The boiling points or melting points (°C/mmHg or °C) of the new compounds are as follows: PhCD$_2$NHEt, 40/8; *p*-CH$_3$OC$_6$H$_4$CH$_2$NHEt, 131/26; *m*-BrC$_6$H$_4$CH$_2$NHEt, 102/5; *m*-NO$_2$C$_6$H$_4$CH$_2$NHEt, 108/3; *p*-NO$_2$C$_6$H$_4$CH$_2$NHEt, 131/6; PhCD$_2$NH-*i*-Pr, 34/5; *p*-CH$_3$OC$_6$H$_4$CH$_2$NH-*i*-Pr, 72/3; *m*-BrC$_6$H$_4$CH$_2$NH-*i*-Pr, 62/3; *m*-NO$_2$C$_6$H$_4$CH$_2$NH-*i*-Pr, 91–92/5; *p*-NO$_2$C$_6$H$_4$NH-*i*-Pr, 80/5; PhCH$_2$NH-*t*-Bu, 82/5; PhCD$_2$NH-*t*-Bu, 60/3; *p*-CH$_3$OC$_6$H$_4$CH$_2$NH-*t*-Bu, 101/1; *m*-BrC$_6$H$_4$NH-*t*-Bu, 95/0.5; *m*-NO$_2$C$_6$H$_4$CH$_2$NH-*t*-Bu, 113/0.5; *p*-NO$_2$C$_6$H$_4$CH$_2$NH-*t*-Bu, 32.

N-Halobenzylalkylamines were prepared by reaction of the benzylalkylamines with *N*-chloro- or *N*-bromosuccinimide in pentane as described previously.[8]

Methanol was purified by reaction with magnesium and distillation. Solutions of MeONa in MeOH were prepared by adding clean pieces of sodium metal to anhydrous MeOH under nitrogen.

Kinetic Studies of Elimination from 2–5. Kinetic studies of eliminations from 2–5 were carried out as before[8] using a Cary 17D or Pye Unicam SP 500 UV spectrophotometer with thermostated cuvette holders. The pseudo-first-order rate constant was divided by the base concentration to afford the second-order rate constant k_2. For reactions of *N*-bromobenzylalkylamines with MeONa–MeOH, the k_2 values were multiplied by the imine yields to obtain the second-order rate constant for imine formation.

Product Studies for Reactions of *N*-Halobenzylalkylamines with MeONa–MeOH. For reactions of *N*-halobenzylalkylamines with MeONa–MeOH, the absorbances of infinity samples from the kinetic reactions were compared with those of authentic samples of 6. Based upon the starting benzylalkylamines, the yields of 6 were 85–96% from *N*-chloramines 2–5 and 40–80% from the corresponding *N*-bromamines.

The products of reactions of *N*-halobenzylalkylamines with MeONa–MeOH were identified by using more concentrated solutions and the proton magnetic spectral method outlined pre-

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(23) The ν' value of 0.73 was estimated for *sec*-Bu from the relationship between the ν and ν' values for structurally related alkyl substituents.[5,6]

viously.[8]   From reactions of **2a–5a** with MeONa–MeOH, benzylidenealkylamines were obtained as the only products in 72–76% yields.   On the other hand, the reactions of *N*-bromobenzylalkylamines with MeONa–MeOH produced benzylalkylamines in addition to 6.

Control Experiments. The stability of the *N*-haloamines and benzylidenealkylamines under the experimental conditions was demonstrated by the previously used method.[8]

Surface Photochemistry: The CdS-Mediated Reactions of
1,1-Di-*p*-anisylethylene[1]

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The CdS-photomediated reaction of 1,1-di-*p*-anisylethylene (**1b**) leads to the formation of two cyclized (2 + 4) and two open chain dimeric products. All four reactions were quenched by 1,2,4,5-tetramethoxybenzene. Comparison of the product distribution in the CdS-induced reaction with those obtained by using cyanoaromatic sensitizers showed that the CdS distribution fell within the range found in the homogeneous systems by varying the nature of the sensitizer and of the solvent. It can be concluded that in this system, at least, the fact of adsorption on the semiconductor surface plays a minor role in directing the nature of the products. One sample of CdS used, which was of high purity, appeared able, even when washed, to induce the acid-catalyzed "dark" dimerization of **1b**. This sample yielded, on irradiation, the same four dimeric materials obtained previously, together with 1,2-dimethyltetra-*p*-anisylethane.

