

- (7) C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London*, **235**, 518 (1956).
- (8) H. E. Zimmerman, T. P. Cutler, V. R. Fitzgerald, and T. J. Weigt, *Mol. Photochem.*, in press.
- (9) S. S. Hixson, *J. Am. Chem. Soc.*, **98**, 1271 (1976).
- (10) (a) H. E. Zimmerman and R. D. Little, *J. Am. Chem. Soc.*, **96**, 5143 (1974); (b) see also ref 16.
- (11) (a) Since quantum yields are the ratio of excited singlet reaction rate to the total decay rate, these are not always safely correlated to reaction mechanism and structure;<sup>11b,c</sup> (b) H. E. Zimmerman and A. A. Baum, *J. Am. Chem. Soc.*, **93**, 3646 (1971); (c) H. E. Zimmerman and N. Lewin, *ibid.*, **91**, 879 (1969).
- (12) H. E. Zimmerman, D. P. Werthemann, and K. S. Kamm, *J. Am. Chem. Soc.*, **96**, 439 (1974).
- (13) (a) A more extensive description can be found in ref 2 and 13b; (b) H. E. Zimmerman and W. T. Gruenbaum, *J. Org. Chem.*, **43**, 1997 (1978).
- (14) (a) J. A. Pople, *Trans. Faraday Soc.*, **49**, 1275 (1953); (b) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953).
- (15) R. J. Buenker and S. D. Peyerimhoff, *Theor. Chim. Acta*, **35**, 33 (1974).
- (16) H. E. Zimmerman and B. R. Cotter, *J. Am. Chem. Soc.*, **96**, 7445 (1974).
- (17) (a) H. E. Zimmerman and V. R. Sandel, *J. Am. Chem. Soc.*, **85**, 915 (1963); (b) H. E. Zimmerman and S. Somasekhara, *ibid.*, **85**, 922 (1963); (c) E. Havinga, *Pure Appl. Chem.*, **16**, 137 (1968).
- (18) Precise comparisons are inexact in any case. The cyclopropyldicarbonyl diradical formed by aryl migration (e.g., 41\* in Chart III) has lost aromaticity but still has pentadienyl delocalization.
- (19) (a) Just a few examples are given in ref 19b-f; (b) H. E. Zimmerman and J. W. Wilson, *J. Am. Chem. Soc.*, **86**, 4036 (1964); (c) H. E. Zimmerman, R. D. Rieke, and J. R. Scheffer, *ibid.*, **89**, 2033 (1967); (d) H. E. Zimmerman, R. C. Hahn, and M. C. Wani, *ibid.*, **87**, 1138 (1965). (e) In these examples, an aryl group migrates to the  $\beta$  carbon of an  $n-\pi^*$  triplet moiety. Considerable activation energy is involved, however (10 kcal/mol<sup>19f</sup>). (f) H. E. Zimmerman and W. R. Elser, *J. Am. Chem. Soc.*, **91**, 887 (1969).
- (20) H. E. Zimmerman, "Quantum Mechanics for Organic Chemists", Academic Press, New York, N.Y., 1975, Chapter 5.
- (21) W. T. Borden, "Modern Molecular Orbital Theory for Organic Chemists", Prentice-Hall, Englewood Cliffs, N.J., 1975.
- (22) (a) There is a problem in deciding which orbitals of the six-ring to observe. Inclusion of the  $sp^2$  hybrid seems particularly apt since this plus the C-1 p orbital together give  $sp^5$  hybrids involved in three-ring formation. Inspection of only the six p orbitals would lead to inclusion of only one component of the equivalent  $\sigma$  bonds to C-1 in the diradical. The alternative is to focus attention on the pentadienyl radical forming system. (b) The energies given ignore the concerted nature of the reaction with three-ring opening beginning. Also, the total bridging energy is negative despite the local rise in energy.
- (23) S. S. Hixson, *Tetrahedron Lett.*, 1155 (1972).
- (24) H. E. Zimmerman, P. Baekstrom, T. Johnson, and D. W. Kurtz, *J. Am. Chem. Soc.*, **96**, 1459 (1974).
- (25) H. E. Zimmerman and R. T. Klun, *Tetrahedron*, in press.
- (26) (a) H. E. Zimmerman, Abstracts, 17th National Organic Symposium, Bloomington, Ind., 1961, p 31; (b) H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, **83**, 4486 (1961); (c) *ibid.*, **84**, 4527 (1962).
- (27) All melting points were determined on a hot-stage apparatus calibrated with known compounds. Proton nuclear magnetic resonance spectra were taken on Varian T-60, JEOL MH100, or Bruker WH-270 spectrometers. Mass spectra were obtained using an AE1 MS-320 mass spectrometer at 70 eV. High-pressure liquid chromatography used a Waters Associates Inc. ALC-100 chromatograph equipped with 254-nm ultraviolet detector. Gas chromatographic analyses used a Varian Aerograph series 2100 chromatograph with flame ionization detectors. Column chromatography was done with Vycor columns and Sylvania phosphors mixed with the packing to monitor bands with a hand-held UV lamp.
- (28) A. Hoffman, *J. Am. Chem. Soc.*, **51**, 2542 (1929).
- (29) E. E. Blaise and I. Herman, *Ann. Chim. Phys.*, **23**, 432 (1913).
- (30) J. Corse, and E. Rohrmann, *J. Am. Chem. Soc.*, **70**, 370 (1948).
- (31) J. Colonge and L. Pichat, *Bull. Soc. Chim. Fr.*, 177 (1949).
- (32) C. F. Koelsch and P. R. Johnson, *J. Org. Chem.*, **6**, 538 (1941).
- (33) A. Sonada, I. Moritani, S. Yasuda, and T. Wada, *Tetrahedron*, **26**, 3075 (1970).
- (34) This compound was also obtained by Griffin; see ref 4a.
- (35) W. H. Starnes, *J. Org. Chem.*, **33**, 3767 (1968).
- (36) H. E. Zimmerman and P. S. Mariano, *J. Am. Chem. Soc.*, **91**, 1718 (1969).
- (37) H. Pines and D. Wunderlich, *J. Am. Chem. Soc.*, **80**, 6001 (1958).
- (38) H. Kuntzel, H. Wolf, and K. Schaffner, *Helv. Chim. Acta*, 868 (1971).
- (39) D. Seyferth, J. M. Burlitch, R. J. Minasz, J. Y.-P. Mui, H. D. Simmons, A. J. H. Treiber, and S. R. Dowd, *J. Am. Chem. Soc.*, **87**, 4259 (1965).
- (40) D. Seyferth and R. L. Lambert, *J. Organomet. Chem.*, **16**, 21 (1969).
- (41) H. E. Zimmerman, T. R. Welter, D. Tartler, and R. A. Bunce, unpublished results.
- (42) L. Meites and T. Meites, *Anal. Chem.*, **20**, 984 (1948).
- (43) H. E. Zimmerman, D. P. Werthemann, and K. S. Kamm, *J. Am. Chem. Soc.*, **97**, 3718 (1975).
- (44) J. N. Murrell and K. L. McEwen, *J. Chem. Phys.*, **25**, 1143 (1956).
- (45) H. E. Zimmerman and M. G. Steinmetz, unpublished results.
- (46) J. Hinze and H. H. Jaffe, *J. Am. Chem. Soc.*, **84**, 540 (1962).
- (47) K. Nishimoto and L. Forster, *Theor. Chim. Acta*, **4**, 155 (1966).
- (48) R. L. Flurry, "Molecular Orbital Theories of Organic Molecules", Marcel Dekker, New York, N.Y., 1968.
- (49) R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).
- (50) L. E. Sutton, "Tables of Interatomic Distances and Configurations in Molecules and Ions", *Chem. Soc., Spec. Publ.*, **No. 11** (1958); and **No. 18** (1965).
- (51) L. D. Kispert, C. Dyas, and C. U. Pittman, *J. Am. Chem. Soc.*, **93**, 6948 (1971).

## Photochemical Electron-Transfer and Triplet Reactions of 1,2-Diphenylcyclopropene-3-carboxylate<sup>1</sup>

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**Abstract:** In nonpolar solvents singlet-excited 9,10-dicyanoanthracene (<sup>1</sup>DCA\*) and methyl 1,2-diphenylcyclopropene-3-carboxylate (CP) form an emitting exciplex and yield the exo Diels-Alder adduct **1**. In polar solvents <sup>1</sup>DCA\* reacts with CP at a diffusion-controlled rate leading to the formation of the radical ions CP<sup>•+</sup> and DCA<sup>•-</sup>. Recombination of this radical ion pair partially gives <sup>3</sup>CP\*, which reacts with CP to give the dimer **3**. The triplet yield in this reaction is increased by more than an order of magnitude when 1,2,4,5-tetracyanobenzene (TCNB) is added in small amounts. This effect is due to a secondary electron transfer from DCA<sup>•-</sup> to TCNB, followed by recombination of TCNB<sup>•-</sup> and CP<sup>•+</sup>, which leads to a higher triplet yield than that from the corresponding reaction with DCA<sup>•-</sup>. Further support for this electron-transfer/triplet mechanism is obtained from quenching of CP<sup>•+</sup> by compounds having low oxidation potentials and from quenching and chemical trapping of <sup>3</sup>CP\*. In connection with the latter experiments the preparative and kinetic aspects of the triplet reactions of CP with dimethyl fumarate (F) and *p*-cyanocinnamate esters (CNC) are investigated. The main products of these reactions are the bicyclopentane derivatives **4-6** and **11-13**, respectively. The radical cation CP<sup>•+</sup>, formed in polar solvents, tautomerizes to the enol radical cation (E<sup>•+</sup>), which adds to DCA<sup>•-</sup> and, upon reketonization of the product, the endo Diels-Alder adduct **2** is obtained. This mechanism is supported by a deuterium isotope effect, incorporation of deuterium in the product on irradiation in the presence of *t*-BuOD, and other experiments. The intermediate E<sup>•+</sup> can be trapped with F and CNC giving different products (**8-10** and **14**, respectively) from those obtained from the reaction of <sup>3</sup>CP\* with these reactants. Irradiation of DCA and CP in polar solvents in the presence of O<sub>2</sub> leads, in a chain process, to several oxidation products. This oxidation probably proceeds via reaction of CP<sup>•+</sup> with oxygen.

### Introduction

Reactions of exciplexes and electron transfer are currently attracting considerable interest in organic photochemistry.

Photochemical charge-transfer (exciplex) and electron-transfer (radical ions) reactions are controlled by redox potentials, excitation energy, and solvent polarity.<sup>2</sup> Whereas excited complexes and exciplexes are usually formed in nonpolar sol-

vents, the formation of solvated radical ions requires irradiation in polar solvents.<sup>2,3</sup>

Of the photochemical electron-transfer reactions, those of aromatic hydrocarbons with amines and of carbonyl compounds with amines are more extensively investigated.<sup>4</sup> Few photoinduced electron-transfer reactions of olefins are reported and the scope and limitations of these reactions are not yet well defined. A number of olefins are known to dimerize via the photochemically produced radical cation.<sup>5-9</sup> Among these is an example of mixed addition of different olefins.<sup>7b</sup> Some of these dimerizations proceed via a chain reaction, in which the chain propagation step is electron transfer from a monomeric olefin to a dimeric radical cation.<sup>5,7b,8a</sup> When such electron-transfer reactions are carried out in the presence of nucleophiles, such as alcohols and cyanides, anti-Markownikoff addition products are obtained.<sup>6,10</sup> Photosensitized electron-transfer reactions of phenylacetylene<sup>11</sup> give a dimer (1-phenylnaphthalene) and a 2:1 addition product to acetonitrile (2,6-diphenylpyridine).

In continuation of our effort to explore the scope of photoinduced electron-transfer chemistry, we investigated the reactions of methyl 1,2-diphenylcyclopropene-3-carboxylate (CP).<sup>12</sup>

### Results and Discussion

In this study 9,10-dicyanoanthracene (DCA) is used as a sensitizer, for it has a relatively low reduction potential and can be excited at wavelengths longer than 400 nm. Thus, by the proper use of filters, excitation of other starting materials and photoproducts can be easily avoided.

For comparison with the electron-transfer products, the photoreaction of DCA with the diphenylcyclopropene derivative (CP) is also studied in a nonpolar solvent (benzene), where no solvated radical ions are expected to be formed.

**Reactions in Benzene.** The cyclopropene CP quenches the fluorescence of DCA very efficiently. In degassed benzene, the slope of the plot of  $(\phi_0/\phi)_f$  vs. [CP] is 32 L mol<sup>-1</sup>. The lifetime of <sup>1</sup>DCA\* in benzene was determined by Ware et al.<sup>14</sup> as 12.4 ns. Thus, the fluorescence of DCA is quenched by CP at a rate of  $2.6 \times 10^9$  L mol<sup>-1</sup> s<sup>-1</sup>. The actual reaction constant for exciplex formation will be even higher if this process is reversible. An emitting exciplex is formed with maximum at 510 nm (see Figure 1). The excitation spectrum for this structureless band is identical with that for the residual fluorescence of DCA.

