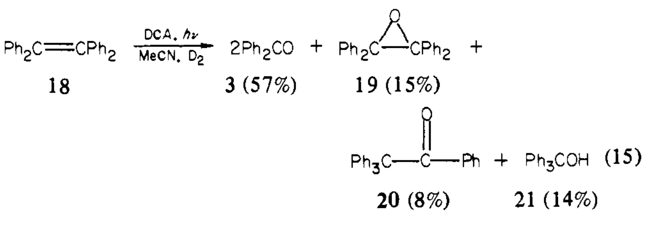
$$(\text{sens}^{-}\cdot + D^{-}\cdot)_{1-F} \rightarrow \rightarrow \text{sens} + D' + \text{other products} \quad \text{back-transfer of the electron and formation of other products}$$

Table II. Rate Constants for Product Formation and Fluorescence Quenching for Phenyl-Substituted Alkenes[a]

alkene	sens	$10^{10}k_D$,[b] $M^{-1}\,s^{-1}$	$10^{10}k_D$,[c] $M^{-1}\,s^{-1}$
1	DCA	0.74 ± 0.15	0.85 ± 0.02
12	DCA	2.0 ± 0.4	1.9 ± 0.1
12	CNA	0.48 ± 0.10	0.36 ± 0.02
18	DCA	2.0 ± 0.4	1.8 ± 0.1

[a] In MeCN at room temperature. [b] Rate constant for product formation, obtained from substrate concentration dependence of product formation, see text. [c] Rate constant for fluorescence quenching from Stern–Volmer plot.[6]

Tetraphenylethylene (18). As described in our preliminary paper,[15] irradiation of an oxygen-saturated MeCN solution of **18** and DCA at wavelengths (>400 nm) where only DCA absorbs the light gave the mixture of oxidation products shown in eq 15.



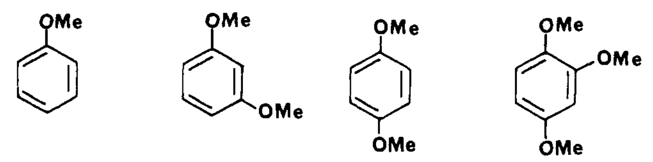
18 3 (57%) 19 (15%)

20 (8%) 21 (14%) (15)

Absolute yields were determined by GLPC analysis using internal standards.

In addition, an unknown compound (~1%) and small amounts of PhCHO and PhCOOH were detected. The products were separated by column chromatography and identified from their spectral data and by comparison with authentic samples.[29-31] DCA was not consumed in the reaction, and no photooxygenation could be detected in less polar solvents such as diethyl ether, ethyl acetate, CCl_4, *p*-dioxane, benzene, or cyclohexane.[15] Possible mechanisms for formation of carbonyl cleavage product and epoxide (**3** and **19**) have been discussed above. Formation of **20** is probably due to cationic rearrangement of **19**; **21** is probably derived from degradation of **20**.

Chart I



MB m-DMB p-DMB TMB

Table III. Quenching of the DCA-Sensitized Photooxygenation of *trans*-Stilbene (12) and Tetraphenylethylene (18) by Methoxybenzenes[a]

donor[b]	$E_{1/2}{}^{ox}D$,[c] V vs. SCE	obsd quenching, %	ΔG^{ET},[d] kcal/mol
MB[e]	1.76	2	+6.2
m-DMB[e]	1.49	10	0.0
p-DMB[e]	1.34	89	−3.5
TMB[e]	1.12	94	−8.5
m-DMB[f]	1.49	(0)[g]	+3.7
p-DMB[f]	1.34	70	+0.2
TMB[f]	1.12	91	−4.8

[a] In MeCN/O_2 at room temperature. $E_{1/2}$ (**12**/**12**$\cdot^+$) = 1.49 V vs. SCE;[16] $E_{1/2}$ (18/18$\cdot^+$) = 1.33 V vs. SCE (J. D. Stuart and W. E. Ohnesorge, *J. Am. Chem. Soc.*, 93, 4531 (1971)). [12] = 2 × 10^{-2} M; [18] = 10^{-2} M. [b] [Donor] = 10^{-3} M. [c] Oxidation potential of donor.[6] [d] Free-energy change for electron transfer: D + substrate$^{+}\cdot$ → $D^{+}\cdot$ + substrate (eq 5). [e] **12** as substrate. [f] **18** as substrate. [g] A minor enhancement of the reaction was observed, perhaps indicating reverse electron transfer.