Introduction

Although the study of photochemically induced electron-transfer organic reactions has received much attention in recent years the parallel study of the mediation of photostimulated semiconductors in such processes has

attracted much less. Aside from oxidation/reduction processes,[2] examples of semiconductor induced reactions now include dimerization,[3,4] cis–trans isomerization,[5] va-

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(1) Publication No. 380 from the Photochemistry Unit, Department of Chemistry, University of Western Ontario.

(2) (a) Fox, M. A. *Acc. Chem. Res.* **1983**, *16*, 314. (b) Pincock, J. A.; Pincock, A. L.; Fox, M. A. *Tetrahedron* **1985**, *41*, 4107. (c) Fox, M. A.; Chen, C. C.; Park, K. H.; Younathan, J. N. In *Organic Transformations in Nonhomogeneous Media* Fox, M. Ed.; ACS Symposium Series 278; American Chemical Society: Washington, DC, 1985; p 69.

Table I. Yields of Products Obtained with CdS and Organic Sensitizers[a]

products	CdS(α)[b] (CH$_2$Cl$_2$)	CdS(α,β)[c] (CH$_2$Cl$_2$)	DCA[d] (CH$_2$Cl$_2$)	DCA[e] (MeCN)	DCA[f,g] (MeCN)	CN[h] (MeCN)
5	33	48	58	57	(33)	23
6	43	38	17	43		67
4b	12	8	25		(66)	
3b	12	6			i	

[a] 1b (0.1 M) was irradiated under argon. [b] λ > 420 nm, conversion 30%. [c] λ > 420 nm, conversion 50%. [d] λ > 400 nm, conversion 30%. [e] λ > 400 nm conversion 40%. [f] Reference 19. [g] With 2,6,9,10-tetracyanoanthracene (ref 19, footnote 10) 5% 5, 60% 4b, and 30% 3b were obtained. [h] Reference 18, incorrectly reported in ref 19, footnote 11. [i] Trace.
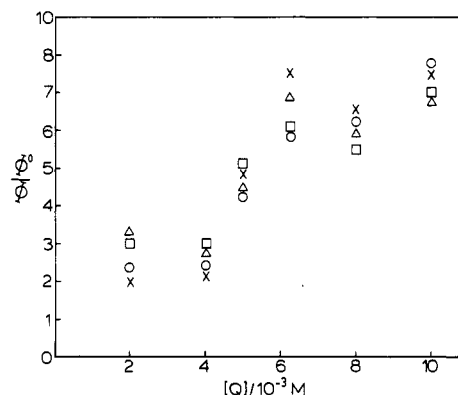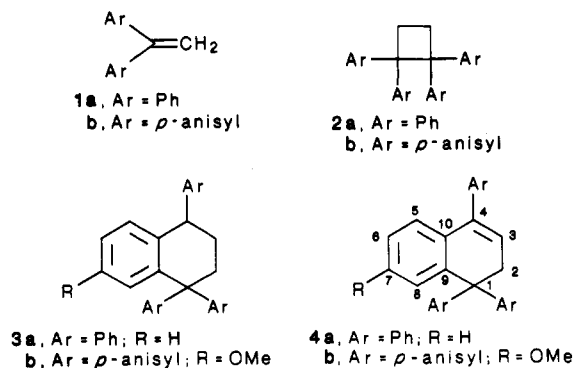
Chart I

Figure 1. The plot of $\phi°/\phi$ vs [Q] for the photoproducts: di-p-anisyl ketone (O), 5 (X), 6 and 3b ($\square$), and 4b ($\triangle$).