Irradiation ( $\lambda \geq 405$  nm) of a saturated solution of DCA in benzene containing CP (0.05 M) leads to the formation of the adduct **1** ( $\phi \approx 0.002$ ) besides traces of the dimer<sup>12</sup> of CP. The NMR spectrum (270 MHz) of **1** shows two AA'BB' systems for the aromatic protons of the anthracene moiety, which is consistent with a symmetry along the long axis of the anthracene moiety (position 1 = 4, 2 = 3, 5 = 8, 6 = 7). The cyclo-

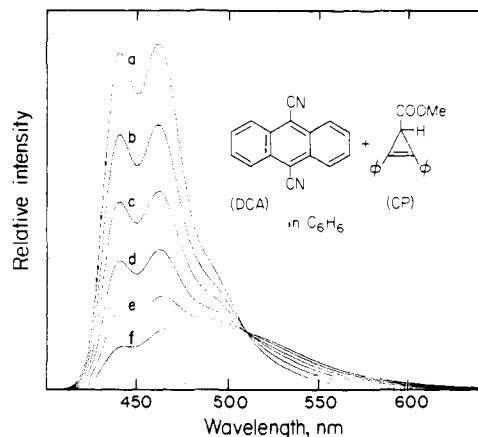
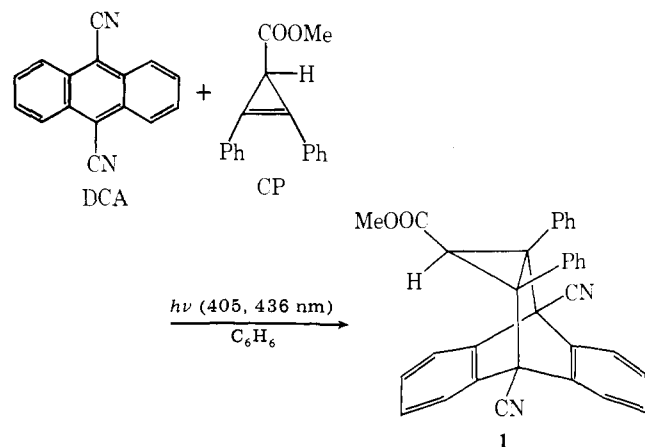
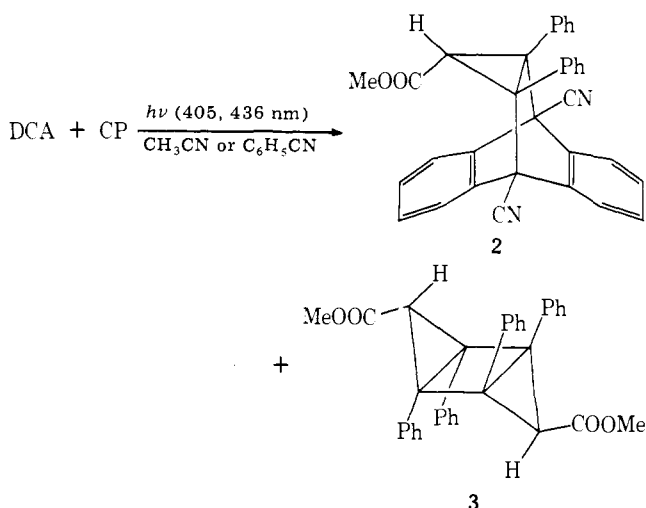


Figure 1. Uncorrected emission spectra of DCA (1.1 mM) in degassed benzene containing CP at concentrations of 0, 0.01, 0.025, 0.05, 0.1, and 0.2 M (a-f, respectively).  $\lambda_{\max}$  of the corrected exciplex emission is 510 nm.

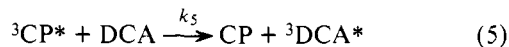
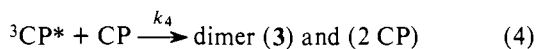
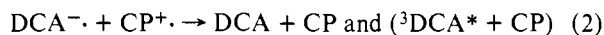
propyl proton in **1** appears at a relatively high field ( $\delta$  2.03), which indicates that it is strongly shielded by the aromatic ring current of the anthracene moiety. The adduct **1** undergoes thermal decomposition to its components as shown by gas chromatography. In addition, the major cleavage in the mass spectrometer is that leading to the radical cation of CP. The structure of compound **1** is likely to be a reflection of the configuration of the exciplex. For steric reasons stronger orbital overlap is obtained from a configuration in which the cyclopropyl proton of CP faces the DCA moiety.

**Reactions in Acetonitrile and Benzonitrile.** In degassed acetonitrile a plot of  $(\phi_0/\phi)_f$  vs. [CP] for the fluorescence quenching of DCA gives a slope of 235 L mol<sup>-1</sup>. The lifetime of <sup>1</sup>DCA\* in this solvent is 15.2 ns.<sup>14</sup> Thus, the rate of quenching of the fluorescence of DCA by CP is  $1.55 \times 10^{10}$  L mol<sup>-1</sup> s<sup>-1</sup>, which is approximately diffusion controlled. As expected, no exciplex emission is observed in this polar solvent. Irradiation in acetonitrile or benzonitrile leads to the isomeric adduct **2** and the dimer of CP (**3**).<sup>12</sup> In the NMR spectrum (270 MHz) adduct **2** also shows two AA'BB' systems different from those of **1** for the aromatic protons of the anthracene moiety. The cyclopropyl proton is not as shielded as in **1**, but the signal of the carbomethoxy group is not much shifted to higher field either. In contrast to adduct **1**, compound **2** does



not cleave thermally to its components. This compound remains unchanged after heating it for 1 h at 250 °C in an evacuated and sealed tube. Its structure is confirmed, however, by x-ray crystallographic analysis to be the endo Diels-Alder adduct.

**Dimerization Mechanism.** The data presented below are best explained in terms of the following mechanism for the dimerization of CP.



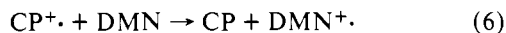
Weller et al.<sup>2</sup> have shown that the feasibility of an electron-transfer process, as in reaction 1, can be determined from the gain in free energy ( $-\Delta G_1$ ) as calculated from

$$\Delta G_1 = (E_{\text{D}^{\text{ox}}} - E_{\text{A}^{\text{red}}}) - \Delta E({}^1\text{A}^*) \quad (I)$$

$E_{\text{D}^{\text{ox}}}$  and  $E_{\text{A}^{\text{red}}}$  are the electrochemically determined potentials for the one-electron oxidation of the donor and reduction of the acceptor, respectively.  $\Delta E({}^1\text{A}^*)$  is the zero-zero transition energy of the lowest excited singlet state of the acceptor.

Since an irreversible electrochemical oxidation wave is obtained for CP, no accurate determination of  $\Delta G$  can be made, but a rough estimate on the basis of this irreversible potential (1.69 V),<sup>15</sup> the reduction potential of DCA (-0.88 V),<sup>16</sup> and the singlet excitation energy of DCA (68 kcal/mol) indicates that reaction 1 is exothermic by ca. 9 kcal/mol.

In agreement with the proposed electron-transfer reaction, compounds having low oxidation potentials, such as 1,4-dimethoxynaphthalene (DMN),<sup>17</sup> substantially (>80%) quench the dimer (3) and the adduct (2) formation at very low concentrations relative to that of CP (DMN:CP ~ 1:100). Under these conditions direct quenching of  ${}^1\text{DCA}^*$  by DMN is only about 1% since CP reacts with  ${}^1\text{DCA}^*$  at a diffusion-controlled rate.



The triplet formation via recombination of radical ion pairs is spectroscopically well established.<sup>18</sup> The free energy associated with such a process as reaction 3 ( $-\Delta G_3$ ) can be calculated from eq II, derived by Weller et al.<sup>18</sup>

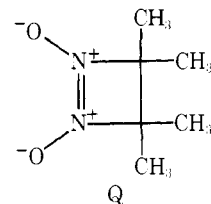
$$\Delta G_3 = \Delta E({}^3\text{D}^*) - (E_{\text{D}^{\text{ox}}} - E_{\text{A}^{\text{red}}}) \quad (II)$$

The second term of eq II gives the free enthalpy stored in the solvated radical ion pair and is equal to the first term in eq I.  $\Delta E({}^3\text{D}^*)$  is the triplet energy of the electron donor. From the electrochemical data and the triplet energy of CP (~53 kcal/mol),<sup>19</sup> it can be estimated that reaction 3 is exothermic (negative  $\Delta G_3$ ) by ~6 kcal/mol.

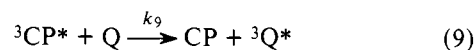
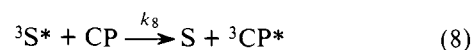
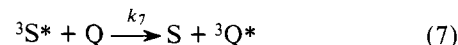
Experimental evidence for the intermediacy of such a process (reaction 3) is obtained from the fact that the dimer formation decreases with increasing concentrations of DCA. The triplet energy of DCA is expected to be lower or similar to that of anthracene, i.e., about 40 kcal/mol, which is much lower than that of CP; hence, the efficient quenching of  ${}^3\text{CP}^*$  by DCA (reaction 5).

A stronger support for the intermediacy of the triplet-excited cyclopropene ( ${}^3\text{CP}^*$ ) in the above-mentioned dimerization is obtained from quantitative quenching experiments, which are compared with those using Michler's ketone (MK) as a triplet sensitizer. 3,3,4,4-Tetramethyl-1,2-diazetene 1,2-dioxide (Q), reported by Ullman<sup>20</sup> as a suitable quencher for low-lying triplets, is used in these experiments.

In the Michler's ketone (MK) sensitized reactions, the quencher (Q) can affect the quantum yield of dimerization at



two stages, that is, interception of the triplet-excited sensitizer ( ${}^3\text{S}^*$ ), reaction 7, which competes with energy transfer to CP, reaction 8, and interception of  ${}^3\text{CP}^*$ , reaction 9, which competes with the dimerization, reaction 4.



At high enough concentrations of CP, the unimolecular decays of  ${}^3\text{S}^*$  and  ${}^3\text{CP}^*$  are negligible compared to the rate of the bimolecular reactions 8 and 4, respectively.<sup>21</sup> The quantum yield dependence on [Q] is given by eq III, which can be rearranged to eq IV.

$$\frac{\phi_0}{\phi} = \left(1 + \frac{k_7}{k_8} \frac{[\text{Q}]}{[\text{CP}]}\right) \left(1 + \frac{k_9}{k_4} \frac{[\text{Q}]}{[\text{CP}]}\right) \quad (III)$$

$$\left(\frac{\phi_0}{\phi} - 1\right) \frac{[\text{CP}]}{[\text{Q}]} = \left(\frac{k_7}{k_8} + \frac{k_9}{k_4}\right) + \left(\frac{k_7 k_9}{k_8 k_4}\right) \frac{[\text{Q}]}{[\text{CP}]} \quad (IV)$$

The ratio of  $k_7/k_8$  is determined from flash photolysis experiments by monitoring the decay rate of  ${}^3\text{MK}^*$  in the presence of CP and in the presence of Q. The values of  $k_7$  and  $k_8$  so determined are  $5 \times 10^9$  and  $6.6 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ , which give a ratio of  $k_7/k_8$  of 0.76. By dividing each value of  $\phi_0/\phi$  by the corresponding  $(1 + 0.76[\text{Q}]/[\text{CP}])$  and plotting the product,  $\phi_0/\phi'$ , vs.  $[\text{Q}]/[\text{CP}]$ , a slope, which is equal to  $k_9/k_4$ , of 10.1 is obtained (Figure 2).

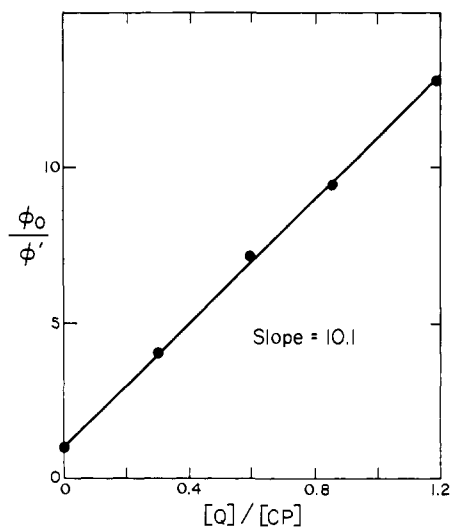
To check the consistency of this experiment, the function on the left side of eq IV is plotted vs.  $[\text{Q}]/[\text{CP}]$ . The intercept and slope of this linear plot are equal to the sum of the two ratios  $k_7/k_8$  and  $k_9/k_4$  and to their multiple, respectively. The experimentally determined intercept and slope are 11.1 and 7.7, respectively (Figure 3). From these data the two ratios are equal to 0.74 and 10.4, which are in good agreement with the values of 0.76 and 10.1 mentioned above.