Quantum Yields. The quantum yield for disappearance of **1** in the DCA-sensitized photooxygenation of **1** in MeCN/O_2 was determined at 405 nm by using a potassium ferrioxalate actinometer and the procedure of Calvert and Pitts.[32] The high value obtained (ϕ(−**1**) = 0.8, Table I) indicates that deactivation pathways such as back-transfer of the electron in the exciplex or the solvent-separated ion pair are quite unimportant in this reaction, at least under O_2.

The reaction of compound **1** was used for the determination of relative quantum yields for disappearance of starting material in the DCA-sensitized photooxygenation of **12**, **14**, and **18**; the values are summarized in Table I.

Kinetic Treatment. The kinetic scheme, Scheme IV, may be considered for the formation of a product (DO_2) in the sensitized electron-transfer photooxygenation of a donor molecule (D).

If F is the fraction of the radical ion pair (sens$^{-}\cdot$ + $D^{+}\cdot$) which forms DO_2, the quantum yield (ϕ) for formation of DO_2 obtained by steady-state treatment is given by eq 16. The relative amount

$$\phi = F\,\frac{k_D[D]}{k_f + k_d + k_{ST} + k_O[O_2] + k_D[D]} \tag{16}$$

(P) of product formed is proportional to ϕ, giving eq 17, where

$$\frac{1}{P} = K\left(1 + \frac{k_f + k_d + k_{ST} + k_O[O_2]}{k_D}\,\frac{1}{[D]}\right) \tag{17}$$

the proportionality constant (K) includes F. The term $k_O[O_2]$ is easily obtained from the quenching of DCA fluorescence by O_2, and $k_f + k_d + k_{ST} = \tau_{sens}{}^{-1}$, which has been measured.[6] Thus, a plot of P^{-1} vs. $[D]^{-1}$ allows determination of k_D. If the proposed electron-transfer mechanism is correct, the k_D obtained from eq 17 should be identical with k_q, the fluorescence quenching rate constant, for the same donor.[6] Values of k_D were determined by monitoring the formation of the major product (**3** form **1** and **18** and **13** from **12**) in the photosensitized oxygenation in oxygen-saturated MeCN. Table II lists values of k_D and k_q. Within

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(29) Spectral data on **19**: ν_{CCl_4} 3100, 1605, 1490, 1445, 1075, 1030, 898, 860, 717, 695 cm^{-1}; $\delta_{CCl_4}{}^{Me_4Si}$ 7.13 (s), 7.17 (s), 7.18 (s). These data and the GLPC retention time were identical with those of an authentic sample of **19** prepared by reaction of **3** with the anion of diethylphosphite in THF and HMPA: J. F. Normant, *Bull. Soc. Chim. Fr.*, 3601 (1966).

(30) Spectral data on **20**: ν_{CCl_4}: 3100, 1695, 1600, 1495, 1440, 1210, 1180, 1080, 1035, 1010, 940, 837, 700, 695 cm^{-1}; $\delta_{CCl_4}{}^{Me_4Si}$ 7.55–7.68 (m), 7.18 (s). These data were identical with those of authentic **20** prepared independently by acid-catalyzed rearrangement of benzpinacol obtained by photolysis of **3** in 2-propanol: W. E. Bachman, "Organic Syntheses", Collect. Vol. II, Wiley, New York, 1943, pp 71, 73.