lence isomerization,[6,7] cycloreversion[8,9] sigmatropic rearrangement,[7,10] and (2 + 4) cycloaddition.[11] One of the important questions of interest which may be posed is that of the effect of the semiconductor surface on the electron-transfer process and, indeed, on the overall chemistry, as compared with reactions photoinduced by electron transfer for sensitizers in homogeneous systems. For instance, it has already been reported several times that homogeneous sensitizers may be, themselves, incorporated chemically into the products, as well as play the role of a photocatalyst;[12] such incorporation is a process not available to reactions utilizing a semiconductor. It is also possible that the chemistry available to the adsorbed radical ion may differ in some degree from that of the free radical ion, as does that of the free radical ion from that of the ion pair.[2c,13] For these purposes a reaction was required where the mechanistic probe could be the pattern of products obtained. A reaction which appeared suitable was the cyanoaromatic-sensitized dimerization of 1,1-di-

phenylethylene[13-15] which was first reported by Arnold[14] (using methyl 4-cyanobenzoate) and then further investigated (by using 9,10-dicyanoanthracene, DCA) by Farid[13] who was able to clarify details of the mechanism leading to the products shown in Chart I. Unfortunately, 1,1-diphenylethylene, with CdS, the semiconductor of choice because of its band gap and position of its conduction band,[16] (aerated) gave only benzophenone and when deaerated gave only polymeric material. Attention was, therefore, turned to the use of the better electron donor, the anisyl derivative 1b.[18] We describe below our results, which include the observation of (2 + 4) "cycloaddition".

Results and Discussion

Irradiation (λ > 420 nm) of an aerated suspension of CdS (band gap, 2.4 eV; ~530 nm) in CH$_2$Cl$_2$ containing 1b (0.1 M) gave five products (conversion 30%) separated by flash chromatography and TLC in a ratio of 51:16:21:6:6 (Table I). These were identified (see Experimental Section) as the known di-p-anisyl ketone, 5, 6, 4b, and 3b, respectively: under deaerated conditions only 5, 6, 4b, and 3b were formed. Appropriate control experiments indicated that both light and CdS were required for reaction. The overall consumption of starting material was faster in the presence of oxygen, but the di-p-anisyl ketone predominated. These results are compatible with previous observations[3,4,6-9] wherein it seems most probable that the hole/electron recombination is slowed, and thus the life-

(3) Draper, A. M.; Ilyas, M.; de Mayo, P.; Ramamurthy, V. *J. Am. Chem. Soc.* **1984**, *106*, 6222.

(4) Al-Ekabi, H.; de Mayo, P. *Tetrahedron* **1986**, *42*, 6277.

(5) (a) Al-Ekabi, H.; de Mayo, P. *J. Chem. Soc., Chem. Commun.* **1984**, 1231. (b) Al-Ekabi, H.; de Mayo, P. *J. Phys. Chem.* **1985**, *89*, 5815. (c) Hasegawa, T.; de Mayo, P. *J. Chem. Soc., Chem. Commun.* **1985**, 1534. (d) Hasegawa, T.; de Mayo, P. *Langmuir* **1986**, *2*, 362. (e) Kodama, S.; Yabuta, M.; Kubokawa, Y. *Chem. Lett.* **1982**, 1671. (f) Kodama, S.; Yabuta, M.; Anpo, A.; Kubokawa, Y. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 2307. (g) Yanagida, S.; Mizumota, K.; Pac, C. *J. Am. Chem. Soc.* **1986**, *108*, 647.

(6) Al-Ekabi, H.; de Mayo, P. *J. Phys. Chem.* **1986**, *90*, 4075.

(7) Okada, K.; Hisamitsu, K.; Takahashi, Y.; Hanaoka, T.; Miyashi, T.; Mukai, T. *Tetrahedron Lett.* **1984**, *25*, 5311.

