binding is reduced by denaturing the DNA or by adding Mg^{2+}. For BPDE in denatured DNA and in native DNA stabilized with Mg^{2+}, the overall, pseudo-first-order rate constants are 8.3–50 times smaller than the rate constants measured in native DNA without Mg^{2+}. For BPO, they are 29 and 100 times smaller. For BAO, they are 14 and 33 times smaller. Like the parallel between the rate constants and the association constants, the results indicating that the rate constants measured in denatured DNA and in native DNA stabilized with Mg^{2+} are smaller than the rate constants measured in native DNA without Mg^{2+} support the conclusion that physical binding plays a key role in determining the overall reactivities of aromatic epoxides in systems containing DNA.

Comparison of the Abilities of BPDE, BPO, and BAO to Form DNA Adducts. Previous investigations have indicated that the genotoxic activity of DNA-alkylating agents sometimes correlates with the abilities of these molecules to modify DNA.[83] However, the data in Table III indicate that, in reactions with native DNA that are run to completion, BPO forms higher levels of adducts than does BPDE. For reactions in native DNA without Mg^{2+}, 14.9% of the BPO forms adducts. Under the same conditions, 10.1% of the BPDE forms adducts. For reactions in native DNA with 0.10 mM Mg^{2+}, 11.2% of the BPO and 7.6% of the BPDE forms adducts.

Interestingly, the kinetics of reactions of BPO that yield adducts exhibit much higher sensitivity to reaction conditions than do the reactions of BPDE. At short reaction times, this sensitivity can significantly alter the relative amounts of adducts formed from the three metabolites. For example, after 10 min, reactions of BPDE run in denatured DNA and in native DNA stabilized with Mg^{2+} yield 9.8 and 7.1% adducts, respectively, while reactions of BPO yield only 1.4 and 1.3% adducts.

The rate at which BAO adduct formation occurs also exhibits high sensitivity to reaction conditions. After 10 min, reactions of BAO run in native DNA without Mg^{2+} yield 2.9% adducts, while reactions in denatured DNA or in native DNA with Mg^{2+} yield only 0.3 and 0.1% adducts.

The larger overall, pseudo-first-order rate constant of BPDE in DNA stabilized with Mg^{2+}, compared to the rate constants for reactions of BPO and BAO, run under the same conditions, may contribute to the higher genotoxic activity of BPDE, compared to that of BPO or BAO. In cells, DNA is stabilized by millimolar concentrations of Mg^{2+} and polyamines,[84] and pathways by which reactive metabolites of polycyclic aromatic hydrocarbons modify DNA compete with detoxification pathways.[21-23] In the present experiments, reactions run in Mg^{2+} mimic this physiological environment better than reactions run without Mg^{2+}. The observation that, in reactions with stabilized DNA run at short reaction times, BPDE yields 5.6 and 49 times more adducts than BPO or BAO, combined with the observation that BPO and BAO are better substrates for detoxifying enzymes than BPDE, may be important for understanding the high genotoxic potency of BPDE compared to the low potency of BPO and BAO.[13,16b,c]

Acknowledgment. Support of this work by the Petroleum Research Fund, administered by the American Chemical Society (Grant No. 21314-AC), The National Cancer Institute of the National Institutes of Health (Grant No. CA41432), The American Cancer Society (Grant No. CN-37), and Cray Research, Inc., is gratefully acknowledged. Computer access time has been provided by the Computer Center of the University of Illinois at Chicago, the Cornell National Supercomputer Facility, and the National Center for Supercomputing Applications at the University of Illinois at Urbana–Champaign. A.V.B. has been supported by a Petroleum Research Fund Summer Faculty Research Fellowship. We thank Prof. Robert Moriarty, Dr. Kenzabu Tasaki, and Mr. Mark Domroese for technical assistance.

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Oxidative Photofragmentation of α,β-Amino Alcohols via Single Electron Transfer: Cooperative Reactivity of Donor and Acceptor Ion Radicals in Photogenerated Contact Radical Ion Pairs

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Abstract: The studies presented in this paper show that α,β-amino alcohols undergo a very clean C–C bond cleavage upon SET (single electron transfer) oxidation by photoexcited electron acceptors in a process which generally culminates in two-electron reduction of the acceptors. For a number of different α,β-amino alcohols, the oxidative fragmentation occurs in a high chemical yield (>90%), yet with low to medium quantum efficiencies (0.0001–0.1) which vary strongly depending on the properties of electron donor (D), acceptor (A), and solvent. The net quantum efficiency reflects the competition between back electron transfer and the chemical redox process. Detailed mechanistic studies were carried out to investigate the visible light induced oxidative fragmentation of α,β-amino alcohols in the presence of electron acceptors including thioindigo (TI), 9,10-dicyanoanthracene (DCA), 2,6,9,10-tetracyanoanthracene (TCA), and 1,4-dicyanonaphthalene (DCN). Cosensitized (biphenyl) photoredox leads to free ions, A^- and D^+, and moderately efficient unassisted fragmentation of D^+. Quenching of $^1A^*$ by electron donor (D) to give a solvent separated radical ion pair (SSRIP) leads to a very inefficient reaction. In contrast, quenching to give a contact radical ion pair (CRIP) gives a relatively efficient reaction. This reaction is sensitive to the stereochemistry of the amino alcohol, suggesting a preferred anticoplanar configuration during the C–C bond cleavage process. The critical matching of reactivity of acceptor and donor ion radicals allows a rapid reaction to occur in the relatively narrow time window between formation and decay of the contact radical ion pair.

Introduction

Photoinduced electron-transfer reactions have been the topic of widespread recent investigation. On the one hand, a number of studies have indicated that single electron transfer (SET) quenching of excited states is a very general phenomenon which can mechanistically unify a diverse array of previously reported

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photochemical reactions including both net redox reactions and other nonredox processes.[1-3] On the other hand, a systematic study of light-induced electron-transfer reactions has led to the development of novel reactions that are readily associated with the facile generation of potentially reactive radical ions. In most of the latter cases, the "chemical activation" achieved by photochemical electron transfer can be associated with enhancement of the reactivities of the individual radical ions with respect to their parent neutral molecules.[4-14] For example, a number of reactions have been attributed to enhanced acidity of cation radicals generated by excited state SET.[15-17] In a number of other cases it has been shown that strong covalent C–C or C–heteroatom bonds in parent neutral molecules can be selectively labilized by photoinduced SET processes.[18-20] This has been found to be especially prominent for radical cations. A number of experiments and calculations have indicated that strong covalent C–C bonds with dissociation energies of 60–100 kcal/mol for the neutral molecules[21,22] can experience sharp and selective reduction in bond dissociation energy upon oxidation to the cation radical.[23,28a] The role of this selective labilization of C–C bonds in cation radicals has been indicated for a number of diverse photoreactions.[24-29]

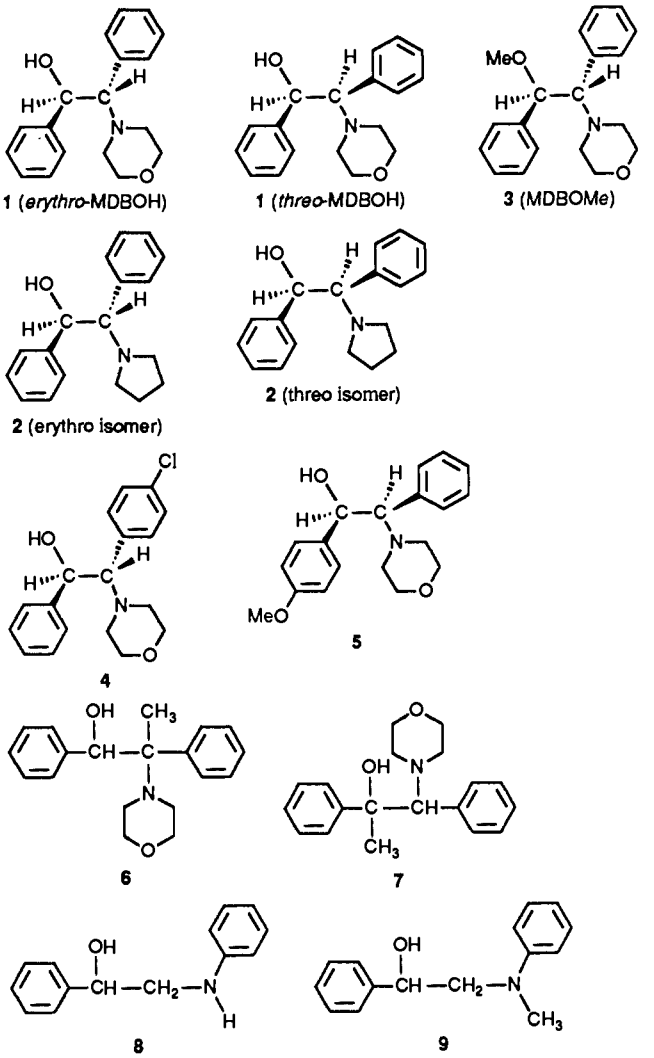

Figure 1. Structures of α,β-amino alcohol donors used in this study.