(31) Spectral data on **21**: ν_{CCl_4} 3090, 1600, 1480, 1440, 1155, 1025, 1010, 890, 698 cm^{-1}; $\delta_{CCl_4}{}^{Me_4Si}$ 2.45 (s, 1 H), 7.28 (s, 15 H); m/e 260 (M^+), 183 (M^+ − Ph), 166, 165, 155, 154, 106, 105 (100%, $PhCO^+$), 91, 77. These data were identical with those of authentic **21** (MC and B).

(32) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry", Wiley, New York, 1966, p 780.

experimental error, k_D equals k_q for all systems investigated, which strongly suggests that fluorescence quenching is also involved in the first step of product formation, as required by the proposed electron-transfer mechanism.

Competitive Electron-Transfer. The electron-transfer mechanism for the sensitized photoxygenation of phenyl-substituted alkenes predicts that addition of small amounts of donor molecules with oxidation potentials less than that of the alkenes should quench the photooxygenations by electron transfer from the donor molecules to the alkene radical cation (see eq 18). Conversely,

$$\text{alkene}^{+}\cdot + \text{D} \rightarrow \text{alkene} + \text{D}^{+}\cdot \qquad (18)$$

donor molecules with oxidation potentials greater than that of the alkene should not greatly affect the photooxygenation of the alkene. The free-energy change involved in this electron transfer is given by eq 19, which contains the oxidation potentials of the

$$\Delta G^{\text{ET}}\ (\text{kcal/mol}) = -23.06\left(E_{1/2}{}^{\text{ox}}(\text{alkene}) - E_{1/2}{}^{\text{ox}}(\text{donor})\right) \qquad (19)$$

alkene and donor molecules. It should be noted that the added donor molecules will also quench the fluorescence of the sensitizer (DCA or CNA) in competition with the alkene. This would result in apparent quenching of the photooxygenation. However, if the ratio [alkene]/[D] is kept high, this competitive quenching by D will be minimal. Very similar considerations have recently been put forward by Farid et al.[9]

The methoxybenzenes, Chart I, were used as donor molecules since they were themselves comparatively unreactive toward DCA-sensitized photooxygenation in MeCN/O_2.

The quenching of the photooxygenation of **12** and **18** was studied by using DCA as sensitizer and [substrate] = $(1-2) \times 10^{-2}$ M and [D] = 10^{-3} M. Thus, from competitive fluorescence quenching alone, ≤5–10% quenching of the photooxygenation could be expected. Table III gives the observed quenching efficiencies of the various donors and ΔG^{ET} calculated from eq **5** by using $E_{1/2}{}^{\text{ox}} = +1.49$ V vs. SCE for **12** and 1.33 V for **18**.[6] It is clear that cases for which the electron transfer is calculated to be exothermic result in very efficient quenching. Hardly any quenching is observed where the calculated electron transfer is endothermic, while isoenergetic electron transfer results in intermediate quenching efficiency.

These findings strongly support the electron-transfer mechanism and the involvement of the alkene radical cation in the photooxygenations of **12** and **18**. The greater efficiency observed in the isoenergetic quenching of $\mathbf{18}^{+}\cdot$ than of $\mathbf{12}^{+}\cdot$ may indicate a longer lifetime of $\mathbf{18}^{+}\cdot$ than of $\mathbf{12}^{+}\cdot$ under the reaction conditions. Attempts to trap the radical cation of **1** by the methoxybenzenes failed, suggesting a much shorter lifetime of $\mathbf{1}^{+}\cdot$ than of $\mathbf{12}^{+}\cdot$ or $\mathbf{18}^{+}\cdot$. Thus, the indicated order of lifetimes ($\mathbf{1}^{+}\cdot < \mathbf{12}^{+}\cdot < \mathbf{18}^{+}\cdot$) agrees with the expected order of steric hindrance to attack on the radical cations, with the observed order of quantum yields for photooxygenation (Table I), and with the observed cation lifetimes in flash photolysis.[14]