In the DCA-sensitized reaction, the Stern-Volmer expression for the quantum yield of dimerization of CP is given by eq V assuming that the unimolecular decay of  ${}^3\text{CP}^*$  is negligible<sup>21</sup> compared to the bimolecular reaction (4).

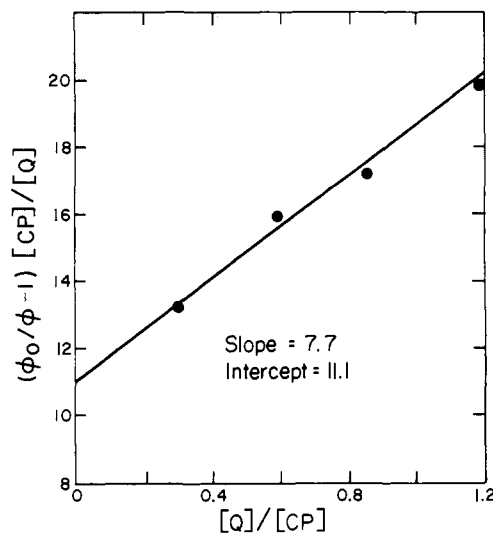
$$\frac{\phi_0}{\phi} = 1 + \frac{k_9}{k_4[\text{CP}] + k_5[\text{DCA}]} [\text{Q}] \quad (V)$$

Addition of Q (up to 0.026 M) to acetonitrile solutions of CP (0.1 M) containing solid DCA (solubility at room temperature; ~0.55 mM) has, as expected, negligible effect on the formation of adduct 2, but it diminishes that of the dimer. The measured quenching efficiency,  $\phi_0/\phi$ , is subjected to a minor correction to account for the interception of  ${}^1\text{DCA}^*$  by Q, which takes place at a rate one-third of the rate of quenching by CP. A plot of the corrected  $\phi_0/\phi$  vs. [Q] has a slope of  $70 \text{ L mol}^{-1}$  (Figure 4).

According to eq V, a determination of  $k_9/k_4$  requires an estimate for the ratio of  $k_5[\text{DCA}]$  to  $k_4[\text{CP}]$ . As shown in the following discussion, this ratio is very small. Error in its estimation is, therefore, not critical. The reaction constant for the exothermic energy transfer from  ${}^3\text{MK}^*$  to Q,  $k_9$ , is 10 times larger than  $k_4$  but is slightly smaller than reaction constants for energy transfer from  ${}^3\text{MK}^*$  to other molecules such as CP



**Figure 2.** Plot of  $\phi_0/\phi'$  for the dimerization of CP vs.  $[Q]/[CP]$ , where  $\phi_0/\phi' = \phi_0/\phi (1 + 0.76 [Q]/[CP])^{-1}$ , from irradiations of degassed  $\text{CH}_3\text{CN}$  solutions of CP (0.02 M), sensitized with MK (0.9 mM).

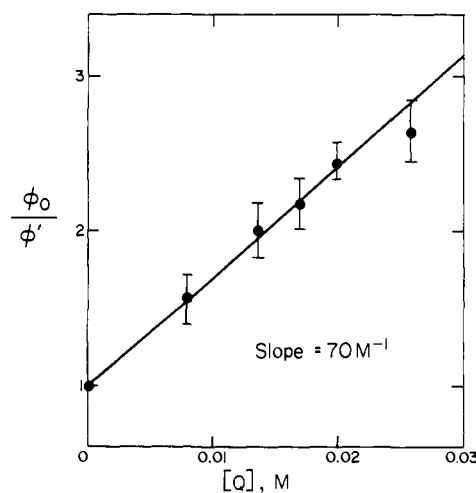
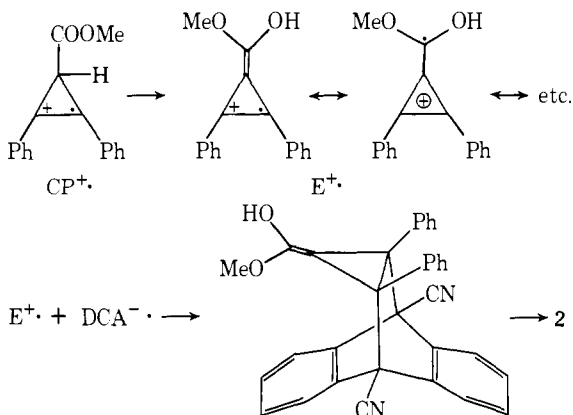


**Figure 3.** Plot of  $(\phi_0/\phi - 1) [CP]/[Q]$  for the dimerization of CP vs.  $[Q]/[CP]$  from irradiations of degassed  $\text{CH}_3\text{CN}$  solutions of CP (0.02 M), sensitized with MK (0.9 mM).

and *p*-cyanocinnamate esters (mentioned below). The reaction constant for the exothermic energy transfer,  $k_5$ , is expected, therefore, to be between 10 and 20 times larger than  $k_4$ . However, since the concentration of CP (0.1 M) is much higher than that of DCA (0.55 mM), then  $k_5[\text{DCA}]$  is only  $8 \pm 3\%$  of  $k_4[\text{CP}]$ . From this value and the slope of  $70 \text{ L mol}^{-1}$  for the plot of  $\phi_0/\phi$  vs.  $[Q]$  (Figure 4), a value for  $k_5/k_4$  of  $7.6 \pm 0.2$  is obtained. This ratio is somewhat smaller than the corresponding ratio of 10.1 obtained from the MK-sensitized reaction. The difference between the two values could be accounted for, if ca. 10% of the dimer in the DCA-sensitized reaction were formed via a nontriplet route, e.g., directly from the radical cation. As a result of such an unquenchable fraction of the dimer, the Stern–Volmer plot, which at low concentrations of Q could still be approximated to a linear one, would have a smaller slope; hence, the apparent lower value of  $k_5/k_4$ .

These experiments and several others mentioned below show, however, that the dimer is mainly formed via the proposed electron-transfer/triplet mechanism.

**Mechanism of Endo Adduct (2) Formation.** In nonpolar solvents the exciplex  $^1(\text{DCA}/\text{CP})^*$  leads to the exo adduct **1**, which is an expected product from an intermediate having the cyclopropyl hydrogen and not the carbomethoxy group of CP facing the DCA moiety. An attractive rationalization for the formation of the sterically unfavorable endo adduct (**2**) on irradiation in polar solvents is that the radical cation  $\text{CP}^{\cdot+}$ , from reaction 1, would enolize. The driving force for such a process would be the higher stability of the resulting cyclic two-electron radical cation ( $\text{E}^{\cdot+}$ ). Reaction of such a radical

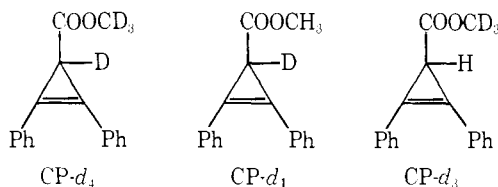


**Figure 4.** Plot of  $\phi_0/\phi'$  for the dimerization of CP vs.  $[Q]$ , where  $\phi_0/\phi' = \phi_0/\phi (1 + 0.35 [Q]/[CP])^{-1}$ , from irradiations of degassed  $\text{CH}_3\text{CN}$  solutions of CP (0.1 M) sensitized with DCA (0.55 mM).

cation with  $\text{DCA}^{\cdot-}$  would lead to an adduct in the enol form, which upon ketonization would be protonated from the least hindered side thus forcing the carbomethoxy group to the endo position.

There are several observations in support of this enolization hypothesis. Addition of nonnucleophilic protic solvents, such as *tert*-butyl alcohol (10%), leads to an increase in quantum yield of adduct **2** formation,<sup>22</sup> which agrees with a solvent-assisted keto–enol tautomerization. In 10% *t*-BuOD/ $\text{CH}_3\text{CN}$ , 80% monodeuterated adduct **2** is formed. Furthermore, the quantum yield of adduct **2** formation decreases with decreasing temperature,<sup>23</sup> an observed deuterium isotope effect indicates that this is due to an activation barrier in the enolization step. To measure this isotope effect, double labeling of the cyclopropene is necessary, since subsequently, the enolic intermediates will undergo D/H exchange with *t*-BuOH.

Equimolar amounts of CP and CP- $d_4$  as well as of CP- $d_1$  and CP- $d_3$  were irradiated in the presence of DCA at  $-10^\circ\text{C}$  in 10% *t*-BuOH/ $\text{CH}_3\text{CN}$ . In both cases the ratio of the adduct derived from the ring-unlabeled to that from the ring-deuterated cyclopropene is 2.3:1. The possibility that this deuterium isotope effect could be in the reaction of  $^1\text{DCA}^*$  with the cy-



cyclopropene is excluded since the rate of fluorescence quenching of DCA is the same for the labeled and unlabeled cyclopropene isotopic isomers.

**Multiple Electron Transfer and Cosensitization.** An interesting observation is made when the radical anion  $\text{DCA}^{\cdot-}$  is intercepted with 1,2,4,5-tetracyanobenzene (TCNB). Reversible reduction potentials<sup>16</sup> in acetonitrile vs. SCE of  $-0.88$  and  $-0.64$  V are measured for DCA and TCNB, respectively. Electron transfer from  $\text{DCA}^{\cdot-}$  to TCNB is, therefore, exothermic. Addition of TCNB to the reaction mixture quenches, as expected, the formation of adduct **2** but leads to about a 15-fold increase in the quantum yield of dimerization of CP ( $\phi = 0.025$ ). These results can be explained in terms of a secondary electron-transfer reaction leading to  $\text{TCNB}^{\cdot-}$  (reaction 10), which then reacts with  $\text{CP}^+$  to give a higher yield of  $^3\text{CP}^*$  (reaction 11) than that from reaction 3.



However, if reaction 3 is exothermic by  $\sim 6$  kcal/mol, as estimated above, reaction 11 would be almost isoenergetic. This apparent paradox, however, can be explained on the basis of one or both of the following points: (a) The reaction of  $\text{CP}^+$  with  $\text{DCA}^{\cdot-}$  can lead to much less  $^3\text{CP}^*$ , owing to competing formation of  $^3\text{DCA}^*$  (reaction 2) as compared with the corresponding reaction of  $\text{CP}^+$  with the radical anion  $\text{TCNB}^{\cdot-}$ . The formation of  $^3\text{TCNB}^*$  in the latter reaction is energetically unlikely. (b) In the absence of TCNB,  $^3\text{CP}^*$  is formed in the vicinity or active sphere of DCA, which can lead directly to non-diffusion-controlled "static quenching",<sup>24</sup> whereas in the presence of TCNB, only the diffusion-controlled dynamic quenching of DCA is competing with the dimerization.

Quenching experiments indicate that this effect of TCNB is in fact mainly due to an increase of triplet formation.<sup>25</sup> In the presence of TCNB, the quencher Q suppresses the dimerization by a magnitude similar to that obtained in the absence of TCNB. A detailed kinetic study of the sensitization with DCA in the presence of TCNB is given below using a *p*-cyanocinnamate ester as a reactant for  $^3\text{CP}^*$ .

A similar effect to that of TCNB, namely, increase of  $\phi_{\text{dimer}}$  and quenching of adduct **2** formation, is achieved by using 1,4-naphthoquinone, which has a reduction potential<sup>26</sup> similar to that of TCNB.

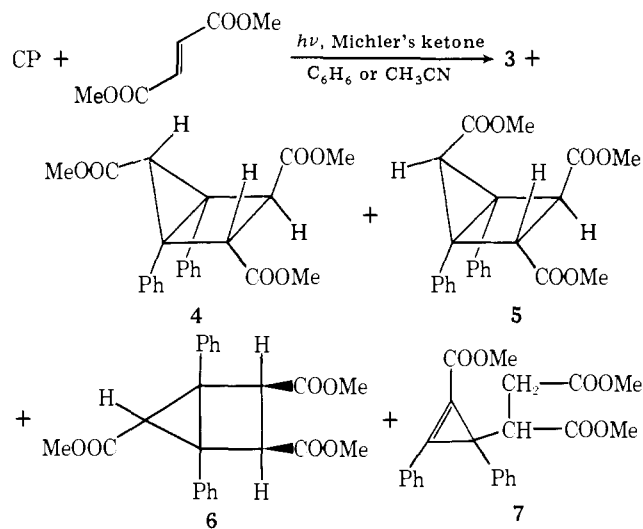
It should be emphasized that the cosensitization effect of TCNB and 1,4-naphthoquinone in this reaction is mechanistically different from that reported earlier<sup>7b</sup> for endothermic electron transfer. In both cases, however, increased quantum yields, induced by the presence of non-light-absorbing compounds (cosensitizers), are achieved by multiple electron-transfer processes.