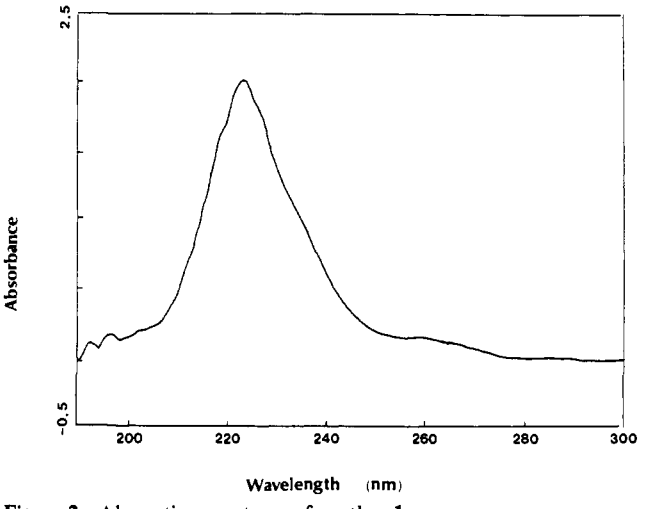

Figure 2. Absorption spectrum of *erythro*-**1**.

While bond activation by photoinduced electron transfer in solution is a fairly well established process, the mechanistic details and efficiencies of these reactions are frequently controlled by a number of other processes occurring in competition with a uni-

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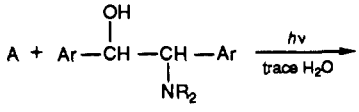
molecular dissociation of an ion radical. Unlike the very commonly observed fragmentation of organic cation radicals in the gas phase,[30-32] photoinduced SET reactions may be complicated by cation–anion and ion–solvent interactions. The frequent photogeneration of SET intermediates as ion–radical pair generates potentially reactive intermediates; however competition between highly exergonic reverse electron transfer provides a clock that can often overwhelm all but the most rapid of the possible reaction channels.[33-35] As an understanding of the factors controlling rates of back electron transfer has been gained, several strategies for overcoming the back electron transfer clock have been developed. Solvent–ion interactions can potentially enhance or reduce reactivity; recent studies have indicated selective enhancement of reactivity can be obtained in certain cases.

An example where oxidative photofragmentation can be induced through excitation of UV and visible light absorbing electron acceptors is the reaction of amino alcohols as outlined in eq 1.



$$AH_2 + ArCHO + Ar'CHO + R_2NH \quad (1)$$

As reported in recent communications,[24] this reaction occurs cleanly for a wide variety of amino alcohols and can be initiated by photoexcitation of acceptors such as thioindigo or cyanoaromatics in a variety of solvents such as benzene, acetonitrile, or acetonitrile–water. While the reaction appears quite general, the quantum efficiency shows a strong dependence upon acceptor, amino alcohol structure, and solvent, which suggests a more complex reaction than simple fragmentation of an electron transfer quenching generated donor cation radical. In the present paper we report a detailed study of the factors controlling this reaction when it is initiated by quenching of excited singlets of TI and the cyanoaromatics in organic solvents of low to moderate polarity. These results indicate that in these solvents overall reactivity is controlled to a large extent by the type of radical ion pair and, especially for contact radical ion pairs (CRIP), the reactivity of both the acceptor anion radical, A^-, and the donor cation radical, D^+.

Results

Overall Aspects of Photoreactivity of α,β-Amino Alcohols with Electron Acceptors. The α,β-amino alcohols used in these studies are shown in Figure 1. They were synthesized either by reaction of a secondary amine with the appropriate epoxide or by a sequence of benzoin condensation and chlorination followed by amine substitution and reduction. The individual diastereomers (*erythro*- and *threo*-2-morpholino-1,2-diphenylethanol (**1**) or 2-pyrrolidinyl-1,2-diphenylethanol (**2**)) were prepared by reacting the secondary amines with *trans*- or *cis*-stilbene epoxide, respectively. The detailed procedures are summarized in the Experimental Section.

All of these compounds absorb primarily in the far UV (Figure 2) and have no absorption in the visible. Direct irradiation of the α,β-amino alcohols in vacuum degassed benzene or acetonitrile solution at 280 and 330 nm, the wavelengths used for photolysis in the "photosensitized" experiments (see below) and where there is only small end absorption for most of the amino alcohols, does not produce observable spectral changes, and no photoproducts were detected by HPLC or NMR analysis even upon prolonged (>10 h) photolysis. Irradiation of these compounds at the same wavelengths in the presence of the polymerizable monomer, methyl methacrylate, does not produce any detectable polymerization; under the same conditions molecules generating even relatively short lived free radicals upon photolysis give substantial polymerization.[36-38]

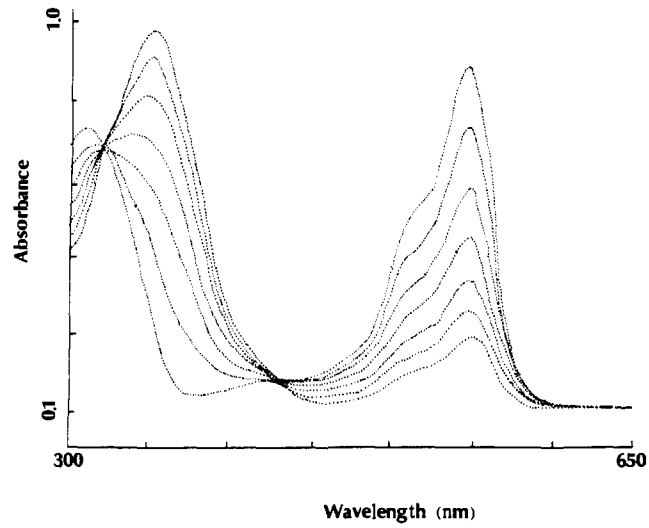


Figure 3. Absorbance change of TI during continuing photolysis in the presence of *erythro*-**1** (every 5 min).

Although the α,β-amino alcohols are unreactive under direct photolysis, they are quite reactive when solutions containing the α,β-amino alcohols together with various electron acceptors having strong absorption in the near ultraviolet or visible are irradiated at wavelengths absorbed only by the electron acceptors.[39] Electron acceptors that can be used to promote reaction include thioindigo (TI), a number of polypyridyl–ruthenium complexes, cyanoaromatics, and various quinones. As will be discussed below, the overall reaction of the α,β-amino alcohol is remarkably independent of the acceptor used and its excited state multiplicity; however, the quantum efficiency of the process is strongly acceptor dependent. In the present paper we focus on reaction initiated by quenching of acceptor excited singlet states. Thus, while reaction has been observed for several other acceptors not discussed in this study,[40] this study compares reactivity initiated by irradiation of thioindigo (TI), 9,10-dicyanoanthracene (DCA), 2,6,9,10-tetracyanoanthracene (TCA), and 1,4-dicyanonaphthalene (DCN). Upon irradiation of these acceptors in deaerated solution (benzene, acetonitrile, methylene chloride) in the presence of moderate concentrations of the α,β-amino alcohols these acceptors undergo "permanent" photochemical reaction which is characterized by bleaching of the long-wavelength absorption due to the acceptor and increase of absorption at shorter wavelengths. In each case, the photoproducts produced by bleaching of the electron acceptors are stable in the absence of oxygen, but quantitatively revert to regenerate the absorption spectrum of the starting electron acceptor upon exposure to air for various lengths of time (recovery of TI requires only a few seconds; however, regeneration of the cyanoaromatics in solution occurs over a period of days). In typical experiments, irradiation

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Table I. Photooxidative Fragmentation Products of α,β-Amino Alcohols

α,β-amino alcohol	products,[a] comments
1	benzaldehyde, morpholine (2:1) for both isomers; no other products were detected after 80% conversion
3	trace amount of benzaldehyde[b]
4	benzaldehyde, *p*-chlorobenzaldehyde, morpholine (1:1:1)
5	benzaldehyde, *p*-methoxybenzaldehyde, morpholine (1:1:1)
6, 7	benzaldehyde, acetophenone, morpholine (1:1:1)
8, 9	benzaldehyde; no formaldehyde was detected

[a] Photoproducts were obtained through irradiation of benzene solution containing TI as the electron acceptor (10^{-3} M for NMR sample, 10^{-4} M for regular sample in a Pyrex test tube) and various α,β-amino alcohols for 15–24 h to reach over 50% conversion. All samples were vacuum degassed through freeze–pump–thaw cycles and selaed under vacuum. Products were analyzed by HPLC and NMR. Photolysis was conducted by using a 200-W Hg lamp with 3–73 (cut-off filter) and 5–56 (band-pass filter) to isolate the peak at 540 nm. Products were obtained in the range 60–87% with cyclohexane as an internal standard. [b] Prolonged irradiation of ca. 3 days for detection of benzaldehyde. No other products were identified under this condition.

of vacuum degassed benzene solutions of TI in the presence of the α,β-amino alcohols leads to the disappearance of the thioindigo absorption at 546 nm concurrent with the appearance of a strong absorption in the ultraviolet centered at 386 nm in benzene (Figure 3). This peak has previously been shown to be characteristic of the 2e, $2H^+$ reduction product *leuco*-thioindigo (TIH_2).[41] Two isosbestic points, at 320 and 422 nm, were maintained during irradiation, suggesting that the photoreaction proceeds cleanly to produce a single product or a mixture of products in a constant ratio. Irradiation of cyanoaromatics under the same conditions in benzene leads to a similar bleaching of the absorption due to the electron acceptor during continuing photolysis; however, the overall rate of the bleaching is drastically reduced for the cyanoaromatics compared to TI under the same conditions.