(8) Okada, K.; Hisamitsu, K.; Mukai, T. *J. Chem. Soc., Chem. Commun.* **1980**, 941.

(9) Barber, R. A.; de Mayo, P.; Okada, K. *J. Chem. Soc., Chem. Commun.* **1982**, 1073.

(10) de Mayo, P.; Wenska, G. *J. Chem. Soc., Chem. Commun.* **1986**.

(11) This work appeared after the submission of this manuscript for publication: Fox, M. A.; Sackett, D. D.; Younathan, N. *Tetrahedron* **1987**, *43*, 1643.

(12) See, for example: (a) Arnold, D. R.; Wong, P. C.; Maroulis, A. J.; Cameron, T. S. *Pure Appl. Chem.* **1980**, *52*, 2609. (b) Ichinose, N.; Mizuno, K.; Hiromoto, Z.; Otsuji, Y. *Tetrahedron Lett.* **1986**, *27*, 5619. (c) Albini, A.; Fasani, E.; Mella, M. *J. Am. Chem. Soc.* **1986**, *108*, 419.

(13) Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* **1983**, *105*, 1386.

(14) Neunteufel, R. A.; Arnold, D. R. *J. Am. Chem. Soc.* **1973**, *95*, 4080.

(15) Majima, T.; Pac, C.; Nakasone, A.; Sakurai, H. *J. Am. Chem. Soc.* **1981**, *103*, 4499.

(16) CdS could be excited by light of wavelength not absorbed by the organic chromophores involved. In addition the use of the oxide semiconductors (ZnO, TiO$_2$) led to oxidation of the hydrocarbon.[17]

(17) Fox, M. A.; Chen, C. C. *J. Am. Chem. Soc.* **1981**, *103*, 6757.

(18) A brief comment in a footnote (Mizuno, K.; Ishii, M.; Otsuji, Y. *J. Am. Chem. Soc.* **1981**, *103*, 5570) had indicated that 1b, with 1-cyanonaphthalene, gave 5 and 6. After completion of our work but before submission of our manuscript Mattes and Farid[19] reported their work on the DCA- and TCA-sensitized transformation of 1b discussed in the text.

(19) Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* **1986**, *108*, 7356.

time of the CdS "hole" initiating the reaction prolonged, by the trapping of the conduction band electron as superoxide[20] ion, as shown in the sequence in eq 1, where D is the donor **1b**.

$$CdS \xrightarrow{h\nu} CdS(h/e) \xrightarrow{O_2} CdS(h/OO^-) \xrightarrow{D}$$
$$CdS(OO^-) + D^{\bullet+} \quad (1)$$
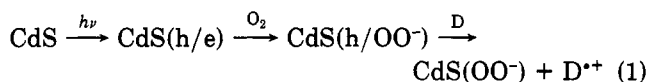
The reaction is sensitive to water content and was very inefficient using undried CH_2Cl_2 (BDH; 400 ppm of H_2O, Karl Fischer titration), but after a partial drying (80 ppm) activity was recovered. No detectable difference in the reaction rate was observed when the molecular sieves 3A or 4A were used for drying. A simple, tentative, rationalization could be that the active sites are preferentially occupied by bound water, but concomitant modification of surface states and hence the lifetime of the electron/hole pair is not excluded.

Since there was produced by the CdS-mediated reaction an array of products—though the cyclobutane **2b**, the consequence of formal (2 + 2) cycloaddition, was absent[21]—it was required to be shown that all these products were derived from the radical cation **1b**[•+]. Such could be achieved by the addition of a quencher in the form of a better donor than **1b**.[3-6,10] 1,2,4,5-Tetramethoxybenzene (TMB, E^{ox} = 0.81 V vs. SCE[22]) fulfilled this requirement and furthermore could not function as an energy transfer, singlet or triplet, quencher in this system, both processing being endothermic. In the event, it was not possible to obtain data precise enough in this heterogeneous system to permit plots to be made of $\phi°/\phi$ (Figure 1), but it is evident that all product formation is efficiently quenched. It should be pointed out that in such a heterogeneous system the Stern–Volmer plots are not necessarily linear. This is because more than one mode of quenching may be occuring, i.e., collision between radical cation and quencher molecules which are surface bound (Langmuir–Hinshelwood kinetics) or between adsorbed radical cations and quencher molecules in solution (Eley–Rideal System).[4,5d,6] The similarity of the quenching data suggests to us that the *order* of the quenching process is the same for all products. If this tentative assumption be correct, then the formation of **5** by the dimerization of **1b**[•+],[23b] followed by the loss of two protons, as suggested for **1a**[+] generated under strong acid conditions,[23a] is improbable.