Nonsinglet Oxygen Mechanism. It is necessary to examine whether a mechanism involving $^1O_2$ sensitized by DCA and CNA could explain the observed photooxygenation of phenyl-substituted alkenes. Indeed, $^1O_2$ reacts with electron-rich substrates such as enamines[33] and vinyl ethers[34] to produce dioxetanes. For the following reasons, however, a $^1O_2$ mechanism is not consistent with the present DCA- and CNA-sensitized photooxygenations:

(a) Compounds **1**, **12**, **14**, and **18** do *not* react with $^1O_2$ to any appreciable extent. Thus, no products were detected in oxygen-saturated MeCN solutions of **1**, **12**, **14**, or **18**, containing the singlet oxygen sensitizer rose bengal irradiated at λ > 500 nm, even at times and light fluxes long by comparison with those used with DCA. In MeOH/O_2 and, more slowly, in CH_3CN, however, methylene blue (but not rose bengal) did sensitize a very slow conversion of **12** to **13**.[35] We also found that **13** quenched the weak fluorescence of methylene blue but not of rose bengal.[35] Clearly, the methylene blue-sensitized conversion of **12** to **13** is not a simple $^1O_2$ mechanism either, and we have suggested an electron-transfer mechanism also in this case.[35] These findings warn that dye-sensitized photooxygenations cannot blindly be interpreted as $^1O_2$ reactions, especially when the reactions are slow or high substrate concentrations are used.

(b) The DCA-sensitized photooxygenation of the phenyl-substituted alkenes takes place only in highly polar solvents (MeCN or MeOH). A $^1O_2$ mechanism would not be expected to show such severe solvent polarity dependence.

(c) The agreement between the rate constants for product formation (k_D) and fluorescence quenching (k_q) (Table II) would be completely fortuitous in the case of a $^1O_2$ mechanism.

(d) Addition of small amounts of methoxybenzenes to the photoxygenations of **12** and **18** would not be expected to have any appreciable effect in the case of a $^1O_2$ mechanism, and no correlation between ΔG for electron transfer from the methoxybenzene to the alkene radical cation and the observed quenching efficiencies (see Table III) should be observed.

Thus, it can safely be concluded that $^1O_2$ is not involved to any appreciable extent in the DCA- and CNA-sensitized photoxygenation of phenyl-substituted alkenes. The electron-transfer mechanism suggested previously[15] involves the superoxide anion formed by electron transfer from $\text{DCA}^{-}\cdot$ or $\text{CNA}^{-}\cdot$ to $^3O_2$. An alternative mechanism (eq 20) suggested recently in similar systems[9,37] involves attack by $^3O_2$ on the substrate radical cation followed by back-transfer of the electron at a later stage and does not involve $O_2{}^{-}\cdot$.

$$[\text{sens}^{-}\cdot + \text{D}^{+}\cdot] \xrightarrow{^3O_2} [\text{sens}^{-}\cdot + \text{DO}_2)^{+}\cdot] \xrightarrow{-\text{sens}} \text{DO}_2 \qquad (20)$$

At this point our data are consistent with both mechanisms. In the absence of further data, however, we favor the $O_2{}^{-}\cdot$ mechanism, since the electron transfer from $\text{DCA}^{-}\cdot$ or $\text{CNA}^{-}\cdot$ to O_2 is calculated to be exothermic (see above) and thus should occur at close to diffusion-controlled rates. Flash photolysis data recently reported[14] also favor this mechanism.

Experimental Section

^{1}H NMR spectra were recorded on a Varian T-60 NMR spectrometer with tetramethylsilane (Me_4Si) internal standard. Infrared spectra were determined on a Perkin-Elmer 137 infrared spectrophotometer in CCl_4 solutions. Ultraviolet spectra were recorded on a Cary Model 15 spectrophotometer while mass spectra were taken by Dr. K. Fang on a MS-9.

Fluorescence spectra were determined on a Spex Fluorolog spectrofluorometer equipped with a photon-counting detection system. The fluorescence quenching experiments, measurements of reduction potentials by cyclic voltammetry, and lifetime determination by single-photon counting have been described.[6] The singlet lifetime obtained in MeCN/N_2 for DCA (15.3 ± 0.1 ns[6]) agrees with the reported value of 15.2 ns.[8c] Melting points are uncorrected.