The products produced by photobleaching of the electron acceptors in the presence of the α,β-amino alcohols were shown to be the two-electron reduction products (AH_2) in most cases. These could be analyzed and quantitatively determined from their absorption spectra and NMR spectra. The absorption spectrum of TIH_2 generated photochemically from irradiation of thioindigo with amino alcohols such as **1** was essentially identical with that of the two-electron reduction product of TI formed during reductive electrolysis.[41] The photoreduction products of the cyanoaromatics such as DCA in benzene were shown also to be the corresponding dihydro compounds, by comparison with authentic samples produced as described previously.[42] These compounds are relatively more stable than TIH_2, and the solids, which precipitate out of irradiated solutions, can be directly isolated in several cases. In the case of irradiation of TCA with **1** (or other amines) in acetonitrile or aqueous acetonitrile solutions, there is a buildup of absorption in the visible which can be ascribed to the anion radical TCA^-. As reported elsewhere,[43,44] this anion radical is relatively stable in the absence of air and accumulates as a permanent product in moderately polar solvents concurrent with the oxidation of **1**.

The photoproducts derived from the α,β-amino alcohol consist of the carbonyl compound resulting from oxidation of the alcohol concurrent with cleavage of the C–C bond, a secondary amine and a second carbonyl compound. The latter two probably result from the corresponding iminium product; the reactions were typically carried out with ca. 3% water added to hydrolyze the iminium ion.[45-47] Thus, the net reaction is an extremely clean conversion of the amino alcohol to carbonyl compounds and free secondary amine as outlined in eq 1.

The stoichiometry was determined by correlating rates of bleaching of the acceptor (UV–vis absorption spectrum) with appearance of the oxidation products (HPLC, NMR, or GC analysis) from the amino alcohol. Analysis by NMR or HPLC indicated only the products as indicated in eq 1. For example, when **1** or **2** and TI are irradiated in an NMR tube new proton signals due to the aldehyde hydrogen of benzaldehyde and α_{C-H} of morpholine (ratio 1:2) appear as the photolysis proceeds. The yields of benzaldehyde from **1** and conversion of TI to TIH_2 (1.9:1) are consistent with the stoichiometry of eq 1. When TI is irradiated with **4** or **5**, proton signals for benzaldehyde, the substituted benzaldehyde, and the α_{C-H} of morpholine appear in the ratio 1:1:4; in all cases no signals due to *N*-benzylmorpholine or other possibly anticipated products from the amine can be detected. A summary of the products obtained from photolysis of TI with several different α,β-amino alcohols is given in Table I. Preparative scale photolysis of TI and **1** and a workup of the benzaldehyde produced in the reaction led to its recovery in 90% chemical yield. In

Table II. Quantum Yields of Photooxidative Fragmentation of *erythro*-**1** with or without Biphenyl in Acetonitrile[a]

	acetonitrile[b]		acetonitrile/biphenyl[b]	
donor/acceptor	ϕ_{red}	ϕ_{ox}	ϕ_{red}	ϕ_{ox}
erythro-**1**/DCA	*c*	0.0017	0.46	1.10
erythro-**1**/TCA	0.035	0.073	0.29	0.26

[a] Determinations were made with vacuum degassed solutions of the donor and acceptor (5×10^{-5} M). For the direct quenching experiments the donor concentration was calculated for 50% quenching, but the quantum yields were corrected to 100% quenching. For the biphenyl cosensitized studies, donor concentration was 5×10^{-3} M and biphenyl concentration was 0.25 M. Irradiation was performed with use of an Hanovia 450-W Hg lamp in a merry-go-round. Absorbance change was recorded on a Hewlett Packard 8451A Diode array spectrophotometer. Formation of benzaldehyde was analyzed on a Waters-990 HPLC. Quantum yields were determined with use of potassium ferrioxalate actinometry. [b] ϕ_{red} for DCA samples is the quantum yield of acceptor bleaching; ϕ_{red} for TCA samples is the quantum yield of growth of $TCA^{\bullet-}$. ϕ_{ox} is the quantum yield of benzaldehyde formation. [c] No observable reaction was detected.

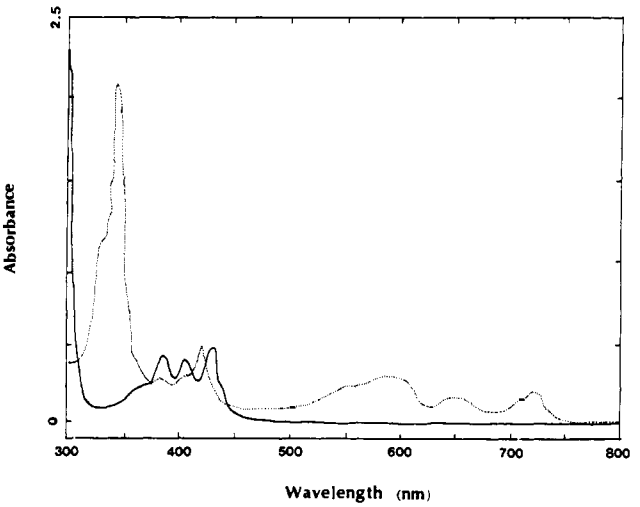

Figure 4. Absorbance of TCA in acetonitrile before irradiation (solid). Absorbance of TCA^- formed during photolysis with *erythro*-**1** in the presence of BP (0.25 M) in acetonitrile (broken curve).

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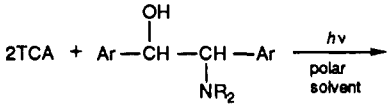
Table III. Anodic Peak Potentials of Various α,β-Amino Alcohols and the Corresponding Quenching Constants for Quenching Singlet TI through ET by These Donors

electron donors	oxidation peak potential,[a] eV vs SCE	quenching constant[b] k_q, M^{-1} s^{-1}	$-\Delta G^*$,[c] kcal/mol benzene	$-\Delta G^*$,[c] kcal/mol CH_3CN
erythro-**1**	1.05	2.13×10^9	9.50	19.15
threo-**1**	1.21	1.36×10^9	6.04	15.70
erythro-**2**	0.89	9.08×10^9	13.42	22.84
threo-**2**	0.95	5.32×10^9	12.04	21.46
3	1.20	2.53×10^9	6.27	15.70
4	1.10	2.89×10^9	8.58	18.00
5	1.11	2.62×10^9	8.35	17.77
6	1.11	2.72×10^9	8.35	17.77
7	1.09	2.76×10^9	8.81	18.23
8	0.83	1.03×10^{10}	14.80	24.23
9	0.79	1.26×10^{10}	15.73	25.15

[a] Oxidation potential peaks (the maximum oxidation peak for the irreversible anodic reaction) were measured in purified acetonitrile. The substrate concentration was ca. 1–3 mM. Tetrabutylammonium tetrafluoroborate (TBA·BF_4, 0.1 M) was used as the electrolyte. [b] Quenching experiments were carried out in benzene. TI was used as the electron acceptor (5×10^{-5} M in each case) with excitation at 546 nm. Dry argon was bubbled through the sample solutions for 20–30 min prior to each measurement. [c] Free energies for electron-transfer quenching of excited singlet TI as calculated by equations derived by Weller (ref 62a). Since oxidation of amino alcohols is irreversible, the oxidation potential of these α,β-amino alcohols should be lower than the oxidation peak potential. So, the photoinduced ET should be more exergonic than the ΔG^* listed in this table. $E_{red}(TI) = -0.45$ eV vs SCE. $E_{S0\rightarrow S1} = 2.28$ eV.

analytical-scale photolyses with cyclohexane as an internal standard, products according to eq 1 were obtained in the range of 60–87%.

Although *erythro*-**1** reacts very inefficiently under irradiation of DCA or TCA in acetonitrile solution, "cosensitization" with biphenyl (BP) leads to relatively efficient photoredox. Irradiation of DCA in the presence of biphenyl (0.25 M) and *erythro*-**1** (0.005 M) leads to rapid bleaching of the long-wavelength absorption of DCA and to efficient ($\phi = 1.1$) formation of benzaldehyde (Table II). Evidently reaction according to eq 1 is facilitated by the addition of biphenyl under conditions where it dominates the quenching of DCA.[48] For irradiation of TCA/*erythro*-**1** (0.005 M)/acetonitrile in the presence of 0.25 M biphenyl moderately efficient formation ($\phi = 0.26$) of benzaldehyde is observed together with bleaching of the absorption due to TCA; however in this case a clean accumulation of TCA^-, readily detected by its characteristic absorption spectrum, is observed (Figure 4). Thus the cosensitized reaction between TCA and *erythro*-**1** is as shown in eq 2. Biphenyl cosensitization with *threo*-**1** leads



$$2TCA^- + ArCHO + Ar'CHO + R_2NH \quad (2)$$

to the same quantum efficiency (within experimental error) as for the erythro isomer; the erythro ether **3** reacts under DCA–biphenyl cosensitization to give DCA bleaching with a quantum efficiency of 0.16.