**Reactions with Electron-Poor Olefins.** To further confirm the role of  $^3\text{CP}^*$  in the dimerization reported above, we sought to obtain a "chemical evidence" by trapping this intermediate in the form of products, which could be compared with those from a triplet-sensitized reaction.

No mixed adducts of the cyclopropene (CP) are reported; Arnold,<sup>27</sup> however, found that triplet-sensitized 1,2,3-triphenylcyclopropene reacts with dimethyl fumarate (F) to give adducts of cyclobutane structure. We investigated, therefore, the triplet-sensitized reactions of CP with dimethyl fumarate (F) and with other electron-poor olefins, such as *p*-cyanocin-

namate esters (CNC). As shown below, these reactions yield several cyclobutane adducts. In agreement with the triplet mechanism in the DCA-sensitized reaction, addition of these electron-poor olefins decreases the quantum yield of dimerization and leads to the formation of the cyclobutane adducts. Unexpectedly, however, these reactions yield also other addition products, not formed in the conventionally triplet-sensitized reaction.

**A. Dimethyl Fumarate.** Irradiation of a benzene or acetonitrile solution of CP and dimethyl fumarate (F) sensitized with Michler's ketone (MK) leads to the dimer (**3**) and several CP/F addition products. These include three isomeric cyclobutane derivatives (**4**, **5**, and **6**), with adduct **4** being the major isomer. In addition, the substitution addition product **7** and one



or two other minor, not yet identified, products are also formed. Although there is no evidence that some of these compounds may be secondary products, this cannot be ruled out conclusively.

In accordance with the *trans* configuration of the carbomethoxy groups of the fumarate moiety in compounds **4** and **5**, the cyclobutane protons and the carbomethoxy groups are not equivalent. A weak coupling (ca. 1 Hz) between the cyclopropane proton and one of the cyclobutane protons in compound **5** confirms the given structure.<sup>28</sup> Such coupling is absent in compound **4**. In compound **6**, the cyclobutane protons and two of the COOMe groups appear as singlets in accordance with a *cis* configuration. Only one of the four possible *cis* configurations can be eliminated for compound **6**, namely, the one in which the cyclopropane and cyclobutane protons are in *exo* positions, since no long-range coupling between these protons is detectable. The structure of compound **7** is supported by the unusual IR  $\text{C}=\text{C}$  frequency at  $1812 \text{ cm}^{-1}$ , which agrees with literature data<sup>29</sup> for phenylcarboxyl-substituted cyclopropenes. The absorption spectrum resembles that of methyl cinnamate, and the NMR spectrum indicates that the phenyl groups are not equivalent and supports the presence of a  $\text{CHCH}_2$  group with nonequivalent  $\text{CH}_2$  protons. Since this molecule contains two asymmetric carbon atoms, two diastereomers are possible. Only one isomer, however, has been isolated and identified. Details of the NMR and mass spectral data of compounds **4**–**7** are given in the Experimental Section.

Addition of F to an acetonitrile solution of CP sensitized with DCA leads, as expected, to a decrease in the quantum yield of dimerization, although F does not quench the fluorescence of DCA. Furthermore, compound **4**, which is the major product of the triplet-sensitized reaction of CP and F, is also formed in the DCA-sensitized reaction. In fact the ratio of compound **4** to dimer **3** at equimolar concentrations of CP

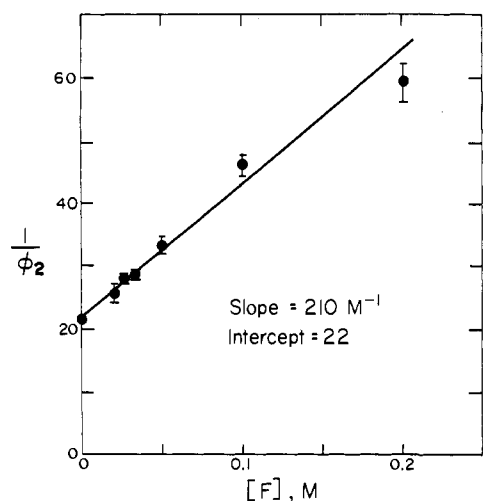
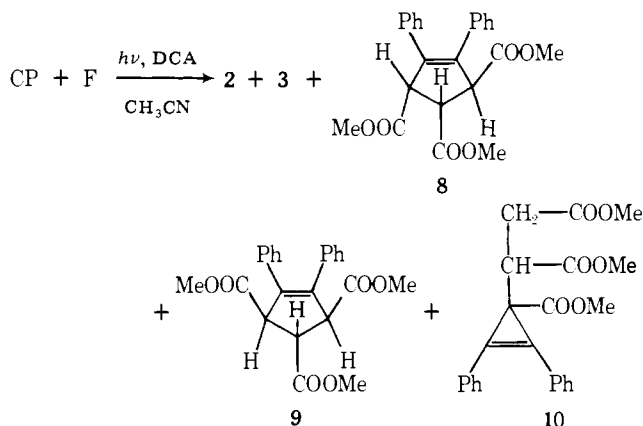


Figure 5. Plot of  $1/\phi_2$  of adduct **2** vs.  $[F]$  from irradiations of degassed 10% *t*-BuOH/CH<sub>3</sub>CN solutions of CP (0.05 M) at varying concentrations of F.

and F is about 1:3, which is the ratio of these products from the corresponding MK-sensitized reaction. These data are in accordance with the proposed triplet mechanism (eq 1-4).

Surprisingly, however, the major products of the DCA-sensitized reaction are three other CP/F addition products (**8-10**); none of them is formed in the triplet-sensitized reac-



tion. For structural elucidation see the Experimental Section.

There are strong indications that compounds **8-10** share a common intermediate with adduct **2**. For example, the formation of compounds **8-10**, which increases with  $[F]$ , is accompanied by quenching of adduct **2**. In quantitative terms, a plot of  $1/\phi_2$  vs.  $[F]$  gives a straight line with a slope of 210 L mol<sup>-1</sup> and an intercept of 22 (Figure 5) and a plot of  $1/\phi_{8-10}$  vs.  $1/[F]$  gives a straight line with a slope of 2.7 mol L<sup>-1</sup> and an intercept of 24 (Figure 6). These intercepts give the reciprocal of the quantum yield of adduct **2** in absence of F and that of compounds **8-10** extrapolated to infinite  $[F]$ , respectively. The measured values for these intercepts are very similar, indicating that with increasing  $[F]$ , adduct **2** is simply replaced by **8-10**. In fact, the sum of  $\phi_2 + \phi_{8-10}$  gives a constant value of ca. 0.045 regardless of  $[F]$ . Furthermore, compounds **8-10** are similarly affected by the same reaction conditions which influenced adduct **2** formation. As with **2**, the quantum yield of compounds **8-10** increases in the presence of protic solvents such as *t*-BuOH, and deuterium is incorporated in these compounds on irradiation in the presence of *t*-BuOD; a deuterium isotope effect of ca. 2.3 at -10 °C is observed on using mixtures of the labeled cyclopropenes mentioned above. Similarly, the overall yield of **8-10** increases with increasing

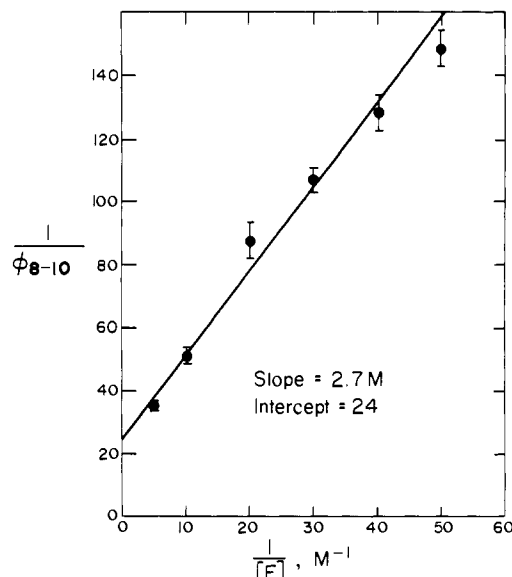


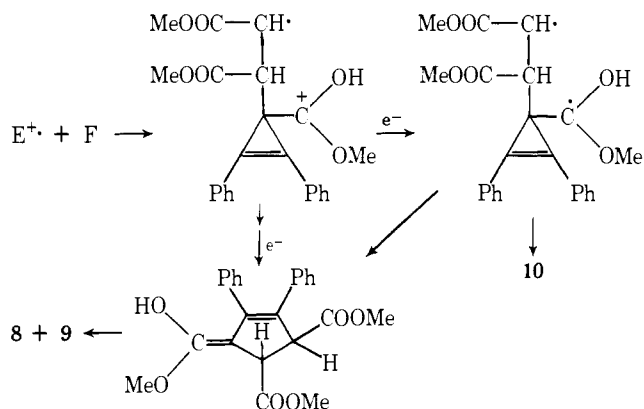
Figure 6. Plot of  $1/\phi$  of compounds **8-10** vs.  $1/[F]$  from irradiations as described under Figure 5.

temperature,<sup>30</sup> but the ratio (**8 + 9**):**10** also increases with temperature with the net effect that the quantum yield of **10** is virtually temperature independent.

These data indicate that the formation of compounds **8-10** is also preceded by enolization of CP<sup>+</sup> to E<sup>+</sup>, as discussed above for adduct **2** formation. Compounds **8-10** cannot be formed, however, via reaction of E<sup>+</sup> with F<sup>-</sup> because the fumarate radical anion is unlikely to be formed in this reaction owing to the strong endothermicity of electron transfer from DCA<sup>-</sup> to F.<sup>31</sup> This view is further strengthened from the fact that addition of TCNB leads to an increase<sup>32</sup> in the quantum yield of compounds **8-10**. As mentioned above, electron transfer from DCA<sup>-</sup> to TCNB is exothermic and TCNB is accordingly an efficient quencher for adduct **2** formation. Electron transfer from TCNB<sup>-</sup> to F would have been even more endothermic than that from DCA<sup>-</sup> to F.

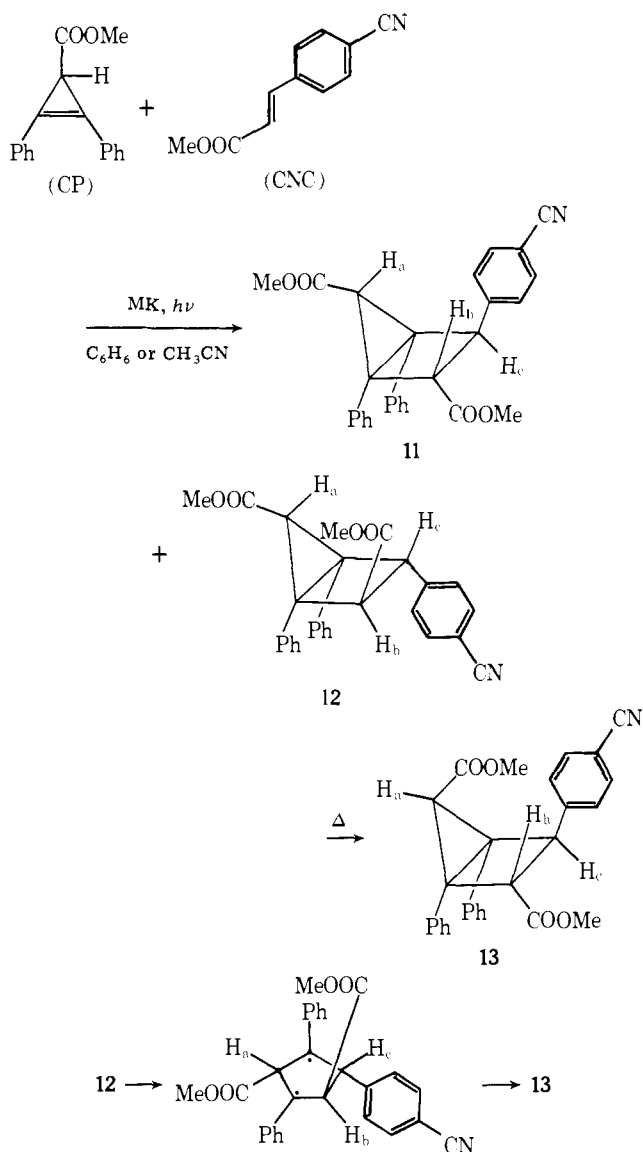
A triplet mechanism in which <sup>3</sup>E\* would be produced via reaction of E<sup>+</sup> with DCA<sup>-</sup> (or TCNB<sup>-</sup>) followed by addition to F is also unlikely because no quenching of compounds **8-10** is observed when compound Q is added to the reaction mixture.