Materials. Compounds 1 (Aldrich), 12 (Eastman), and 14 (Aldrich) were used as received. Compound 18 (Aldrich, or prepared[38] from Ph_2CCl_2 and Cu) is a yellow powder. Recrystallization from benzene/EtOH (1:1) gave yellow crystals, mp 222–223 °C. Norit has little effect on the color of the obtained crystals. Purification by column chromatography (Silica Gel, eluant hexane/benzene, 3:1), however, gave a white solid, which, after recrystallization from hexane/benzene (1:1) gave white crystals, mp 222-223 °C, with no absorption above 400 nm. This purified sample of 18 was used in all quantitative runs. MeCN was spectrograde (MC and B) and was used as received.

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(33) C. S. Foote, A. A. Dzakpasu, and J. W.-P. Lin, *Tetrahedron Lett.*, 1247 (1975); C. S. Foote and J. W.-P. Lin, *ibid.*, 3267 (1968).

(34) P. D. Bartlett and A. P. Schaap, *J. Am. Chem. Soc.*, **92**, 3223 (1970); S. Mazur and C. S. Foote, *ibid.*, 92, 3225 (1970); A. P. Schaap and P. D. Bartlett, *ibid.*, **92**, 6055 (1970); P. D. Bartlett, G. D. Mendenhall, and A. P. Schaap, *Ann. N.Y. Acad. Sci.*, 171, 79 (1970).

(35) L. Manring, J. Eriksen, and C. S. Foote, *J. Am. Chem. Soc.*, **102**, 4275 (1980). Rio and Berthelot[36] also observed very slow conversion of **1** to **3**, **12** to **13**, and **18** to **3** in methylene blue-sensitized photooxygenation in MeOH/O_2. Although the reactions could not be sensitized by rose bengal, these authors suggested a $^1O_2$ mechanism.[36]

(36) G. Rio and J. Berthelot, *Bull. Soc. Chim. Fr.*, 3609 (1969).

(37) R. Tang, H. J. Yue, J. F. Wolf, and F. Mares, *J. Am. Chem. Soc.*, **100**, 5248 (1978). See also R. K. Haynes, *Aust. J. Chem.*, **31**, 121 (1978).

(38) R. E. Buckles and G. M. Matlack, "Organic Syntheses", Collect. Vol. IV, Wiley, New York, p 914, 1963.

Photochemical Instrumentation. All photolyses were carried out by using a 1200 W medium-pressure Hanovia lamp in a water-cooled immersion well. A 1-*cm* pathlength filter solution consisting of 27.0 g of $CuSO_4 \cdot 5H_2O$, 30.0 g of $NaNO_2$, and 50 mL of concentrated NH_4OH diluted with water to 1000 mL was used. This filter isolates the Hg lines at 405 and 436 nm (ref 32, p 737).

Irradiation Procedures. All solutions for analytical photolyses were placed in matched Bausch and Lomb Spectronic 20 test tubes (capacity ~5 mL). Concentrations of substrates were $(1-2) \times 10^{-2}$ M and of DCA or CNA, 10^{-4} M. The tubes were stoppered with serum caps, and O_2 or N_2 was bubbled through the solutions for 3 min prior to irradiation. During photolysis, the tubes rotated around the light source on a merry-go-round. After irradiation, an appropriate substrate was added for internal standardization in the GLPC analysis, carried out on a Hewlett-Packard Model 5720A gas chromatograph using a 50 cm × $^1/_8$ in. stainless-steel column packed with 10% UC-W 98 on 80–100 mesh WAW-DMCS or a 120 cm × $^1/_8$ in. stainless-steel column packed with 10% Carbowax 20M on 80 × 100 mesh Chromsorb W. For all quantitative determinations, the GLPC analyses were carried out in triplicate. In these experiments, the conversion of substrate was always kept below 10%. Irradiation times leading to >90% conversion were 30 min for **1**, 60 min for **12** and **14**, and 180 min for **18** under these conditions.