Mechanistic Investigations of Photooxidative Fragmentation of α,β-Amino Alcohols via Quenching of Acceptor Excited Singlets. (a) Fluorescence Quenching. The reaction of excited singlet TI with α,β-amino alcohol donors was investigated by fluorescence quenching in both benzene and acetonitrile. Only the monomer emission of *trans*-TI was detected. No trans–cis photoisomerization of TI was observed under conditions where the amine concentrations were adjusted to quench more than 50% of the excited singlet TI. In all cases, fluorescence quenching showed typical Stern–Volmer behavior, from which the rate constant, k_q, for the quenching step was calculated, and the data are summarized in Table III. The lifetimes of unquenched excited singlet TI were measured as 9.1 and 13 ns in acetonitrile and benzene, respectively; these are consistent with reported values.[49]

Table IV. Quenching Rate Constants[a] of Excited Singlet Acceptor by *erythro*-**1**

electron acceptor	k_q in benzene, M^{-1} s^{-1} *erythro*-**1**	k_q in benzene, M^{-1} s^{-1} *threo*-**1**	k_q in CH_3CN, M^{-1} s^{-1} *erythro*-**1**	k_q in CH_3CN, M^{-1} s^{-1} *threo*-**1**
TI	2.1×10^9	1.4×10^9	1.3×10^{10}	1.1×10^{10}
DCA	4.1×10^9	3.9×10^9	1.4×10^{10}	1.2×10^{10}
TCA	9.9×10^9	9.1×10^9	3.2×10^{10}	2.8×10^{10}
DCN	7.8×10^9	7.2×10^9	1.3×10^{10}	1.2×10^{10}

[a] All samples were degassed by passing through dried argon gas for 30 min and sealed with parafilm prior to each measurement. The quenching experiments were carried out with 5×10^{-5} M acceptors and various concentrations of diastereomer **1**, 0.005–0.05 M. The quenching constants were obtained from more than five data points in each case by a Stern–Volmer plot.

For the cyanoaromatics, in the absence of an electron donor, fluorescence emission is observed from the first excited singlet state of cyanoaromatic monomer, with a single exponential decay. At low concentrations of donor (<0.05 M), only cyanoaromatic monomer emission was observed in benzene, and the quenching of the excited monomer follows a Stern–Volmer relationship, from which the rate constant was obtained (Table IV). A second emitting component was observed at high donor concentration in benzene, and two fluorescent lifetimes can be determined. One component is ascribed to monomer emission from the excited singlet cyanoaromatic, and its lifetime is significantly reduced as the concentration of donor increases. The second component appears at relatively longer wavelengths and can be attributed to an exciplex between ground state donor and excited cyanoaromatic.[50] Exciplex emission accompanies DCA fluorescence quenching by α,β-amino alcohols (**1**, **2**, **4**, **5**, **8**, and **9**) and by the α,β-amino ether (**3**). The emission is generally weak and appears at longer wavelengths; the exciplex fluorescence λ_{max} increases as E_{ox} decreases, and the emission intensity varies with the donor. The exciplex formed between excited DCA and the N-aromatic-substituted α,β-amino alcohols (**8** and **9**) shows over 100 times more intense exciplex emission than that of the exciplex between DCA and *N*-alkyl-substituted amino alcohols (**1**, **2**, and **4**) although **8** and **9** are better electron donors. The strongest emission was observed when **3** was used as a donor (concentration of DCA is 5×10^{-5} M, concentration of donor is 0.05 M (limited by the low solubility of **3** in benzene); under this low concentration condition, exciplex fluorescence is too weak to be detected for **1**, **2**, **4** and **5**. Exciplex fluorescence lifetimes in benzene with *erythro*-**1** as the donor are 8.6, 7.5, and 15.1 ns for DCA, TCA, and DCN, respectively; these lifetimes are independent of the concentration of donor. No exciplex emission could be detected in acetonitrile for any of the amino alcohols.

(b) Diastereomeric Selectivity in Photofragmentation. Amino alcohols **1** and **2** were investigated as individual diastereomers and their reactivity compared under photolysis of the different acceptors. It was found that in each case, for equivalent concentrations of individual diastereomers, there is a greater efficiency for reaction of the erythro over the threo isomer. For example, for irradiation of dilute solutions of TI with 0.05 M donor in benzene reactivity ratios, erythro/threo, are 6.0 for **1** and 6.7 for **2**. As data in Table III indicate, for both **1** and **2** the erythro isomer is a more efficient quencher of acceptor fluorescence than the threo isomer. This parallels the difference in oxidation potential and is general for all four fluorescent acceptors used in this investigation. The difference in oxidation peak potentials for

(48) Fluorescence quenching rate constants for DCA and TCA with biphenyl in acetonitrile are 3.6×10^9 and 2.0×10^{10} M^{-1} s^{-1}, respectively. Biphenyl (0.25 M) quenches 92% $^1DCA^*$ and 98% $^1TCA^*$ via electron transfer process, respectively, which efficiently compete with direct electron transfer between DCA or TCA and donor. Under these conditions, the majority of the photooxidative fragmentation is initiated through cosensitization.

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Table V. The O–H Stretching Frequencies in Diastereomers of α,β-Amino Alcohols

stereoisomer	O–H stretching freq, cm^{-1} in CH_2Cl_2 solution[a]		O–H stretching freq, cm^{-1} in solid phase[b]	
erythro-**1**	3428.6	120.3	3472.6	127.3
threo-**1**	3308.3		3345.3	
erythro-**2**	3436.4	191.5	3471.4	196.5
threo-**2**	3244.9		3274.8	

[a] Infrared spectra were measured in purified CH_2Cl_2 with the same amine concentration as that in photolysis experiments, where 50% of the excited TI was quenched in each case, i.e. *erythro*-**1** was 0.0236 M and *threo*-**1** was 0.0506 M. [b] Solid samples were prepared by mixing amine donors (1–3 mg) with dried KBr. The measurement was conducted under N_2 atmosphere.

Table VI. Quantum Efficiency[a] and Diastereomeric Selectivity of Photooxidative Fragmentation at Various Temperatures

temp, °C	$\Phi_{frag(erythro\text{-}1)}$	$\Phi_{frag(threo\text{-}1)}$	$\Phi_{(erythro\text{-}1)}/\Phi_{(threo\text{-}1)}$
−63	8.6×10^{-3}	2.1×10^{-4}	42.1
−20	1.9×10^{-2}	1.3×10^{-3}	15.4
0	3.3×10^{-2}	4.1×10^{-3}	8.2
21	4.4×10^{-2}	7.9×10^{-3}	5.6
35	7.7×10^{-2}	4.6×10^{-2}	1.7
55	9.5×10^{-2}	8.4×10^{-2}	1.12
75	0.13	0.12	1.13

[a] Samples were prepared in toluene and vacuum degassed through freeze–pump–thaw cycles. TI (5×10^{-5} M) used as electron acceptor was irradiated at 540 nm. The concentration of donor was adjusted through quenching correction at each temperature to ensure 50% of the excited TI was quenched in each case. Quantum yields were obtained by the method described in the Experimental Section.

the erythro and threo diastereomers of **1** and **2** may be correlated with differences in the infrared spectra of the two isomers[51,52] which clearly show intramolecular hydrogen bonding for the two threo isomers characterized by an O–H stretch appearing at lower frequencies for both solid and solution samples with a broadened peak and enhanced intensity, compared with the erythro isomers (Table V).

Although differences in fluorescence quenching rate constants should account for part of the increased reactivity of erythro isomers compared to the corresponding threo, the larger part of the difference in overall reaction efficiency is attributed to a difference in reactivity subsequent to the quenching process. To compensate for differences in the quenching step, reaction quantum efficiencies were compared by using concentrations of individual diastereomers producing the same percentage of quenched excited acceptor in each case. For example, for reactions of TI with **1** and **2** there is a net 3- to 4-fold reactivity difference favoring the erythro isomer after correction for the differences in excited state quenching. In the case of reaction between TI and amino alcohol **1**, the quantum efficiencies and diastereomer selectivity were found to show considerable variation when examined over the temperature range −60 to 75 °C in toluene. Data listed in Table VI show that the erythro/threo selectivity (after correction for quenching differences) decreases from 42 to 1.1 as the temperature is increased in this range. The cyanoaromatic electron acceptors also exhibit a preference for reaction of erythro over threo diastereomers for **1** and **2**; Table VII compares the reactivity of the diastereomers of **1** with TI and the cyanoaromatics in benzene. As mentioned above, the diastereomeric selectivity with **1** disappears when the reaction is carried out in acetonitrile via biphenyl cosensitization.

(c) Reactivity of Different Electron Donors. The quantum efficiency of photooxidative fragmentation of the α,β-amino alcohols shows a strong dependence upon the structure of the electron donor. Different efficiencies of acceptor bleaching or fragmentation (as detected by product formation) were observed

Table VII. Quantum Efficiency and Diastereomeric Selectivity in C–C Bond Cleavage of α,β-Amino Alcohols with Different Electron Acceptors

quantum yield[a]	TI	DCA	TCA	DCN
$\Phi_{frag(erythro\text{-}1)}$	4.4×10^{-2}	6.7×10^{-3}	1.4×10^{-3}	6.6×10^{-5}
$\Phi_{frag(threo\text{-}1)}$	7.9×10^{-3}	3.5×10^{-4}	5.2×10^{-5}	1.1×10^{-6}
$\Phi_{(erythro\text{-}1)}/\Phi_{(threo\text{-}1)}$	5.6	19	27	62

[a] All samples were prepared in benzene and vacuum degassed through freeze–pump–thaw cycles. The concentration of electron acceptors used was 5×10^{-5} M, and the concentration of donors was adjusted to quench 50% of the excited electron acceptors in each case. Irradiation at room temperature was carried out under a 200-W Hg lamp with appropriate filters to isolate the maximum absorption band for each electron acceptor. Quantum yields of reduction of electron acceptors were measured by monitoring bleaching of acceptor absorbance, which directly reflects the quantum yields of C–C bond cleavage shown in eq 1. Light intensity was corrected by actinometer.