5   **6**
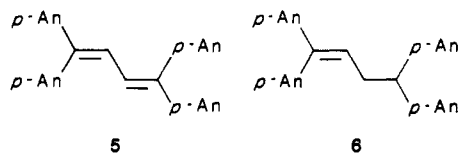
Unlike the organic-sensitized systems there appears to be no hydrogen acceptor, aside from the substrate itself. There is no equivalent to, for instance, the dihydro-9,10-dicyanoanthracene in the DCA sensitized reaction of **1a**,[13] and hence disproportionation must be invoked. Furthermore, the distinction between the free ion and the ion

Scheme I

pair, made successfully in solution,[13] is more obscure on a semiconductor surface. With these factors in mind (and for reaction in the absence of oxygen) the minimal mechanism described in Scheme I can be written. The addition of the radical cation **1b**[•+] to the neutral molecule **1b** gives the 1,4-dimeric radical cation which undergoes both cyclization and loss of a proton. The 1,6-cyclization product after loss of a proton and subsequent disproportionation, or electron transfer followed by proton transfer, gives **3b** and **4b**. On the other hand, loss of proton from the dimeric radical ion gives a radical which upon disproportionation or electron transfer followed by proton transfer gives **5** and **6**.

Comparison of CdS Samples. The experiments just described were performed with CdS in the α form (hexagonal),[24-26] surface area 0.5 m^2/g (Strem Luminescent grade, 99.99% lot no. NATL). Hexagonal CdS is usually prepared from a neutral solution of cadmium salt with hydrogen sulfide at room temperature. The other crystalline form (cubic β) is prepared in acidic solution at 100 °C.[25] Since the purpose of our enquiry was the function of the semiconductor surface we chose to examine the behavior of another CdS sample. That chosen, Strem Ultrapure ($\alpha + \beta \sim$ 1:1, $\geq$99.99% lot no. 16693-s) had surface area 7.1 m^2/g.[26] Since its mode of preparation was unknown, but probably involved acidic conditions, a preliminary examination to reveal any dark reaction was made. A suspension of CdS in CH_2Cl_2 containing 0.1 M **1b** was kept in the dark for 24 h. The dimer **7** was obtained (40% yield), identified spectroscopically,[27] and compared with an authentic specimen prepared by treatment of **1b** with trichloroacetic acid in benzene.[28]

A similar experiment conducted with the first sample of CdS yielded no **7**. The yield of **7** from the second sample was unchanged when the CdS was kept in vacuo for 5 days or when washed with conductivity water and subsequently dried. The nature of the bound acid was not established,
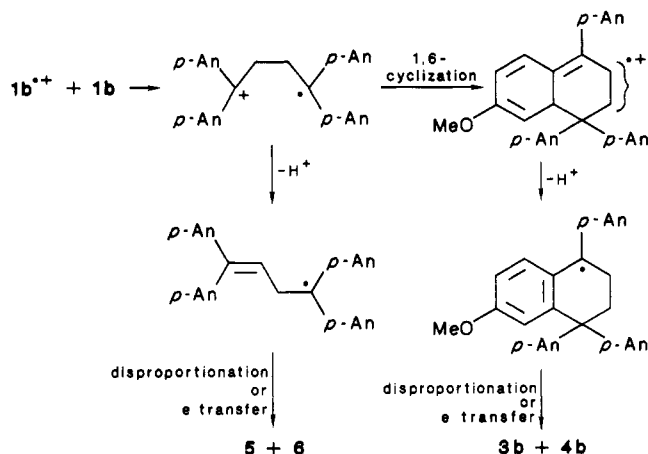
(20) (a) Harbour, J. R., Hair, M. L. *J. Phys. Chem.* **1977**, *81*, 1791. (b) Harbour, J. R.; Hair, M. L. *J. Phys. Chem.* **1978**, *82*, 1397.