In preparative photolyses, tubes of 100- or 500-mL capacity were used. Oxygen was constantly bubbled through the solution during irradiation. Photolysates were concentrated on a rotary evaporator and the residues chromatographed (Silica Gel, 2.5 × 40 cm) and eluted with 0–30% benzene in hexane. Eluted fractions were analyzed by GLPC.

Quantum Yields. Potassium ferrioxalate and the procedure described by Calvert and Pitts were used.[32] The light source was a 200-W Hg–Xe lamp, and the 405-nm line was isolated by a Jarrell-Ash monochromator. The light intensity was determined twice before and once after the actual photolysis. No change in light intensity was detected during these experiments. The photolysis of **1** and DCA were carried out to ~10% conversion of **1**. The photolysate was analyzed by GLPC using an internal standard and determination of GLPC response factors. The quantum yields were determined three times. The photooxygenation of **1** was used as an actinometer for the measurements of the quantum yields for the photooxygenation of **12**, **14**, and **18**, which were irradiated on the merry-go-round.

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Photoaddition of Biacetyl and Alkenes. Reaction Stereochemistry, Multiplicity, and Photokinetics

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Abstract: Quantum yields are reported for the photoaddition of biacetyl with the alkenes indene, 2,3-dimethyl-2-butene, furan, and 1,2-dimethoxyethene in benzene solution. The dependence of quantum efficiencies on alkene concentration is consistent with a photoaddition mechanism involving biacetyl triplets. The quenching of fluid solution biacetyl phosphorescence has been observed, and quenching constants correlate with the electron-donor ability (ionization potentials) of the alkenes. Photoaddition of biacetyl and 1,2-dimethoxyethene is nonstereospecific, and oxetane formation is accompanied by the isomerization of the starting alkene. Stereochemical results are used to estimate relative rates of cleavage, closure, and stereorandomizing bond rotation in biradicals, proposed intermediates in photoaddition. Exciplexes of triplet biacetyl and alkenes are proposed as primary photochemical intermediates (precursors to biradicals) on the basis of the stereochemical, emission quenching, and other data.

The solution photochemistry of biacetyl and related dicarbonyl compounds appears to be dominated by reactions involving hydrogen abstraction from solvent or another reagent followed by varied combination of the photogenerated radicals.[1] On the other hand, a number of recent reports[2,3] have described photoaddition of biacetyl and unsaturated substrates under circumstances where hydrogen abstraction might have taken place but did not prevail. Thus, the conjugated dicarbonyl functionality appears to join the larger class of simple alkanones and alkanals which readily participate in the Paterno–Buchi (cycloaddition) and related reactions.[4]

The quantitative aspects of this comparison of dicarbonyls and other aldehydes and ketones are not well understood although the mechanism of biacetyl addition is partially known. Several alkenes have been shown to quench the phosphorescence of biacetyl,[2a,d,e] but in a number of cases biacetyl fluorescence emission can also be quenched.[5] These results in general permit that either singlet or triplet states of biacetyl may be reactive. Emission quenching and quantum yield results indicate that a triplet path is dominant for biacetyl/1,2-diethoxyethene photoaddition.[2e] Labeling studies[2a] further show that 1,4 biradicals may be important intermediates which follow the initial interaction of biacetyl and quenchers and lead to oxetane and "ene-type" addition products.

In the spirit of earlier mechanistic analyses[4,6] of alkanone and alkanal addition, we have examined in detail the interaction of excited biacetyl with a variety of unsaturated compounds. Luminescence results and the profile of quantum yield of photoaddition as a function of the concentration of addends allow the assignment of the reactive excited state. A stereochemical test provides information on the nature of penultimate intermediates involved in photoaddition.

Cycloaddition reactions which employ visible absorbing chromophores as sensitizers or substrates are currently of interest as

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