Table VIII. Structural Dependence of C–C Bond Cleavage of α,β-Amino Alcohols

α,β-amino alcohol	Φ_{frag}[a]	α,β-amino alcohol	Φ_{frag}[a]
erythro-**1**	4.4×10^{-2}	**5**	2.6×10^{-2}
threo-**1**	7.9×10^{-3}	**6**	9.0×10^{-2}
erythro-**2**	11.0×10^{-2}	**7**	9.3×10^{-2}
threo-**2**	4.3×10^{-2}	**8**	1.8×10^{-3}
4	4.1×10^{-2}	**9**	9.7×10^{-4}

[a] Samples were prepared in benzene with TI (5×10^{-5} M) as the electron acceptor and vacuum degassed through freeze–pump–thaw cycles. Concentration of various α,β-amino alcohols was adjusted through quenching correction to ensure 50% of the excited TI was quenched in each case. Parallel photolysis (at room temperature) was conducted in merry-go-round with appropriate filters to isolate the peak at 540 nm. Φ_{frag} was measured by HPLC analysis of C–C bond cleavage products, carbonyl compounds (benzaldehyde, substituted benzaldehyde, and acetophenone). Light intensity was monitored by a secondary actinometer described in the Experimental Section.

Table IX. Isotope Effect on C–C Bond Cleavage of α,β-Amino Alcohols

isotope effect[a]	TI	DCA	TCA	DCN
ϕ_H/ϕ_D(*erythro*-**1**)[b]	1.34	1.70	2.13	3.67
ϕ_H/ϕ_D(*threo*-**1**)	1.26	2.50	3.28	4.01

[a] Samples were prepared in benzene by adding either 3% H_2O or D_2O, vacuum degassing through freeze–pump–thaw cycles, and sealing at $p < 3 \times 10^{-6}$ Torr. Concentration of acceptor was 5×10^{-5} M, and concentration of donors was adjusted to quench 50% of the excited acceptor in each case. Irradiation was carried out at room temperature under a Hg lamp with filters to isolate the maximum absorption peak for different acceptors. The rate of C–C bond cleavage was obtained by measuring the bleaching of absorbance of acceptor. [b] $k_H/k_D = \phi_H/\phi_D$, according to eq 10, since $k_{BET} \gg k_{frag}$ in this case.

for the different amino alcohols with TI in benzene after correction for differences in quenching rate constants (Table VIII). The variation of reactivity with amino alcohol structure shows three general trends: higher reactivity is always observed for an erythro isomer over a threo isomer as discussed above; higher reactivity is also observed for **6** or **7**, compared to **1**, **2**, **4**, and **5**, by introducing a methyl group on the C–C bond which is cleaved, and lower reactivity is observed when compounds **8** and **9** are used as electron donors (*N*-aromatic-substituted amino alcohols), compared with *N*-alkyl-substituted amino alcohols.

There is also a pronounced isotope effect on reactivity in benzene as indicated in Table IX. From NMR it can be shown that the addition of 3% D_2O to a benzene solution results in exchange of the O–H to O–D as the only proton exchange. For all the acceptors used in this study this deuterium for hydrogen substitution results in a decrease in reactivity as reflected in the ratio of quantum efficiencies for nondeuterated vs deuterated samples. The magnitude of this isotope effect increases in the series TI, DCA, TCA, and DCN and is somewhat larger for *threo*-**1** compared to *erythro*-**1**. Attempts were made to determine whether the isotope effect persists in acetonitrile; however, the quantum

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Table X. Solvent Effect on C–C Bond Cleavage of α,β-Amino Alcohol **1** with TI

quantum yield[a]	benzene	CH_2Cl_2	CH_3CN
$\Phi_{frag(erythro\text{-}1)}$	4.4×10^{-2}	1.1×10^{-2}	2.9×10^{-5}
$\Phi_{frag(threo\text{-}1)}$	7.9×10^{-3}	1.2×10^{-3}	1.5×10^{-6}
$\Phi_{(erythro\text{-}1)}/\Phi_{(threo\text{-}1)}$	5.6	9.4	19.3

[a] All samples were vacuum degassed through freeze–pump–thaw cycles. Irradiation was conducted at room temperature under a 200-W Hg lamp with filters to isolate the peak at 540 nm. TI was used as the electron acceptor with a concentration of 5×10^{-5} M. The concentration of donors was adjusted to quench 50% of the excited TI in each case. Quantum yields of the reduction of TI were obtained by monitoring absorbance changes during continuous photolysis (less than 15% conversion) according to the method described in the Experimental Section. Light intensity was corrected by a secondary actinometer.

efficiency is so low that efforts to measure an isotope effect were inconclusive. Deuterated and nondeuterated samples of *erythro*-**1** were found to react at the same rate, within experimental error, with DCA in acetonitrile.

(d) Dependence of Reactivity on Electron Acceptor. As indicated by data in Table VII, reaction quantum efficiencies show a strong variation with electron acceptor and the general trend, typified by data with *erythro*- and *threo*-**1** as indicated in the Table VII, is that reactivity in benzene decreases in the series TI, DCA, TCA, and DCN. Compared with TI, all three cyanoaromatics are better electron acceptors in their excited states, and electron-transfer quenching of cyanoaromatic fluorescence occurs in each case with near diffusion controlled rates, but with a small erythro/threo preference (Table IV). The erythro/threo selectivity of the fragmentation in benzene also shows an increase as the reaction efficiency decreases in the series of acceptors, as described above.

(e) Solvent Dependence of the Photofragmentation. Although reaction occurs cleanly as described in eq 1 for the various combinations of amino alcohol donors and fluorescent electron acceptors, reaction efficiency for TI as the acceptor shows a strong sensitivity to solvent as indicated in Table X. As to cyanoaromatics, the reaction efficiency for DCA also decreases with solvent polarity, and no observable reduction of DCA can be detected in acetonitrile. In contrast, the reaction efficiency for TCA increases sharply as the solvent is changed from benzene to acetonitrile (Table II). For benzene solutions, addition of water, while not effecting the chemical reaction observed as shown in eq 1, produces a sharp decrease in reaction efficiencies.

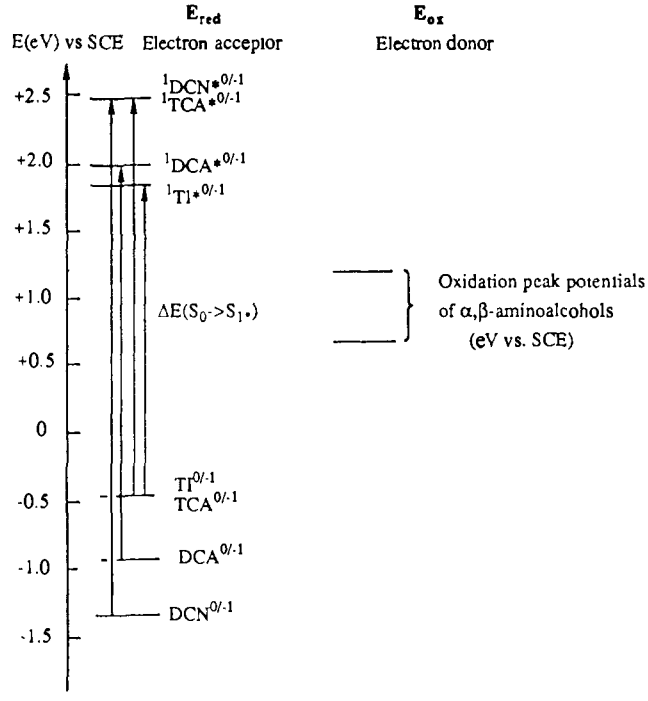
(f) Chemical and Electrochemical Oxidation of α,β-Amino Alcohols. As indicated in Table III, all the amino alcohols used in this study show electrochemical oxidations that are electrochemically irreversible in the range 0.8–1.2 eV vs SCE. Electrochemical oxidation of **1** in argon-saturated tetrahydrofuran leads to the relatively clean production of benzaldehyde and morpholine; a similar experiment with **4** leads to detection of equimolar amounts of benzaldehyde, *p*-chlorobenzaldehyde, and morpholine as detected by gas chromatography–mass spectrometry.

1 was also subjected to chemical oxidation by O_2SbF_6 (a very strong oxidant)[53] in $CHClF_2$ (−125 °C) and in CH_2Cl_2 (−90 °C) in the absence of oxygen.[54] After the solution was warmed to room temperature and subsequent evaporation of the solvent, the residue was found to contain benzaldehyde (NMR) as a major product. Although morpholine was also detected, several unidentified products were also present, suggesting that this oxidation may be accompanied by other reactions.

Discussion

All of the photoreactions investigated in this study are initiated by excitation of the electron acceptors, since none of the donors involved absorb beyond 300 nm. The quenching of acceptors in excited singlet states by the amino alcohol donors involves electron transfer and appears reasonable from the energetics presented in

Scheme I. Energetic Diagram of Redox Properties of Electron Donor and Acceptor



Scheme I. Application of the "Weller equation"[62d] indicates that electron-transfer quenching should be favorable on energetic grounds (Table III); since the oxidation of amino alcohols **1–7** is not electrochemically reversible, the use of these potentials in determining the energetics of the overall electron transfer must be made with some caution. On the other hand, the observation that cations of the amino alcohols are unstable and give fragmentation products identical with those observed in the photolysis (vide infra) gives support to an electron-transfer mechanism for the oxidative photofragmentation.