A possible mechanism for the formation of compounds **8-10**



is addition of E<sup>+</sup> to F followed by electron transfer from DCA<sup>-</sup> (or TCNB<sup>-</sup>) to the intermediate radical cation. Alternatively these compounds could be formed from the reaction of E<sup>+</sup> with a charge-transfer complex between F and DCA<sup>-</sup> (or TCNB<sup>-</sup>). The electron density on the fumarate in such a complex will be higher, which might increase its reactivity toward the radical cation E<sup>+</sup>.

**B. *p*-Cyanocinnamate Esters.** From the Michler's ketone sensitized irradiation of CP and methyl *p*-cyanocinnamate (CNC) in benzene or acetonitrile three cyclobutane addition products (**11-13**) are obtained. Compounds **11** and **12** are

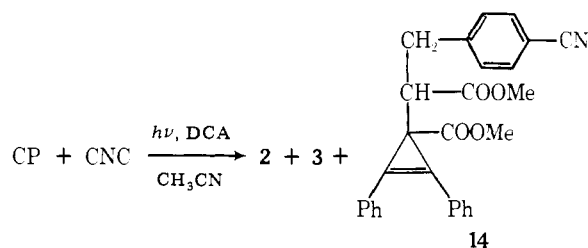


primary photoproducts and can be detected in the NMR spectrum of the reaction mixture prior to workup. The addition product **13**, however, is a secondary product; at 60–70 °C compound **12** rearranges, almost quantitatively, to **13**, whereas compound **11** remains unchanged. Arnold<sup>27</sup> observed a similar rearrangement with triphenylcyclopropene/fumarate addition products.

The stereochemistry of these products is elucidated from the NMR spectra. The signals of  $H_c$  are differentiated from those of  $H_b$  by a broadening of the  $H_c$  protons due to long-range coupling with protons on the cyanophenyl group, as confirmed by a decoupling experiment. A long-range coupling (0.9 Hz) between  $H_a$  and  $H_c$  in compound **13** shows that these two hydrogen atoms are in exo positions of the bicyclopentane structure.<sup>28</sup> The lack of such coupling between  $H_a$  and  $H_b$  in this compound indicates that  $H_b$  is in an endo position; hence, the trans configuration of the cyanophenyl and carbomethoxy groups. Consequently, the structure of compound **12**, the precursor of **13**, can be determined on the basis of the rearrangement mechanism,<sup>27</sup> which involves the cleavage of the inter-ring bond of the bicyclopentane. The structure of **11** is only tentatively reached from the lack of long-range couplings with  $H_a$  and the fact that the  $H_b$ – $H_c$  coupling is very similar

to those in **12** and **13**. A cis configuration for compound **11**, although it cannot be ruled out entirely, is unlikely for a major product.

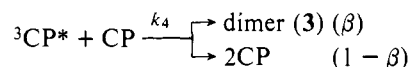
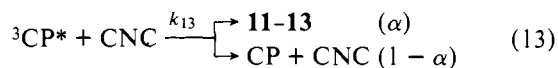
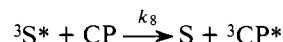
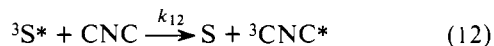
Irradiation of an acetonitrile *tert*-butyl alcohol solution of CP and CNC sensitized with DCA yields compound **14** as the



major CP/CNC addition product. This compound is analogous to compound **10** from the DCA-sensitized reaction of CP with F and is probably formed in a similar mechanism. Compounds with cyclopentene structures analogous to **8** and **9**, however, if formed, must be in very low yields. Electron transfer from  $\text{DCA}^-$  to CNC is highly unlikely because of the high reduction potential of CNC (–1.46 V).<sup>16</sup>

We have shown that in the DCA-sensitized reactions of CP in  $\text{CH}_3\text{CN}$  the yield of  $^3\text{CP}^*$  can be considerably increased in the presence of low concentrations of TCNB. Consequently, the “triplet products” of the CP/CNC reaction, namely, the cyclobutane adducts **11**, **12**, and the thermolysis product of the latter (**13**), become major products when the irradiation is carried out in the presence of TCNB.

The kinetic analysis of this reaction gives a good quantitative assessment of the cosensitization role of TCNB. As shown below this study gives unambiguous evidence for the proposed triplet mechanism via multiple electron transfer (reactions 1 and 10) followed by radical ion recombination to give  $^3\text{CP}^*$  (reaction 11). Ethyl cyanocinnamate is used instead of the methyl ester in the kinetic studies for it gives a better separation of the peaks in the gas chromatographic analysis. As expected, both esters behave otherwise very similarly.



In the MK-sensitized reaction the dependence of the quantum yield of dimerization on [CNC] is given by

$$\frac{\phi_0}{\phi} = \left(1 + \frac{k_{12}[\text{CNC}]}{k_8[\text{CP}]}\right) \left(1 + \frac{k_{13}[\text{CNC}]}{k_4[\text{CP}]}\right) \quad (\text{VI})$$

The ratio of  $k_{12}/k_8$  as determined by flash photolysis in 2% *tert*-butyl alcohol/acetonitrile, the solvent mixture used for this study, is 1.25.

Following the procedure mentioned above for quenching with Q, each  $\phi_0/\phi$  for dimerization is divided by the corresponding value of  $(1 + 1.25[\text{CNC}]/[\text{CP}])$ , and the product  $\phi_0/\phi'$  is plotted against  $[\text{CNC}]/[\text{CP}]$  (Figure 7). A slope of 7.1, which is equal to  $k_{13}/k_4$ , is obtained from this plot. Based on this ratio of  $k_{13}/k_4$  and that of  $k_{12}/k_8$  determined by flash photolysis, a plot of  $(\phi_0/\phi - 1)[\text{CP}]/[\text{CNC}]$  vs.  $[\text{CNC}]/[\text{CP}]$  should have an intercept of 8.35 and a slope of 8.88. The experimentally determined values of this function agree well with such a line (Figure 8).

In the DCA/TCNB-sensitized reaction, the dependence of the dimerization quantum yield on [CNC] is given by

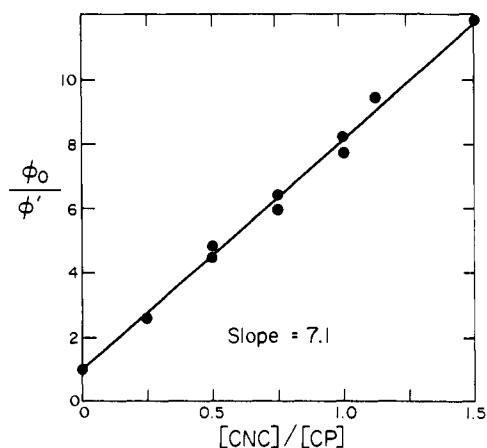


Figure 7. Plot of  $\phi_0/\phi'$  for the dimerization of CP vs.  $[\text{CNC}]/[\text{CP}]$ , where  $\phi_0/\phi' = \phi_0/\phi (1 + 1.25[\text{CNC}]/[\text{CP}])^{-1}$ , from irradiations of degassed 2% *t*-BuOH/CH<sub>3</sub>CN solutions of CP (0.04 M) at varying concentrations of ethyl cyanocinnamate sensitized with MK (0.9 mM).

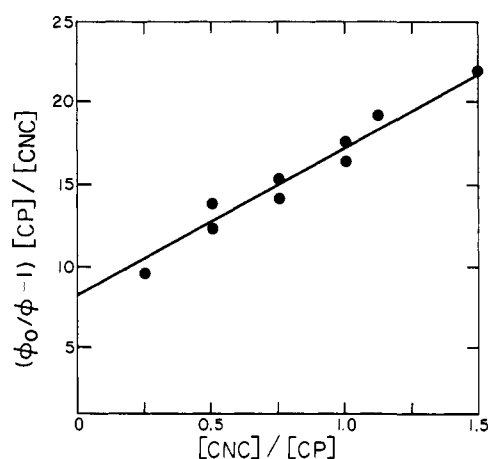


Figure 8. Plot of  $(\phi_0/\phi - 1)[\text{CP}]/[\text{CNC}]$  for the dimerization of CP vs.  $[\text{CNC}]/[\text{CP}]$  from irradiations as described under Figure 7.

$$\frac{\phi_0}{\phi} = 1 + \frac{k_{13}}{k_4[\text{CP}] + k_5[\text{DCA}]} [\text{CNC}] \quad (\text{VII})$$

A plot of  $\phi_0/\phi$  vs.  $[\text{CNC}]$  gives, at low concentrations of  $[\text{CNC}]$ , a slope of  $142 \text{ L mol}^{-1}$  (Figure 9). From this slope, the concentrations of CP (0.04 M) and DCA ( $5.5 \times 10^{-4} \text{ M}$ ) and the estimate of  $k_5/k_4$  of 16, mentioned above, a ratio of  $k_{13}/k_4$  of 6.9 is obtained, which is in excellent agreement with the value of 7.1 derived from the kinetics of the MK-sensitized reaction.

At high  $[\text{CNC}]$  concentrations, however, some deviation from linearity in the plot of  $\phi_0/\phi$  vs.  $[\text{CNC}]$  (Figure 9) is observed. This deviation can be rationalized in terms of a minor, nontriplet path leading to dimerization. The data obtained from two different sets of experiments (Figure 9) seem to fit well curves calculated on the basis of a 0.5% and a 1.3% contribution from such an unquenchable path to the dimer. These curved plots are derived from eq VIII, where  $n$  is taken as 0.7 and 1.85, respectively.

$$\frac{\phi_0}{\phi} = \frac{1 + 142[\text{CNC}]}{1 + n[\text{CNC}]} \quad (\text{VIII})$$

It is interesting to note that these data are consistent with the observation mentioned earlier that, in the absence of TCNB, ca. 10% of the dimer might be formed via a nontriplet path. Since the yield of  $^3\text{CP}^*$  increases by about an order of magnitude on adding TCNB to the reaction mixture, one

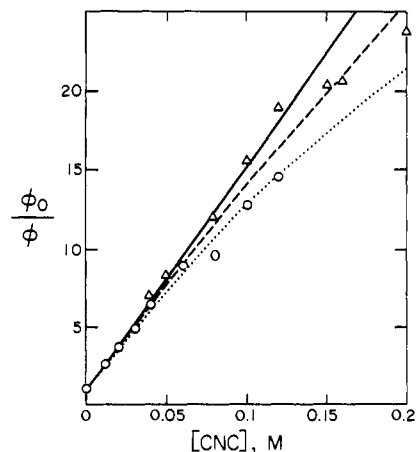


Figure 9. Plot of  $\phi_0/\phi$  for the dimerization of CP vs.  $[\text{CNC}]$  from irradiations of degassed 2% *t*-BuOH/CH<sub>3</sub>CN solutions of CP (0.04 M) at varying concentrations of ethyl cyanocinnamate sensitized with DCA (0.55 mM) in the presence of TCNB (5 mM). The circles and triangles represent data from two sets of experiments. Tangent at low  $[\text{CNC}]$ , slope  $142 \text{ M}^{-1}$ , —, calculated curves for 0.5 and 1.3% dimerization via a path unquenchable with CNC, - - - - and - · - ·, respectively.

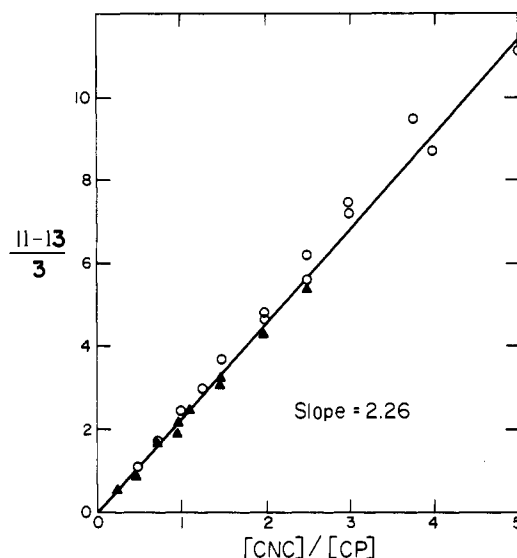


Figure 10. Plot of the product ratio  $(11-13)/3$  vs.  $[\text{CNC}]/[\text{CP}]$  from irradiations of degassed 2% *t*-BuOH/CH<sub>3</sub>CN solutions of CP (0.04 M) at varying concentrations of ethyl cyanocinnamate sensitized with DCA (0.55 mM) in the presence of TCNB (5 mM) (circles) or with MK (0.9 mM) (triangles).

would expect the contribution from a nontriplet path to drop to ca. 1% in the presence of TCNB.