(21) It has been shown that **2a** is thermally unstable, the half-life at 51 °C being 47 min.[19] It is possible that **2b** may have a short half-life at room temperature, alternatively the precursor biradical[13] may not close but revert directly to starting material.

(22) Siegerman, J. *Techniques of Chemistry*; Weinberg, N. L., Ed.; Wiley: New York, 1975; Vol. 5, Part 2, p 792.

(23) (a) Haynes, R. K.; Probert, M. K. S.; Wilmot, I. D. *Aust. J. Chem.* **1978**, *31*, 1737. (b) Moutet, J. C.; Reverdy, G. *Tetrahedron Lett.* **1979**, 2389.

(24) (a) Milligan, W. O. *J. Phys. Chem.* **1934**, *38*, 797. (b) Aylett, B. J. In *Comprehensive Inorganic Chemistry*; Bailer, J. C., Emeleus, H. J.; Nyholm, R., Trotman-Dickenson, Ed.; Pergamon: Oxford, 1973; p 268.

(25) Mau, A. W.-H.; Huang, C.-B.; Kakuta, N.; Bard, A. J.; Camplon, A.; Fox, M. A.; White, J. M.; Webber, S. E. *J. Am. Chem. Soc.* **1984**, *106*, 6537.

(26) Ilyas, M.; de Mayo, P. *J. Am. Chem. Soc.* **1985**, *107*, 5093.

(27) The acid-catalyzed dimer **7** was identified by its spectral data: ^{1}H NMR (CDCl₃) δ 7.16–7.09 (6 H, m, Ar protons), 6.80–6.65 (10 H, m, Ar protons), 6.64 (1 H, s, olefinic proton), 3.79 (6 H, s, 2OCH₃), 3.78 (3 H, s, OCH₃), 3.77 (3 H, s, OCH₃); MS, m/e 480 (M[•+]), 465 (M[•+] – CH₃), 372, 345, 253, 227; precise mass calcd 480.2301, found 480.2280.

(28) (a) Evans, A. G.; Gones, N.; Jones, P. M. S.; Thomas, J. H. *J. Chem. Soc.* **1956**, 2757. (b) Tadros, W.; Sakla, A. B.; Abdou, S. E. *J. Chem. Soc.* **1972**, 2839.
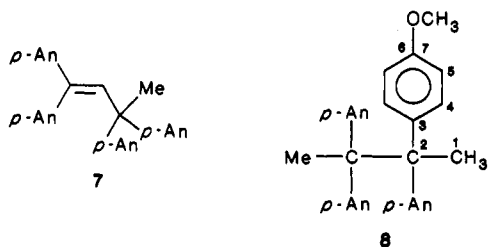
but its undoubted presence shown chemically and photochemically (see following) must be a warning with regard to the interpretation of CdS induced chemistry.

Irradiation (λ > 420 nm) of a degassed suspension of the second CdS sample in CH_2Cl_2 gave **3b**, **4b**, **5**, and **6**, together with a small amount of **7**, (conversion 50%) and a 30% yield of a new product: under aerated conditions this new product was not obtained, but **3b**, **4b**, **5**, and **6** were accompanied by di-*p*-anisyl ketone. The new substance was identified spectroscopically as **8** and its mode of formation, which is not relevant to the processes here discussed, will be described elsewhere.[29]