While single electron transfer (SET) quenching of excited singlets of the electron acceptors is a likely starting point for the fragmentation reactions described in this study, the precise intermediates and mechanisms involved can be quite dependent both on the medium and the specific substrate structures involved. Thus, as has been shown in a number of recent investigations, SET quenching processes involving neutral donors and acceptors in organic solvents can lead to at least three different sets of radical ion intermediates, depending chiefly upon solvent polarity for intermolecular reactions in homogeneous solution.[55-62] In solvents of low polarity ($\epsilon < 7$), electron-transfer quenching gives rise primarily to contact radical ion pairs or exciplexes (CRIP); these are the lowest energy species in nonpolar solvents and most photoinduced electron-transfer reactions in these solvents will proceed exclusively via the CRIP. In solvents of moderate polarity ($\epsilon = 7$–40) quenching can involve direct formation of either a CRIP or a solvent separated radical ion pair (SSRIP); generally

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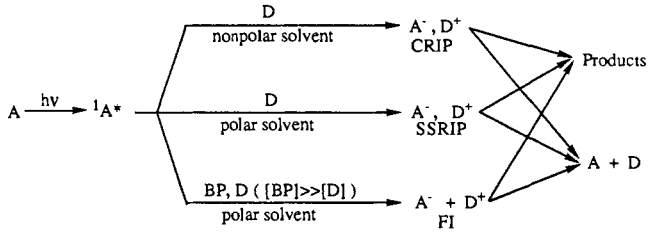
Scheme II. Different Electron Transfer Intermediates from Photolysis of an Acceptor (A) and Quenching of Its Excited Singlet A* by SET in Solution



the latter is of lower energy so that its collapse to a CRIP is unlikely. However the CRIP may undergo "solvation" to generate a SSRIP. Lifetimes of both the CRIP and SSRIP are governed by relatively rapid back electron transfer processes; while back electron transfer rates are subject to the usual "Marcus relationships", differences in the influence of external vs. internal reorganization energies play major roles in controlling the different sensitivities to energetics for the two species. For the donor–acceptor combinations used in this study in the solvents involved (benzene, methylene chloride, and acetonitrile) it is anticipated that these back electron transfer reactions will be much more rapid than cage escape so that all of the reactions except for the biphenyl cosensitization should involve primarily radical ion pairs (vide infra). On the other hand, studies of DCA and TCA with biphenyl (BP) have shown that biphenyl is an effective cosensitizer,[63-66] and its quenching of the cyanoaromatic excited singlet states in acetonitrile leads to free ions (FI) with efficiencies of 0.83 and 0.25, respectively.[67] Since the oxidation potential of biphenyl (1.84 eV vs SCE) is higher than those of the amino alcohols by a sufficient magnitude to ensure complete reaction, it is possible to generate cyanoaromatic radical anions and amino alcohol cation radicals as kinetically free ions through this means (cosensitization shown in eqs 3–6). Thus, by varying the solvent environment

$$A^* + BP \rightarrow A^-, BP^+ \quad (3)$$

$$A^-, BP^+ \rightarrow A^- + BP^+ \quad (4)$$

$$BP^+ + D \rightarrow BP + D^+ \quad (5)$$

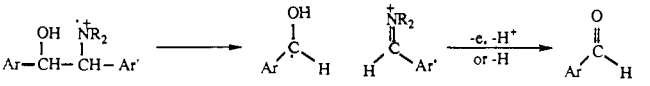
$$\text{net reaction:} \quad A^* + D \xrightarrow{BP} A^- + D^+ \quad (6)$$

and by employing both direct and cosensitized electron transfer quenching paths, for a given donor–acceptor combination the three distinct intermediates can be generated and their reactivity investigated as outlined in Scheme II.

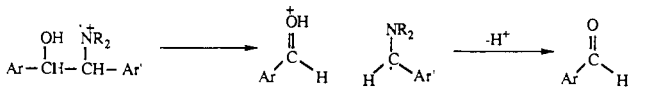
The predominant feature of the overall reaction according to eq 1 is the oxidative fragmentation of the donor amino alcohols. Therefore, it is worth beginning a discussion of the mechanism for the photoreaction with an overview of the reactivity of "free" cation radicals of the amino alcohols. Not surprisingly, we find that both chemical and electrochemical SET oxidation of amino alcohols such as **1** leads to net two electron redox reactions as outlined in eq 1. That these cations should fragment is in accord with both direct experimental and thermochemical studies which indicate the carbon–carbon bond flanked by two heteroatoms should have a very low bond dissociation energy for the cation radical.[23a] It seems most reasonable that the cation radical of amino alcohols such as **1** is centered on nitrogen, since the oxidation potentials of the amino alcohols are more than 0.5 eV lower than those of the corresponding diols.[68] The cleavage of amino

Scheme III. Possible Mechanisms of C–C Bond Cleavage in Radical Cation of α,β-Amino Alcohols

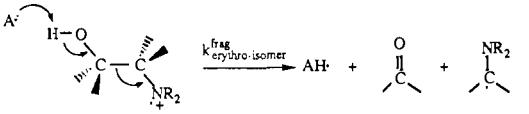
1. Homolytic Cleavage, Followed by Oxidation of Alcohol Fragment



2. Heterolytic Cleavage, Followed by Deprotonation of Oxy Fragment



3. Concerted Cleavage: Concerted Proton Loss and C-C Bond Cleavage



alcohol cation radicals then could be viewed as shown in Scheme III as either a homolytic cleavage or heterolytic cleavage; the former is in accord with the observed fragmentation pattern for these amino alcohol cations in the gas phase (mass spectrometry) while the latter is equally plausible in solution.

That fragmentation of the cation radical of **1** does occur on a reasonable time scale is indicated by the biphenyl (BP) cosensitization experiments of **1** with DCA and TCA. As mentioned above, these cosensitization experiments result in high yields of free ions and, with each cyanoaromatic as the photoexcited electron acceptor and **1** as the "secondary" donor, the quantum yields of benzaldehyde in the cosensitized reaction are significantly increased as anticipated with the increase of yields of free ions. The high efficiency for reaction under conditions where FI are generated in a moderately polar solvent (acetonitrile) is in accord with an expectation that under the relatively low steady state light levels (light intensity = 8.3×10^{-10} einstein s^{-1}), cation–anion annihilation will be too slow to effectively compete with the unassisted fragmentation of $\mathbf{1}^+$. That the acceptor anion radical plays little role under conditions where FI are involved is indicated by the finding that while DCA is ultimately reduced to $DCAH_2$, TCA is simply converted to its one electron reduction product TCA^-. In fact, the quantum efficiency of reaction between TCA and **1** (with BP) is not attenuated by the accumulation of TCA^- up to a concentration $[TCA^-] = 10^{-5}$ M; this suggests that unassisted fragmentation is more rapid than bimolecular back electron transfer. If we assume the rate constant for the latter process is diffusion controlled, this suggests that for the unassisted process, $k_{frag} \geq 10^5$ s^{-1}. Not surprisingly, it is found that *erythro*-**1** and *threo*-**1** give the same quantum efficiency under cosensitization with DCA–BP and even **3**, which is unreactive in the direct quenching experiments, shows moderate efficiency for net reduction of DCA with DCA–BP in acetonitrile.

The low quantum efficiencies for "direct" electron transfer oxidation of **1** or the other amino alcohols by the cyanoaromatics in solvents such as benzene or acetonitrile indicate that FI are not the major products under these conditions. The rate constant for cage escape of oppositely charged cations in acetonitrile is ca. 5×10^8 s^{-1}.[62d,67] For the cyanoaromatics and the various amino alcohols used in this study exothermicities for back electron transfer are in the range −1.5 to −2.5 eV; from studies of back electron transfer rates vs reaction exothermicity for structurally similar donor–acceptor combinations, it has been shown that the maximum rate constants are obtained for SSRIP with rate constants $k \sim 1\text{–}5 \times 10^{10}$ s^{-1} for $\Delta G_{et} \sim -2$ eV.[62e,67b] If we assume similar values for back electron transfer and cage escape from an initially formed SSRIP, about 1–10% of the quenching should

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(68) Cyclic voltammetry measurement of pinacols in acetonitrile gives an irreversible oxidation peak; their peak potentials are E_p = 1.63 and 2.05 eV vs SCE for hydrobenzoin and benzopinacol, respectively.

lead to FI, which accounts for the observed fragmentation in acetonitrile.