The product ratios from the reactions with CNC are also in full agreement with the triplet mechanism when DCA/TCNB is used as a sensitizing system. According to the proposed mechanism the ratio  $(11-13)/3$ , using either DCA/TCNB or MK<sup>33</sup> as sensitizers, is given by

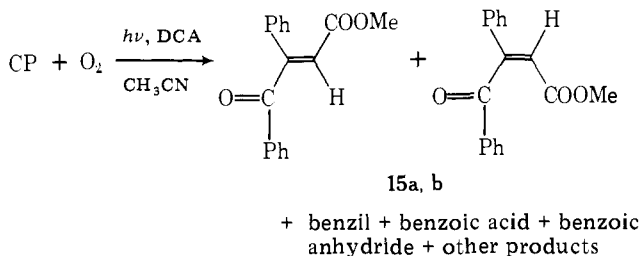
$$\frac{11-13}{3} = \frac{k_{13}\alpha}{k_4\beta} \frac{[\text{CNC}]}{[\text{CP}]} \quad (\text{IX})$$

In both cases, therefore, similar slopes for the plot of  $11-13/3$  vs.  $[\text{CNC}]/[\text{CP}]$  should be obtained; this does occur (Figure 10). The slope of this plot, which gives the ratio  $k_{13}\alpha/k_4\beta$ , is 2.34; thus  $\alpha/\beta = 2.34/7.1 = 0.33$ .

**Reactions with Oxygen.** When air or oxygen is bubbled through an acetonitrile solution of DCA and CP during the irradiation, the amount of adduct **2** formed is considerably



diminished and several oxidation products are formed. The major component of these products is the isomeric mixture **15a,b**. Benzil, benzoic acid, and benzoic anhydride are also



formed besides several unidentified products. The structure of **15a,b** is confirmed by spectroscopic data, by their interconversion, and by an independent synthesis (see Experimental Section). Compounds **15a,b** are also formed in high yields by epoxidation of CP with *m*-chloroperbenzoic acid, a process which probably involves the oxabicyclobutane<sup>34</sup> as an intermediate. These compounds are also formed by photooxygenation using rose bengal as a sensitizer.

In the DCA-sensitized reaction the quantum yield of oxidation increases with increasing [CP]. At a concentration of CP of ca. 0.5 M, quantum yields for the conversion of CP of ca. 20 are measured. This reaction seems, once initiated photochemically, to continue for several minutes after the irradiation is stopped. It is likely that this oxidation is initiated by the reaction of CP<sup>•+</sup> with O<sub>2</sub>, similar to the mechanism we proposed earlier<sup>11</sup> for the photooxidation of diphenylacetylene via electron transfer. In the present reaction, 1,4-dimethoxynaphthalene (DMN), which has a lower oxidation potential than CP, is an efficient quencher for the oxidation. This agrees with the proposed reaction of CP<sup>•+</sup> with O<sub>2</sub>. Other intermediates such as O<sub>2</sub><sup>•-</sup>, which can be formed via electron transfer from DCA<sup>-</sup> to O<sub>2</sub>, singlet oxygen, and free radicals could also be involved in this complex reaction. It is conceivable that superoxide ion is produced via electron transfer from DCA<sup>-</sup> to O<sub>2</sub>.

## Experimental Section

**General.** Acetonitrile (spectroquality, Matheson Coleman and Bell) and benzonitrile (spectrograde, Eastman) were washed through columns packed successively with basic (top), neutral, and acidic activated alumina. Benzene (spectrograde, Eastman) was used without further purification. DCA (Eastman) was recrystallized twice from pyridine, and TCNB (Eastman) was recrystallized from pyridine and then from benzene/acetonitrile. Dimethyl fumarate (F) was recrystallized from benzene. 3,3,4,4-Tetramethyl-1,2-diazetidine 1,2-dioxide<sup>20</sup> and CP<sup>34</sup> were prepared according to literature data. CP-*d*<sub>3</sub> was prepared by refluxing the corresponding acid chloride in CD<sub>3</sub>OD and recrystallizing the product from methanol, mp 83.5–84 °C, isomeric ratios CD<sub>3</sub> (90%), CHD<sub>2</sub> (6%), CH<sub>3</sub> (4%). CP-*d*<sub>1</sub> was prepared according to the procedure described by DeBoer<sup>35</sup> from the reaction of phenylchlorodiazirine with methyl phenylpropiolate and reduction of the resulting chlorocyclopropene with NaBD<sub>4</sub>, mp 83–84 °C, 91% deuterated. CP-*d*<sub>4</sub> was prepared in the same way as CP-*d*<sub>1</sub> starting with trideuteriomethyl phenylpropiolate, mp 83–84 °C, isomeric ratios *d*<sub>4</sub> (87%), *d*<sub>3</sub> (mainly the CHD<sub>2</sub> ester, 11%), *d*<sub>2</sub> (1%), *d*<sub>0</sub> (1%). The cyanocinnamate esters were prepared by the condensation of *p*-cyanobenzaldehyde with malonic acid in pyridine/piperidine followed by esterification with the appropriate alcohol/H<sub>2</sub>SO<sub>4</sub>: methyl ester, mp 120–122 °C; ethyl ester, mp 67–69 °C (lit.<sup>36</sup> 67.5–68.5 °C).

Irradiations on preparative scale were done under continuous bubbling of nitrogen or argon, saturated with the solvent, in an immersion apparatus equipped with one of the following glass filters. For the DCA reactions a GWV<sup>37</sup> filter was used to eliminate the 366-nm line and shorter wavelengths. For the MK-sensitized reactions a GWCa filter<sup>37</sup> was used to eliminate the 334-nm line and shorter wavelengths. The samples for kinetic studies were degassed by three freeze-pump-thaw cycles and irradiated on a Merry-Go-Round mounted on an optical bench. The output of a PEK 200-W sup-

erhigh-pressure mercury lamp was filtered through water-cooled Kodak Wratten ultraviolet 18A and Corning O-52 filters to isolate the 366-nm line (for MK-sensitized reactions) or filtered through Corning CS 5-58 and Corning CS 3-75 filters to isolate the 405- and 436-nm lines (for DCA-sensitized reactions). The irradiations of the DCA-containing samples were interrupted several times for magnetic stirring to ensure a constant concentration of DCA. The photoreaction of 9,10-phenanthrenequinone (10<sup>-3</sup> M) with *trans*-stilbene (0.1 M) in benzene was used as an actinometer for irradiations at 405 and 436 nm. The quantum yield<sup>38</sup> for the disappearance of the quinone, which is monitored by absorption spectroscopy (λ<sub>max</sub> 410 nm, ε 1800), is 0.065. The GC analyses were done on a Hewlett-Packard 7620A chromatograph equipped with an HP 3380 A integrator, using a 1.5% Dexsil on Chromosorb W 80/100 (1/8 in. × 6 ft) column.

**Irradiation of DCA and CP in Benzene.** A suspension of DCA (300 mg) in 50 mL of 0.04 M solution of CP in benzene was irradiated (HPK, GWV filter) under nitrogen for 18 h. The solution was filtered from unreacted DCA (80 mg). The solvent was distilled and 10 mL of acetonitrile was added to the residue, where another 20 mg (mainly DCA and a small amount of dimer **3**) remained insoluble. The solvent was distilled, and the residue was extracted with pentane and then recrystallized from cyclohexane containing a small amount of acetone to give 220 mg of adduct **1**: decomposes to its components without definite melting at ca. 240 °C. Injection of an acetonitrile solution of **1** into the GC (injection port at 300 °C) gave peaks of equimolar amounts of DCA and CP corresponding to an almost quantitative cleavage. NMR (CDCl<sub>3</sub>) δ 2.03 (s, cyclopropyl H), 3.48 (s, -COOCH<sub>3</sub>), 6.82 (m, 4 H, ortho H of the two C<sub>6</sub>H<sub>5</sub> groups), 7.08–7.29 (m, 6 H, meta and para H of the two C<sub>6</sub>H<sub>5</sub> groups), two AA'BB' spectra, one centered at δ 7.43 and 7.58 and the other at 7.48 and 7.74 (two different, equivalently ortho-disubstituted benzene rings); mass spectrum *m/e* (rel intensity) 478 (0.4, M<sup>+</sup>), 451 (1.8, M - HCN), 447 (3.4, M - OCH<sub>3</sub>), 392 (4.8), 391 (3.6), 314 (4), 250 (100, CP), 235 (77, CP - CH<sub>3</sub>), 228 (35, DCA), 191 (45), 105 (81, COC<sub>6</sub>H<sub>5</sub>).

**Irradiation of DCA and CP in Acetonitrile.** A suspension of DCA (400 mg) in 50 mL of 0.04 M solution of CP in acetonitrile containing 10% *t*-BuOH was irradiated (HPK, GWV filter) under nitrogen for 17 h. The solution was filtered from 140 mg of unreacted DCA. The solution was distilled and the residue successively extracted with pentane (total 150 mL). Recrystallization of the insoluble fraction from cyclohexane/acetone yielded 250 mg of adduct **2** and from the mother liquor another 150 mg of a 3:1 mixture of **2** and **3**. Adduct **2**: NMR (CDCl<sub>3</sub>) δ 3.01 (s, cyclopropyl H), 3.33 (s, -COOCH<sub>3</sub>), 6.94–7.27 (m, 10 H, two C<sub>6</sub>H<sub>5</sub> groups), two AA'BB' spectra, one centered at δ 7.35 and 7.67 and the other at 7.45 and 7.75 (two different, equivalently ortho-disubstituted benzene rings); mass spectrum *m/e* (rel intensity) 478 (100, M<sup>+</sup>), 451 (11, M - HCN, m\*), 447 (20, M - OCH<sub>3</sub>), 446 (39, M - HOCH<sub>3</sub>, m\*), 419 (42, M - COOCH<sub>3</sub>), 418 (32, M - HCOOCH<sub>3</sub>, m\*), 392 (22), 341 (28), 314 (15), 250 (22, CP) 237 (49), 235 (27), 228 (15). An x-ray crystallographic analysis of adduct **2** was done by Molecular Structure Corp., College Station, Texas (see paragraph at end of paper regarding supplementary material).

**MK-Sensitized Reaction of CP and F.** A benzene solution (50 mL) of MK (0.2 mM), CP (0.05 M), and F (0.15 M) was irradiated (HPK, UVG filter) under nitrogen for 3 h. The solvent was distilled and the residue was taken into acetonitrile where the dimer of CP is sparingly soluble and was filtered off. The solvent was distilled and the remaining F was sublimed at ca. 50 °C in vacuo. The residue was chromatographed on Florisil (activated for 1 h at 120 °C) with benzene. Unreacted CP and the rest of the dimer were eluted first followed by compound **4**. Further elution of the column with ether/benzene (up to 1:9) yielded fractions enriched in compounds **5**, **7**, and **6**, respectively, which were purified by rechromatography on smaller columns. Compound **4**: NMR (CDCl<sub>3</sub>) δ 3.47, 3.48, and 3.75 (s, three -COOCH<sub>3</sub>), 2.94 (s, cyclopropyl H), 3.47 and 4.07 (AB spectrum, *J* = 4 Hz, two cyclobutyl H); mass spectrum *m/e* (rel intensity) 394 (1, M<sup>+</sup>), 362 (19, M - CH<sub>3</sub>OH), 335 (34, M - COOCH<sub>3</sub>), 334 (21), 330 (11), 303 (100, (M - COOCH<sub>3</sub>) - CH<sub>3</sub>OH), 302 (24), 275 (83), 217 (38), 215 (46); exact mass 394.1375 (calcd for C<sub>23</sub>H<sub>22</sub>O<sub>6</sub>, 394.1415). Compound **5**: NMR (CDCl<sub>3</sub>) δ 3.53, 3.71, 3.83 (s, three -COOCH<sub>3</sub>), 2.79 (cyclopropyl H<sub>X</sub>), 4.24 and 4.48 (cyclobutyl protons, H<sub>A</sub> and H<sub>B</sub>, respectively), *J*<sub>AB</sub> = 4.4 Hz, *J*<sub>BX</sub> ≈ 1 Hz. Compound **6**: NMR (CDCl<sub>3</sub>) δ 3.47 (s, 6 H, two -COOCH<sub>3</sub>), 3.29 (s, 3 H, -COOCH<sub>3</sub>), 2.68 (s, 1 H, cyclopropyl), 3.42 (s, 2 H, cyclobutyl); mass

spectrum (through GC)  $m/e$  (rel intensity) 394 (15,  $M^+$ ), 362 (44,  $M - CH_3OH$ ,  $m^*$ ), 335 (24), 334 (46), 303 (27,  $M - CH_3OH - COOCH_3$ ,  $m^*$ ), 275 (35), 243 (100, (303),  $-HCOOCH_3$ ,  $m^*$ ), 217 (64), 216 (56), 215 (87); exact mass 394.1418 (calcd for  $C_{23}H_{22}O_6$ , 394.1415). Compound **7**: NMR ( $CDCl_3$ )  $\delta$  3.33, 3.65, 3.95 (s, three  $-COOCH_3$ ), 2.57, 2.90, and 4.09 (ABX spectrum,  $-CH_AH_B^*CH_X<$ , respectively,  $J_{AB} = 17.2$ ,  $J_{AX} = 3.8$ ,  $J_{BX} = 10.9$  Hz), ca. 7.3 (m, 8 H, aromatic H), ca. 7.8 (m, 2 H, ortho H of the  $C_6H_5$  group in conjugation with the  $COOCH_3$  group); mass spectrum (20 eV)  $m/e$  (rel intensity) 394 (0.6,  $M^+$ ), 363 (3,  $M - OCH_3$ ), 362 (5,  $M - CH_3OH$ ), 335 (13,  $M - COOCH_3$ ), 334 (9), 321 (100,  $M - CH_2COOCH_3$ ), 303 (25), 302 (67), 289 (11), 275 (25), 274 (11), 249 (16), 243 (24), 221 (13), 217 (14), 216 (13), 215 (25); absorption spectrum (cyclohexane)  $\lambda_{max}$  292 nm; IR (film) 1812 (cyclopropene  $C=C$ ), 1738, 1706, 1435, 1202, 1165  $cm^{-1}$ ; exact mass 394.1410 (calcd for  $C_{23}H_{22}O_6$ , 394.1415).