Homogeneous Sensitization. The distribution of products with the two samples of CdS (aside from **7** and **8**) while not identical were rather similar. The only report in the literature, when these experiments were performed, of a homogeneous electron-transfer-induced reaction of **1b** was that of Mizuno, Ishii, and Otsuji,[18] who obtained, in an attempted reaction of **1b** with furan sensitized by 1-cyanonaphthalene, the open chain dimers **5** and **6** (Table I). Using DCA as a sensitizer in acetonitrile we obtained the same two substances: **3b** and **4b** were not formed. However, bearing in mind the proposed intervention of both ion pairs and free radical ions in the solution mechanism suggested by Farid[13,19,30] and others,[31] it appeared desirable to compare products obtained in the same solvent. Since, in our experience, organic semiconductor-induced reaction frequently proceed better in CH_2Cl_2 than in MeCN, we attempted the DCA-induced reaction in this solvent: again **5** and **6** were formed, but in addition there was obtained **4b**.[32]

The situation for homogeneous reaction is, thus, more complex than previously expected. The nature of the products depends on the solvent, the electron acceptor and the proximity of the counterion: the basicity of the system presumably determines the rate of deprotonation vs. cyclization and disproportionation. Evidently, comparison of the product distribution in the CdS photoinduced reaction with those obtained using cyanoaromatic sensitizers showed that CdS distribution fell within the range found in homogeneous systems by varying the nature of the sensitizer and of the solvent, even on two widely disparate samples of CdS. It must be concluded that, in this system at least, the fact of adsorption plays no major role in the determination of product formation.

(29) Al-Ekabi, H.; Kawata, H.; de Mayo, P., manuscript in preparation. The reaction does not involve CdS.

(30) Mattes, S. L.; Farid, S. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1983; Vol. 6, p 233.

(31) (a) Eriksen, J.; Foote, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 6083. (b) Pac, C.; Ohtsuki, T.; Fukunaga, T.; Yanagida, S.; Sakwai, H. *Chem. Lett.* **1985**, 1855 and references cited therein.

(32) In MeCN Farid reports[19] that DCA gives essentially **4b** and **5** and no **6**. We are at present unable to account for this difference (Table I).

Experimental Section

Chemicals. Methylene dichloride (BDH spectroscopic grade) was used after drying with 3A or 4A molecular sieves. Acetonitrile (Fisher Certified) was used without further purification. 1,1-Diphenylethylene (Aldrich) was distilled before use. 1,1-di-*p*-anisylethylene was prepared from ethyl acetate and *p*-anisylmagnesium bromide.[33] The CdS is described in the text.

General Irradiation Procedure. Typically, **1b** in methylene dichloride (0.1 M; 6 mL) containing CdS (100 mg) was irradiated (λ > 420 nm: Corning 3-72 filter) for 2 h by using a 1000-W PRA xenon lamp run at 840 W. Prior to irradiation the mixture was sonicated for 10 min, and it was stirred during the course of the irradiation. Compressed air was used as a coolant, and a water filter removed IR radiation. Dry argon or nitrogen or degassing by three freeze–thaw cycles were used to remove oxygen for anaerobic samples; others were open to the atmosphere via a condenser. *n*-Hexadecane was used as calibrant. After irradiation the mixture was filtered and the filtrate analyzed by using a Varian 3700 gas chromatograph connected to an H.P. 3390A integrator. The stationary phases used were OV-17 (3%) or OV-101 (10%): both were on Chromosorb W.

CdS(α,β) Photoinduced Reaction. **1b** (250 mg) in CH_2Cl_2 (6 mL) was irradiated under argon in the presence of CdS(α,β) (100 mg) for 4 h. After filtration, the filtrates from two identical experiments were combined and separated by flash chromatography on silica gel (230–400 mesh) using methylene dichloride-hexane (3:1) as eluent. Further separation was achieved by thin-layer chromatography using the same solvent combination. The (known) products were identified by spectral data.