A general mechanism for the radical ion pair fragmentation is given by eqs 7–9 where α represents the fraction of "products"

$$A^* + D \xrightarrow{k_{ET}} (A^-, D^+) \quad (7)$$

$$(A^-, D^+) \xrightarrow[k_{frag}]{\alpha} \rightarrow \rightarrow \text{fragmentation products} \quad (8)$$

$$(A^-, D^+) \xrightarrow{k_{bet}} A + D \quad (9)$$

from the initial process, which competes with back electron transfer, that go on to the final observed products. In this treatment we assume initially that none of the observed reaction can be attributed to FI resulting from cage escape (vide supra); while this may be invalid for acetonitrile solutions or water–acetonitrile, it is surely a reasonable assumption for less polar solvents such as benzene or methylene chloride (vide infra). The observed quantum efficiencies for fragmentation should be given by eq 10 if it is assumed that excited state quenching to form the

$$\Phi_{frag} = \frac{\alpha k_{frag}}{k_{frag} + k_{bet}} \quad (10)$$

radical ion pair (CRIP or SSRIP) is totally efficient and that other decay processes from the radical ion pair (such as exciplex fluorescence from the CRIP) can be neglected.

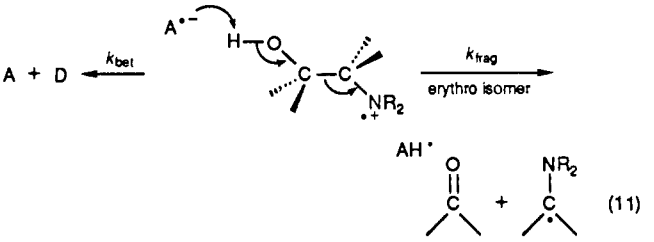
As outlined in Scheme III, there are several possible mechanisms for the fragmentation within the photogenerated radical ion pairs. As pointed out above, the free donor cation radicals could undergo "unassisted" fragmentation, although with the data available it is difficult to estimate the rate of this reaction or how it might be influenced by solvent, etc. The concerted mechanism involves "assistance" from the reduced acceptor and should be sensitive to ion pair separation as well as the basicity or nucleophilicity of A^-.

If we examine reactivity in benzene and toluene, where it is likely that cage escape is very slow ($k \sim 10^6$ s^{-1} or slower),[62d,63] all of the reaction is probably occurring within the CRIP. As results listed in Tables VII and IX indicate, there is a strong dependence of the reaction efficiency on acceptor structure as well as a significant isotope effect upon replacement of the O–H by O–D. These results give strong support for a concerted mechanism as outlined in Scheme III. While the isotope effects listed in Table IX are the ratios of quantum efficiencies, if it is assumed that the reaction efficiency is described by eq 10 and only k_{frag} is subject to an isotope effect, the values observed correspond to small-to-moderate primary kinetic isotope effects. The isotope effect is quite reasonably smaller for "reactive" acceptors such as TI and relatively large (ϕ_H/ϕ_D = 3–4) for the less reactive acceptors TCA and DCN.

The effects of acceptor structure and donor stereochemistry need to be evaluated in terms of eq 11, considering both k_{bet} and k_{frag}. The back electron transfer process is exergonic by 1.5–2.5 eV for the four acceptors and **1**, with the order in increasing exergonicity being TI < TCA < DCA < DCN. For CRIP's it appears reasonable that these exergonicities all should fall into the "inverted" region of free energy dependence and hence the order of k_{bet} should be TI > TCA > DCA > DCN. Clearly this is *not* the order of reaction efficiencies and the observed order reflects a large variation in the values of either α or, more likely, k_{frag}. Similarly, since the oxidation potential of *erythro*-**1** is lower than that of *threo*-**1** (and the same is true for other diastereomeric amino alcohols), the erythro/threo preference for reactivity (after correcting for quenching differences) reflects both a probable back electron transfer ratio ($k_{bet}^{erythro}/k_{bet}^{threo}$) < 1 and hence a ratio ($k_{frag}^{erythro}/k_{frag}^{threo}$) > 1. In other words, the quantum yield ratios can be used to estimate a *minimum* value for the erythro/threo fragmentation reactivity.

Although the base strengths of the acceptor anion radicals (A^-) are not known with certainty, especially in a relatively poorly solvating medium such as benzene, toluene, or methylene chloride, it is reasonable to infer that for three of the acceptors used, the order of increasing base strength is $TCA^- < DCA^- < TI^-$.[24d] This coincides with the order of increasing reactivity in benzene (even when the considerations of k_{bet} dependence discussed above are made) and, taken together with the observed isotope effects, these results provide strong support for a concerted mechanism for fragmentation such as that outlined in Schemes III where A^--mediated deprotonation accompanies the fragmentation. That fragmentation occurs concurrently with proton transfer from alcohol to acceptor radical anion is also supported by the finding that the amino ether (**3**) quenches excited acceptors well (Table III) but gives very inefficient fragmentation according to eq 1.

The larger values of k_{frag} for erythro diastereomers compared to the corresponding threo isomers for **1** and **2** in benzene, toluene, or methylene chloride are consistent with a preference for an anti stereochemistry in the cleavage process (eq 11). A similar diastereomeric selectivity has been observed in "even electron"



(11)

electrophilic fragmentations such as the base-catalyzed solvolysis of γ-hydroxy halides,[69] oxidative electrolysis of γ-hydroxy carboxylic acids,[70] and the gas phase fragmentation of cations.[71–73]

As shown in Table VI the fragmentation quantum efficiencies for *erythro*- and *threo*-**1** mediated by irradiation of TI in toluene show an increase with increase in temperature, together with a decrease in erythro/threo selectivity, after correction for differences in the extent of fluorescence quenching. If we assume that the efficiency is given by eq 10, and that α and k_{bet} are independent of temperature, a plot of ln ϕ_{frag} (quantum efficiency corrected for quenching) vs $1/T$ should be linear, yielding an Arrhenius activation energy for the fragmentation. Such plots show good linearity for both diastereomers over the range −63 to +75 °C and permit estimates of E_a = 2.8 and 4.9 kcal/mol for *erythro*-**1**:TI and *threo*-**1**:TI, respectively. These energies compare reasonably well with, but are somewhat lower than, the 4–8 kcal/mol bond dissociation energies estimated via thermochemical cycle calculations for simple amino alcohol cation radicals.[23a]

To summarize, the behavior observed with the excited singlets of the acceptors TI, DCA, TCA, and DCN and amino alcohols **1**–**7** in nonpolar solvents is consistent with overall reaction according to eq 1, proceeding via electron transfer to give the CRIP, and subsequent reaction as outlined in eqs 12–16. The critical step determining the overall efficiency is the fragmentation which must compete with back electron transfer, which for CRIP's may have rate constants, for $\Delta G \sim -1$ to 2 V, $k_{bet} \sim 10^{11}$ s^{-1} or greater. This suggests $k_{frag} = 10^6$–10^9 s^{-1} (or greater) with the magnitude of the spread largely attributable to reactivity of A^- for the systems investigated.

The striking (>100-fold) decrease in reactivity as the solvent is varied in the series benzene, methylene chloride, and acetonitrile for the pair TI–**1** could be attributed to a number of different factors. Electron-transfer quenching in benzene generates a CRIP with little solvation of the ion radicals; consequently their individual reactivities should be quite high, compared with the partially solvated ions of a CRIP generated in more polar solvents. (Ev-

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idence for solvation of CRIP's is provided by the frequently observed red shifts of exciplex fluorescence as solvent polarity increases.[74-76] However, the complete absence of exciplex fluorescence in acetonitrile, compared to benzene, for amino alcohol–cyanoaromatics suggests that both the yield and lifetime of CRIP's in acetonitrile may be very low. A number of investigations have suggested that direct formation of the SSRIP may occur in more polar solvents.[77] Probably the most reasonable explanation for the drastically lowered reactivity of TI–**1** (and TI with other amino alcohols) in more polar solvents is the change in the predominant electron transfer quenching intermediate from CRIP to SSRIP. This should effectively eliminate or greatly retard the A^- assisted fragmentation outlined in eq 11 since it requires contact between A^- and D^+ while back electron transfer can occur across distances greater than collisional.

Interestingly, while reactivity for the combination TI–**1** decreases as the solvent is changed from benzene to acetonitrile, reactivity increases for TCA with **1**. As noted above, for TCA, considering estimated rate constants for k_{bet} and cage escape in acetonitrile, it is expected that between 1 and 10% of the excited state quenching events should lead to FI. The quantum efficiency for benzaldehyde from **1** with TCA is 0.073; since these should be twice the initial yield of SET products (see eqs 12–16), the values obtained are consistent with most of the reactivity in acetonitrile being attributable to the FI forming via cage escape. Thus, there may be little or no fragmentation occurring in the SSRIP's themselves. It is probably reasonable that the rate constant, k_{frag}, in the SSRIP in acetonitrile is very close to that for FI in the same solvent. If we assume a value close to that estimated above for FI, $k_{frag}^{1+\bullet} \sim 10^6\ s^{-1}$, it is quite reasonable that very little reaction should occur in competition with back electron transfer.

Mechanistically the most significant aspects of this study are the sharp demarcation of reactivity between the different electron transfer intermediates that can be produced from a common donor–acceptor pair together with the demonstration that contact radical ion pairs generated in poorly solvating nonpolar solvents can have enhanced reactivity compared to solvated ions in more polar solvents. "Cooperative" fragmentation in which the acceptor anion radical A^- assists the C–C bond cleavage by proton removal occurs predominantly within the CRIP, while it is not very effective in the SSRIP. On the other hand, it is reasonable to conclude from the cosensitization experiments that the free ions, D^+, generated in acetonitrile have a high probability of fragmentation during the lifetime limited by bimolecular ion recombination. These results together with those from other investigations of rather different donor–acceptor combinations suggest novel and useful chemistry via exciplex reactions may be quite general.