**DCA-Sensitized Reaction of CP and F.** A suspension of DCA (100 mg) in 40 mL of a solution of 600 mg of CP (0.06 M) and 690 mg of F (0.12 M) in acetonitrile was irradiated (HPK, GWV filter) under nitrogen for 20 h. The solution was filtered from unreacted DCA (ca. 60 mg), the solvent evaporated, and the remaining F sublimed at 50 °C. The mixture was chromatographed on activated (120 °C for 1 h) Florisil. Elution with benzene gave 150 mg of unreacted CP followed by the dimer (**3**), adduct **2**, and compound **4**, respectively. Elution with 10% ether in benzene yielded 230 mg of a mixture of the stereoisomers **8** and **9**. The ratio **8:9** decreases with the progressing elution. The ratio **8:9** of the total isolated product is 2.4:1. Further elution with the same solvent mixture yielded 90 mg of compound **10**. Compound **8**: NMR ( $CDCl_3$ )  $\delta$  3.54, 3.57, and 3.77 (s, three  $-COOCH_3$ ), 4.11, 4.47, and 4.85 (AMX spectrum, respectively,  $J_{AM} = 8.8$ ,  $J_{AX} = 9.2$ ,  $J_{MX} = 2.7$  Hz); IR (film) 1737 (broad) 1435  $cm^{-1}$ ; mass spectrum  $m/e$  (rel intensity) 394 (10,  $M^+$ ), 362 (49,  $M - CH_3OH$ ,  $m^*$ ), 334 (100, ( $M - CH_3OH - CO$ ,  $m^*$ ), 303 (31), 302 (22), 276 (16), 275 (37), 217 (30), 216 (30), 215 (80); exact mass 394.1349 (calcd for  $C_{23}H_{22}O_6$ , 394.1415). Compound **9**: NMR ( $CDCl_3$ )  $\delta$  3.67 (s, 6 H, two  $-COOCH_3$  at C-3 and C-5), 3.81 (s, 3 H,  $-COOCH_3$  at C-4), 4.35 and 4.11 ( $A_2B$  spectrum, respectively,  $J_{AB} = 6.5$  Hz). Compound **10**: NMR ( $CDCl_3$ )  $\delta$  2.35 (s, 3 H,  $-COOCH_3$ ), 3.60 (s, 6 H, two  $-COOCH_3$ ), 2.47, 2.63, and 4.07 (ABX spectrum,  $-CH_AH_B^*CH_X<$ , respectively,  $J_{AB} = 16.2$ ,  $J_{AX} = 5.9$ ,  $J_{BX} = 8.4$  Hz); absorption spectrum ( $CH_3CH$ )  $\lambda_{max}$  324 and 308 nm (for comparison, CP in  $CH_3CN$  has  $\lambda_{max}$  at 323 and 307 nm); mass spectrum  $m/e$  (rel intensity) 394 (52,  $M^+$ ), 362 (17,  $M - CH_3OH$ ,  $m^*$ ), 347 (7), 335 (38), 321 (37,  $M - CH_2COOCH_3$ ), 319 (35), 315 (18), 303 (18), 302 (24), 287 (13), 275 (100), 261 (15), 259 (14), 249 (34,  $M - CH(COOCH_3)CH_2COOCH_3$ ), 105 (51,  $COPh$ ); exact mass 394.1451 (calcd for  $C_{23}H_{22}O_6$ , 394.1415).

Irradiation as above in the presence of 10% *t*-BuOD led to mono-deuterated compounds **8-10**. The NMR spectrum of **8-d1** indicates that the H atom at  $\delta$  4.47 is the one replaced by D; the signals at  $\delta$  4.11 and 4.85 appear as an AB multiplet ( $J \sim 9$  Hz). In compound **10-d1** both geminal  $H_A$  and  $H_B$  are partially replaced by deuterium.

**Triplet-Sensitized Reaction of CP and CNC.** A. A toluene solution (50 mL) of fluorenone (0.01 M), CP (0.1 M), and methyl *p*-cyanocinnamate (0.1 M) was irradiated (HPK, GWV filter) under nitrogen for 2 h. The solvent was removed in vacuo and the residue was triturated with acetonitrile (10 mL). A colorless solid (330 mg) was removed by filtration and identified by GC and NMR as the dimer of CP. The mixture of products in the filtrate was separated by ascending column chromatography on 1:1 silica gel/cellulose powder using toluene as eluent. The lower half of the column was divided into three equal fractions, which were washed with ether. The major component of the first fraction (most polar) was identified by NMR as compound **12**. The third fraction contained methyl cyanocinnamate and compound **11**. Recrystallization of this fraction from ethyl acetate/hexane enriched the filtrate in compound **11**. These compounds were further purified by thick layer chromatography (silica gel, 2-mm thickness) using multiple development in toluene for compound **11** and 1:1 toluene/chloroform for compound **12**. Overnight reflux of a sample of **12** in  $CDCl_3$  led to its conversion to compound **13**, as indicated by the NMR spectrum. Compound **11**: NMR ( $CDCl_3$ )  $\delta$  3.35, 3.49 (s, two  $-COOCH_3$ ), 2.62 (s,  $H_A$ ), 3.41 (d,  $H_B$ ), 4.62 (broad d,  $H_C$ )  $J_{bc} = 3.9$  Hz; mass spectrum  $m/e$  (rel intensity) 437 (6,  $M^+$ ), 405 (39,  $M - CH_3OH$ ), 378 (100,  $M - COOCH_3$ ), 377 (33), 346 (33), 319 (28), 318 (56), 240 (23); exact mass 437.1614 (calcd for  $C_{28}H_{23}NO_4$ , 437.1625). Compound **12**: NMR ( $CDCl_3$ )  $\delta$  3.37, 3.69 (s, two

$-COOCH_3$ ), 3.13 (s,  $H_A$ ), 3.54 (d,  $H_B$ ), 3.85 (broad d,  $H_C$ ),  $J_{bc} = 4.6$  Hz; mass spectrum  $m/e$  (rel intensity) 437 (3,  $M^+$ ), 405 (80,  $M - CH_3OH$ ), 378 (100,  $M - COOCH_3$ ), 377 (31), 346 (44), 345 (12), 319 (33), 318 (70), 240 (30); exact mass 437.1628 (calcd for  $C_{28}H_{23}NO_4$ , 437.1625). Compound **13**: NMR ( $CDCl_3$ )  $\delta$  3.25, 3.53 (s, two  $-COOCH_3$ ), 2.83 (d,  $H_A$ ), 4.40 (d,  $H_B$ ), 5.02 (broad q,  $H_C$ ),  $|J_{ac}| = 0.9$ ,  $J_{bc} = 4.0$  Hz; mass spectrum  $m/e$  (rel intensity) 437 (1.6,  $M^+$ ), 405 (82,  $M - CH_3OH$ ), 378 (100,  $M - COOCH_3$ ), 377 (30), 346 (52), 319 (38), 318 (85), 240 (36); exact mass 437.1610 (calcd for  $C_{28}H_{23}NO_4$ , 437.1625).

**B.** An acetonitrile/10% *tert*-butyl alcohol solution (50 mL) of MK (0.4 mM), CP (0.1 M), and methyl cyanocinnamate (0.1 M) was irradiated (HPK, UVG filter) for 6 h under nitrogen. A product mixture similar to that from the irradiation mentioned above, namely, compounds **11** and **12**, was obtained. The product was allowed to reflux overnight in  $CDCl_3$  whereupon the NMR signals of compound **12** disappeared and were replaced by those of compound **13**.

**DCA-Sensitized Reaction of CP and CNC.** A suspension of DCA (200 mg) in 50 mL of a solution of CP (0.06 M) and methyl *p*-cyanocinnamate (0.06 M) in 10% *t*-BuOH/ $CH_3CN$  was irradiated (HPK, GWV filter) for 24 h. Unreacted DCA was filtered off, the solvent distilled, and the residue recrystallized twice from ether to yield colorless crystals of **14**: mp 214–216 °C; NMR ( $CDCl_3$ )  $\delta$  3.53 and 3.61 (s, two  $-COOCH_3$ ), 2.76, 2.78, and 4.05 (ABX spectrum,  $-CH_AH_B^*CH_X<$ , respectively, splittings AX and BX = 6.8 and 8.2 Hz, respectively,  $J_{AB}$  could not be determined owing to very small  $\Delta_{AB}$ ), 7.17 (2H, AA' part of an AA'BB' spectrum of a para-substituted benzene ring, protons ortho to  $CH_2$  group; irradiation at this frequency leads to sharpening of the 2.76 and 2.78 signals but not that at 4.05), 7.98 (2 H, two ortho protons of one of the phenyl groups; note that owing to the asymmetric carbon atom in the molecule the phenyl rings are not magnetically equivalent), 7.69–7.34 (remaining 10 aromatic H); mass spectrum  $m/e$  (rel intensity) 437 (39,  $M^+$ ), 422 (5,  $M - CH_3$ ), 378 (64,  $M - COOCH_3$ ), 321 (100,  $M - CH_2C_6H_4CN$ ), 249 (30,  $M - CH(COOCH_3)CH_2C_6H_4CN$ ), 202 (22), 178 (16,  $C_6H_5C\equiv CC_6H_5$ ), 116 (18,  $CH_2C_6H_4CN$ ), 105 (38,  $C_6H_5CO$ ), 77 (18,  $C_6H_5$ ). Anal. ( $C_{28}H_{23}NO_4$ ) C, H, N. A similar irradiation using ethyl *p*-cyanocinnamate instead of the methyl ester led to the analogous ethyl ester **14a**: mp 168–170 °C; NMR ( $CDCl_3$ )  $\delta$  1.02 and 3.97 (t and q,  $CH_3CH_2OCO$ ), 2.74 and 3.98 (ABX spectrum, very small  $\Delta_{AB}$ ,  $-CH_AH_B^*CH_X<$ , splitting AX  $\approx$  BX  $\approx$  7.5 Hz), 7.13 (2 H, ortho to  $CH_2$  group), 7.89 (2 H, two ortho H of one of the  $C_6H_5$  groups), 7.28–7.61 (remaining 10 aromatic H); mass spectrum  $m/e$  (rel intensity) 451 (44,  $M^+$ ), 436 (5,  $M - CH_3$ ,  $m^*$ ), 392 (70,  $M - COOCH_3$ ), 378 (12,  $M - COOC_2H_5$ ), 335 (100,  $M - CH_2C_6H_4CN$ ), 307 (27, 335  $-CH_2=CH_2$ ,  $m^*$ ), 249 (41,  $M - CH(COOC_2H_5)CH_2C_6H_4CN$ ), 202 (22), 178 (20), 116 (18,  $CH_2C_6H_4CN$ ). Anal. ( $C_{29}H_{25}NO_4$ ) C, H, N.