Spectral data for 5: ¹H NMR (CDCl₃) δ 7.24 (4 H, d, J = 8.9 Hz), 7.16 (4 H, d, J = 8.9 Hz), 6.93 (4 H, d, J = 8.9 Hz), 6.77 (4 H, d, J = 8.8 Hz), 6.66 (2 H, s, olefinic protons), 3.85 (6 H, s, 2OCH₃), 3.77 (6 H, s, 2OCH₃); MS, m/e 478 (M$^{•+}$), 372, 357, 227; precise mass calcd for $C_{32}H_{30}O_4$ 478.2144, found 478.2145.

Spectral data for 6: ¹H NMR (CDCl₃) δ 7.11 (4 H, d, J = 8.7 Hz), 7.04 (4 H, d, J = 8.8 Hz), 6.90 (2 H, d, J = 8.9 Hz), 6.83 (4 H, d, J = 9.0 Hz), 6.78 (2 H, d, J = 9.1 Hz), 5.85 (1 H, d, J = 7.1 Hz), 4.05 (1 H, t, J = 7.6 Hz), 3.87 (3 H, s, OCH₃), 3.80 (9 H, s, 3OCH₃), 2.83 (2 H, t, J = 7.3 Hz); MS, m/e 480 (M$^{•+}$), 372, 357; precise mass calcd for $C_{32}H_{32}O_4$ 480.2301, found 480.2294.

Spectral data for 3b: ¹H NMR (CDCl₃) δ 7.10–6.6 (14 H, Ar protons), 6.2 (1 H, d, Ar), 4.15 (1 H, m) 3.85–3.60 (12 H, s, 4OMe), 2.80 (2 H, m, J = 7.1 Hz), 2.58 (2 H, m); MS, m/e 480 (M$^{•+}$), 372.

Spectral data for 4b: ¹H NMR (CDCl₃) δ 7.10 (2 H, d, J = 8.6 Hz), 7.02 (5 H, d, J = 9.1 Hz) 6.83 (2 H, d, J = 8.9 Hz), 6.78 (4 H, d, J = 9.1 Hz), 6.67 (1 H, dd, $J_{H_6H_8}$ = 2.6 Hz and $J_{H_5H_6}$ = 8.4 Hz), 6.37 (1 H, d, $J_{H_6H_8}$ = 2.7 Hz), 5.79 (1 H, t, J = 4.7 Hz), 3.80 (3 H, s, OCH₃), 3.78 (6 H, s, 2OCH₃), 3.68 (3 H, s, OCH₃), 3.17 (2 H, d, J = 5.0 Hz); MS, m/e 478 (M$^{•+}$), 372, 357, 253, 227; precise mass calcd for $C_{32}H_{30}O_4$ 478.2144, found 478.2140.

Spectral data for 8: ¹H NMR (CDCl₃) δ 6.90 (8 H, br d, J = 9.1 Hz), 6.63 (8 H, d, J = 9.1 Hz), 3.77 (12 H, s, 4OCH₃), 1.91 (6 H, br , 2CH₃); ¹³C NMR 156.60 (C₆), 140.70 (C₃, v br), 132.88 (C₄, v br), 111.08 (C₅, v br), 55.13 (C₇), 53.66 (C₂), 27.64 ppm (C₁, v br); MS, m/e 482 (M$^{•+}$), 430, 242, 240, 227; precise mass calcd for $C_{32}H_{34}O_4$ 482.2457, found 482.2464.

DCA-Sensitized Reaction. A suspension of DCA (15 mg) in 6 mL acetonitrile containing 250 mg of **1b** was irradiated under argon for 2 h. After evaporation to half-volume the mixture was filtered from the precipitated DCA and the filtrate separated by flash chromatography on silica gel (230–400 mesh) using methylene dichloride–hexane (3:1) as eluent. Only **5** and **6** (57:43) were obtained (conversion: 40%). With CH_2Cl_2 as solvent, **4b** was also obtained (58:17:25; conversion 30%).

(33) Allen, C. F. H.; Converse, S. *Org. Synth.* **1941**, *1*, 226.