**DCA-Sensitized Photooxygenation of CP.** A suspension of DCA in 35 mL of an acetonitrile solution of CP (1 g) was irradiated (HPK/GWV filter) for 1 h while oxygen was continuously bubbled. The excess DCA was filtered off. GC analysis showed that the combined yield of **15a** and **15b** was ca. 25% based on consumed CP. The yields of benzoic acid, benzoic anhydride, and benzil were ca. 20, 5, and 2%, respectively. The solvent was removed under reduced pressure and the residue was dissolved in 40 mL of  $CHCl_3$  and extracted with 5% aqueous  $NaHCO_3$  solution. The bicarbonate solution was acidified with hydrochloric acid and reextracted with chloroform to give 120 mg of benzoic acid, which was identified by comparison with an authentic sample using IR, NMR, and GC. The original chloroform solution was chromatographed on an ascending column (1:1 silica gel/cellulose) eluted with benzene. The lower  $\frac{2}{3}$  of the column was divided into four zones. The first zone (most polar) contained a small amount of benzoic acid. The second zone gave almost pure **15a**, recrystallized from methanol/water: mp 85–88 °C; mass spectrum  $m/e$  (rel intensity) 266 (11,  $M^+$ ), 238 (13,  $M - CO$ ,  $m^*$ ), 235 (3.1,  $M - OCH_3$ ), 207 (2.6,  $M - COOCH_3$ ,  $m^*$ ), 206 (3.3), 105 (100,  $C_6H_5CO^+$ ), 77 (26); NMR ( $CDCl_3$ )  $\delta$  3.63 (s,  $-COOCH_3$ ), 6.50 (s,  $>C=CH-$ ), 7.47, 7.97 (m, 10 aromatic H). Anal. ( $C_{17}H_{14}O_3$ ) C, H. The third zone contained a mixture of **15a**, **15b**, and another compound, which was isolated by recrystallization from MeOH [ $C_{17}H_{14}O_3$ , mass spectrum  $m/e$  298 ( $M^+$ ), 267, 121, 105; NMR ( $CDCl_3$ )  $\delta$  3.92 (s,  $OCH_3$ ), 6.55 (s, 1 H), 7.53 (m, 6 H), 8.10 (m, 4 H); IR (KBr)  $\nu_{C=O}$  1765, 1730, 1693  $cm^{-1}$ ]. Compound **15b**: NMR ( $CDCl_3$ )  $\delta$  3.67 (s,  $-COOCH_3$ ), 6.27 (s,  $>C=CH-$ ). The fourth zone contained benzil and traces of DCA. When the extraction with bi-

carbonate was eliminated from the workup, benzoic anhydride (confirmed by GC retention time and IR spectrum) was present together with benzil in the least polar fraction of the chromatographic column.

**Photoisomerization of 15a to 15b.** A solution of **15a** (30 mg) and thioxanthone (2 mg) in 1 mL of  $\text{CDCl}_3$  was irradiated inside a Rayonet photoreactor equipped with 3500-Å lamps. NMR analysis after 20 min irradiation indicated partial isomerization to **15b** (ratio **15a**:**15b** = 75:25). After 5 h irradiation this ratio changed to 53:47, which was also confirmed by GC analysis.

**Reaction of CP with *m*-Chloroperbenzoic Acid.** A solution of CP (2.5 g) and *m*-chloroperbenzoic acid (2.5 g) in 50 mL of methylene chloride was refluxed for 48 h and successively washed with sodium sulfite and sodium bicarbonate solutions. The NMR spectrum and GC of the product are consistent with almost complete conversion to a 2:1 mixture of **15a** and **15b**.

**Synthesis of 15a via Reformatsky Reaction.** A solution of benzil (21 g) and methyl bromoacetate (15 g) in 50 mL of benzene was added over a period of 1 h to 7.8 g of zinc dust. The mixture was refluxed for 1 h, cooled, and extracted with 100 mL of 20% sulfuric acid. The benzene solution was washed with a sodium bicarbonate solution, dried, and evaporated. The residue was recrystallized from pentane to give the alcohol methyl 3-benzoyl-3-hydroxy-3-phenylpropionate. This compound was dissolved in 150 mL of acetic anhydride containing 10 drops of concentrated sulfuric acid. After stirring at 60 °C for 2 h, the mixture was poured onto ice and extracted with ether. Evaporation of the ether left colorless crystals of the dehydrated material, which was identical (NMR, IR, mass spectrum, GC) with **15a**.

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**Supplementary Material Available:** X-ray data of compound **2**: molecular structure, bond lengths, interatomic angles, positional and thermal parameters, observed and calculated structure factor amplitudes, and crystal data (23 pages). Ordering information is given on any current masthead page.

## References and Notes

- (1) For a preliminary communication, see S. Farid and K. A. Brown, *J. Chem. Soc., Chem. Commun.*, 564 (1976).
- (2) (a) A. Weller, *Fast React. Primary Processes Chem. Kinet., Proc. Nobel Symp., 5th, 1967*, 413 (1967); (b) H. Knibbe, D. Rehm, and A. Weller, *Ber. Bunsenges. Phys. Chem.*, **72**, 257 (1968).
- (3) T. Okada, H. Oohari, and N. Mataga, *Bull. Chem. Soc. Jpn.*, **43**, 2750 (1970).
- (4) (a) S. G. Cohen, A. Parola, and G. H. Parsons, Jr., *Chem. Rev.*, **73**, 141 (1973), and references cited therein.
- (5) (a) R. A. Carruthers, R. A. Crellin, and A. Ledwith, *Chem. Commun.*, 252 (1969); (b) A. Ledwith, *Acc. Chem. Res.*, **5**, 133 (1972); (c) A. Ledwith in "The Exciplex", M. Gordon and W. R. Ware, Ed., Academic Press, New York, N.Y., 1975, p 209.
- (6) R. A. Neunteufel and D. R. Arnold, *J. Am. Chem. Soc.*, **95**, 4080 (1973).
- (7) (a) S. Farid and S. E. Shealer, *J. Chem. Soc., Chem. Commun.*, 677 (1973); (b) S. Farid, S. E. Hartman, and T. R. Evans in ref 5c, p 327.
- (8) (a) T. R. Evans, R. W. Wake, and O. Jaenicke in ref 5c, p 345; (b) S. Kuwata, Y. Shigemitsu, and Y. Odaira, *J. Org. Chem.*, **38**, 3803 (1973).
- (9) (a) M. Yamamoto, T. Asanuma, and Y. Nishijima, *J. Chem. Soc., Chem. Commun.*, 53 (1975); (b) T. Asanuma, M. Yamamoto, and Y. Nishijima, *ibid.*, 56 (1975).
- (10) Y. Shigemitsu and D. R. Arnold, *J. Chem. Soc., Chem. Commun.*, 407 (1975).

- (11) S. Farid, K. A. Brown, J. C. Doty, S. E. Hartman, and J. L. R. Williams, Abstracts, VIII International Conference on Photochemistry, Edmonton, Canada, Aug 1975, Abstract Y 1.
- (12) The triplet-sensitized cyclobutadimerization of CP is reported by DeBoer.<sup>13</sup> This dimer undergoes thermal rearrangement to the cyclohexadiene derivative.
- (13) C. D. DeBoer, D. H. Wadsworth, and W. C. Perkins, *J. Am. Chem. Soc.*, **95**, 861 (1973).
- (14) W. R. Ware, J. D. Holms, and D. R. Arnold, *J. Am. Chem. Soc.*, **96**, 786 (1974).
- (15) The oxidation potential of CP is measured by cyclic voltammetry in  $\text{CH}_3\text{CN}/0.1 \text{ M TBABF}_4$  against SCE using a platinum electrode at a scanning rate of 0.1 V/s. An irreversible oxidation wave at  $E_p = 1.72 \text{ V}$  ( $E_{p1/2} = 1.69 \text{ V}$ ) is obtained.
- (16) The reduction potentials are measured against SCE in  $\text{CH}_3\text{CN}/0.1 \text{ M TBABF}_4$  by cyclic voltammetry, using platinum and pyrolytic graphite electrodes, and by polarography. The potential values given are the midpoint potentials between forward and reverse peaks (reversible systems), which agree within 0.01 V with the half-wave potentials from the dropping mercury electrode measurements.
- (17) Oxidation potential (vs. SCE,  $\text{CH}_3\text{CN}/0.1 \text{ M TPAP}$ ) of DMN = 1.1 V [A. Zweig, A. H. Maurer, and B. G. Roberts, *J. Org. Chem.*, **32**, 1322 (1967)].
- (18) (a) A. Weller and K. Zachariasse, "Molecular Luminescence", E. C. Lim, Ed., W. A. Benjamin, New York, N.Y., 1969, p 895; (b) K. H. Grellman, A. R. Watkins, and A. Weller, *J. Phys. Chem.*, **76**, 3132 (1972); (c) H. Schomburg, H. Staerk, and A. Weller, *Chem. Phys. Lett.*, **22**, 1 (1973).
- (19) The triplet energy of CP is determined from the kinetics of reversible energy transfer to low-lying triplet sensitizers (S. Farid and K. A. Brown-Wensley, unpublished results).
- (20) E. F. Ullman and P. Singh, *J. Am. Chem. Soc.*, **94**, 5077 (1972).
- (21) On irradiation in degassed  $\text{CH}_3\text{CN}$  using MK as a sensitizer, no change in the quantum yield of dimerization of CP is detectable between [CP] of 0.1 and 0.02 M.
- (22) The addition of *tert*-butyl alcohol improves considerably the reproducibility of adduct **2** formation. In the absence of such protic solvents, the poor reproducibility is apparently due to the effect of varying amounts of traces of water in the samples.
- (23) A plot of  $\ln(\phi_2)$  vs.  $1/T$  gives a slope of  $-4 \times 10^3 \text{ K}$ .
- (24) Cf. J. B. Birks, "Photophysics of Aromatic Molecules", Wiley-Interscience, New York, N.Y., 1970.
- (25) TCNB quenches the fluorescence of DCA and forms a charge-transfer complex with CP, but under the chosen concentrations the interference from these processes is negligible.
- (26) Reduction potential of 1,4-naphthoquinone (vs. SCE, DMF/0.1 M TEAP) = -0.60 [J. M. Fritsch, S. V. Tatwawadi, and R. N. Adams, *J. Phys. Chem.*, **71**, 338 (1967)].
- (27) D. R. Arnold and R. M. Morchat, *Can. J. Chem.*, **55**, 393 (1977).
- (28)  $^4J_{\text{HH}}$  coupling in rigid systems involving only single bonds (H-C-C-C-H) is observed when these atoms are in a "W" configuration. In bicyclic systems this arrangement corresponds to an "exo-exo" relationship of the hydrogen atoms [cf. M. Barfield and B. Chakrabarti, *Chem. Rev.*, **69**, 757 (1969); S. Sternhell, *Rev. Pure Appl. Chem.*, **14**, 15 (1964); and references cited therein].
- (29) V. V. Razin and V. I. Gupalo, *Zh. Org. Khim.*, **10**, 2342 (1974).
- (30) A plot of  $\ln(\phi_{2,9})$  vs.  $1/T$  gives a slope of  $-2.5 \times 10^3 \text{ K}$ .
- (31) A polarographic half-wave potential of -1.36 V is measured for the reduction of F in  $\text{CH}_3\text{CN}/0.1 \text{ TBABF}_4$  vs. SCE.
- (32) The increase in  $\phi_{2-10}$  in the presence of TCNB is probably due to the decrease of  $[\text{DCA}^-]$ , which is the intermediate in the competing reaction leading to adduct **2**.
- (33) It seems that, in the MK-sensitized reaction, no significant amount of compounds **11-13** is formed via addition of  $^3\text{CNC}^*$  to CP. Under this assumption, the following equation can be derived:
 
$$1/\phi_{11-13} = \text{const} \left\{ \frac{k_4 [\text{CP}]}{k_{13} [\text{CNC}]} + \frac{k_{12} [\text{CNC}]}{k_8 [\text{CP}]} \frac{k_{12} k_4}{k_8 k_{13}} + 1 \right\}$$
 Using the ratios of the reaction constants determined above, it can be shown that, with increasing  $[\text{CNC}]/[\text{CP}]$ ,  $1/\phi_{11-13}$  should first decrease, reach a minimum at  $[\text{CNC}]/[\text{CP}]$  of  $1/3$ , and then increase, which will be almost linear at  $[\text{CNC}]/[\text{CP}] \gtrsim 1$ . Experimentally this did occur.
- (34) R. Breslow, R. Winter, and M. Battiste, *J. Org. Chem.*, **24**, 415 (1959).
- (35) C. D. DeBoer, *J. Chem. Soc., Chem. Commun.*, 377 (1972).
- (36) M. J. D. Brand and B. Fleet, *J. Electroanal. Chem. Interfacial Electrochem.*, **19**, 157 (1968).
- (37) Cf. G. O. Schenck in A. Schönberg, "Preparative Organic Photochemistry", Springer-Verlag, West Berlin, 1968, p 490.
- (38) J. J. Bohning and K. Weiss, *J. Am. Chem. Soc.*, **88**, 2893 (1966).