Experimental Section

Preparation and Purification of Materials. (a) Synthesis. *erythro*-2-Morpholino-1,2-diphenylethanol (1) was prepared through 12 h of reflux of a mixture containing 5 g of *trans*-stilbene oxide and 5 molar equiv of distilled morpholine with vigorous stirring. The reaction was monitored by silica gel TLC analysis until the stilbene epoxide had disappeared. The product was extracted with diethyl ether, and excess morpholine was separated by addition of 20 mL of distilled water. The combined organic layers were washed with distilled water five times to completely remove residual morpholine. Upon drying the solution over anhydrous magnesium sulfate, the solvent was removed on a rotary evaporator. The crude product was recrystallized five times from absolute ethanol, resulting in white plates (75%, mp 123–124 °C). ^{1}H NMR (300 MHz) in $CDCl_3$: δ 2.55 (m, 2 H), 2.68 (m, 2 H), 3.33 (s, 1 H), 3.37 (d, J = 3 Hz, 1 H), 3.76 (m, 4 H), 5.35 (d, J = 3 Hz, 1 H), 6.99 (m, 4 H), 7.38 (m, 6 H). Anal. Calcd for $C_{18}H_{21}NO_2$: C, 76.30; H, 7.57; N, 5.01. Found: C, 76.25; H, 7.55; N, 4.93.

***threo*-2-Morpholino-1,2-diphenylethanol** was made similarly by with *cis*-stilbene oxide. White flake-like powder was obtained after recrystallized 5 times from absolute ethanol (59%, mp 148–150 °C). ^{1}H NMR (300 MHz) in $CDCl_3$: δ 2.42 (m, 2 H), 2.68 (m, 2 H), 3.58 (d, J = 9 Hz, 1 H), 5.07 (d, J = 9 Hz, 1 H), 5.09 (s, 1 H), 7.07–7.24 (m, 10 H). Anal. Calcd for $C_{18}H_{21}NO_2$: C, 76.30; H, 7.57; N, 5.01. Found: C, 76.13; H, 7.49; N, 4.92.

The ether **1-methoxy-2-morpholino-1,2-diphenylethane** (MDBOMe, **3**) was prepared from the corresponding *erythro*-MDBOH with NaH and CH_3I in THF. *erythro*-**1** (3 g, 0.011 mol) was dissolved in 20 mL of purified THF, and the solution was saturated with nitrogen for 20 min to prevent condensation of moisture. Sodium hydride (0.27 g, 0.01 mol) was added once into the solution which had been cooled in an ice–salt bath under N_2. The solution became slightly greenish after 3 h of stirring. Iodomethane (0.7 mL, 0.011 mol) was slowly added with a syringe. The reaction proceeded at room temperature under vigorous stirring for 3 h. Sodium iodide precipitates were removed by filtration, and THF was removed under reduced pressure. The crude product was recrystallized 5 times from absolute ethanol (41%, mp 78–80 °C). ^{1}H NMR (300 MHz) in $CDCl_3$: δ 2.44 (m, 2 H), 2.49 (m, 2 H), 3.22 (s, 3 H), 3.38 (d, J = 6 Hz, 1 H), 3.65 (t, J = 6 Hz, 4 H), 4.75 (d, J = 6 Hz, 1 H), 7.04–7.23 (m, 10 H). Anal. Calcd for $C_{19}H_{23}NO_2$: C, 76.74; H, 7.79; N, 4.70. Found: C, 76.28; H, 7.63; N, 4.59.

***erythro*- and *threo*-2-pyrrolidinyl-1,2-diphenylethanol (2)** were prepared by refluxing *trans*- and *cis*-stilbene epoxide, respectively, with freshly distilled pyrrolidine. The products were recrystallized 5 times from absolute ethanol and dried in a vacuum oven overnight to yield white crystals. *erythro*-**2** (62%, mp 91–92 °C): ^{1}H NMR (300 MHz) in $CDCl_3$: δ 1.86 (m, 4 H), 2.62 (m, 2 H), 2.78 (m, 2 H), 3.31 (d, J = 3 Hz, 1 H), 5.27 (d, J = 3 Hz, 1 H), 6.93–7.16 (m, 10 H). Anal. Calcd for $C_{18}H_{21}NO$: C, 80.86; H, 7.92; N, 5.24. Found: C, 80.95; H, 7.55; N, 5.13. *threo*-**2** (69%): ^{1}H NMR (300 MHz) in $CDCl_3$: δ 1.72 (m, 4 H), 2.51 (m, 2 H), 2.65 (m, 2 H), 3.84 (d, J = 9 Hz, 1 H), 5.02 (d, J = 9 Hz, 1 H), 5.27 (s, 1 H), 7.11–7.27 (m, 10 H). Found: C, 81.30; H, 7.98; N, 5.06.

***erythro*-2-Morpholino-2-(4-chlorophenyl)-1-phenylethanol (4)** was obtained through a four-step synthesis from *p*-chlorobenzaldehyde in 31% overall yield, including a benzoin condensation, chlorination, amine substitution, and reduction of the ketone. The same molecule was also prepared by reaction between the *trans*-4-chloro-substituted stilbene oxide and purified morpholine according to the procedure described above. The product was purified by recrystallization 6 times from absolute ethanol and dried under vacuum oven overnight to yield white crystals (70%, mp 142–144 °C). ^{1}H NMR (300 MHz) in $CDCl_3$: δ 2.35 (m, 2 H), 2.65 (m, 2 H), 3.3 (d, J = 3 Hz, 1 H), 3.38 (s, 1 H), 3.73 (m, 4 H), 5.29 (d, J = 3 Hz, 1 H), 6.86–7.15 (m, 9 H). Anal. Calcd for $C_{18}H_{20}ClNO_2$: C, 68.03; H, 6.34; N, 4.41. Found: C, 68.22; H, 6.45; N, 4.64.

2-Morpholino-2-phenyl-1-(4-methoxyphenyl)ethanol (5) was prepared through a similar procedure starting with *p*-methoxybenzaldehyde; the overall yield was 27%. The last step, reduction of the ketone, was found to be stereoselective, producing only the threo isomer according to NMR spectroscopy. ^{1}H NMR (300 MHz) in $CDCl_3$: δ 2.35 (m, 2 H), 2.65 (m, 2 H), 3.51 (d, J = 9 Hz, 1 H), 3.73 (m, 4 H), 4.99 (d, J = 9 Hz, 1 H), 6.55 (d, J = 6 Hz, 2 H), 7.02 (d, J = 6 Hz, 2 H), 7.05–7.22 (m, 5 H). Anal. Calcd for $C_{19}H_{23}NO_2$: C, 72.82; H, 7.40; N, 4.47. Found: C, 72.57; H, 7.41; N, 4.43.

2-Methyl-2-morpholino-1,2-diphenylethanol (6) and **1-methyl-2-morpholino-1,2-diphenylethanol (7)** were synthesized through epoxidation of α-methylstilbene with *m*-chloroperbenzoic acid (MCPBA) followed by a ring-opening reaction with excess morpholine under high temperature (α-methylstilbene oxide failed to react with morpholine under reflux conditions after 2 days presumably because of the steric hindrance around the epoxide rings). α-Methylstilbene oxide (5 g, 0.023 mol) and morpholine (10 g, 0.11 mol) were placed in a specially designed glass tube for high temperature/high pressure reaction and sealed tightly with a stainless steel screwcap. The mixture was slowly heated to 200 °C in a silicon oil bath and the reaction was maintained at 200 °C with stirring for 3 days. The reaction mixture was quenched by addition of 10 mL of water and 10 mL of diethyl ether and kept in a refrigerator for 2 h. White precipitates (**6**) were collected and recrystallized three times from absolute ethanol and dried under vacuum overnight (33%, mp 158–160 °C). ^{1}H NMR (300 MHz) in $CDCl_3$: δ 1.33 (s, 3 H), 2.65 (m, 4 H), 3.80 (m, 4 H), 4.4 (s, 1 H), 4.83 (s, 1 H), 6.62 (d, J = 9 Hz, 2 H), 6.98–7.18 (m, 8 H). Anal. Calcd: C, 76.74; H, 7.79; N, 4.71. Found: C, 76.53; H, 7.59; N, 4.87.

The filtrate that had been separated from product **6** was subjected to further treatment by addition of 20 mL of diethyl ether. The combined organic extract was washed extensively with water, dried over anhydrous magnesium sulfate, and then concentrated on a rotary evaporator. The same process was repeated five times, enriching compound **7** to as much as 95%. Meanwhile, the precipitate became enriched in compound **6**. ^{1}H NMR (300 MHz) in $CDCl_3$: δ 1.57 (s, 3 H), 2.29 (m, 2 H), 2.6 (m, 2

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H), 3.67 (m, 4 H), 3.7 (s, 1 H), 4.49 (s, 1 H), 6.96–7.29 (m, 10 H).

2-(*N*-Phenylamino)-1-phenylethanol (8) and **2-(*N*-methyl-*N*-phenylamino)-1-phenylethanol (9)** were synthesized by a ring-opening reaction of styrene oxide with the aromatic amines, aniline and *N*-methylaniline, respectively, according to the procedures described above. The products were purified under vacuum distillation through a column packed with glass beads. For the aniline and *N*-methylaniline derivatives, boiling points were 157–159 and 137–138 °C at P = 30 mmHg, respectively.

(b) Materials. Spectrograde acetonitrile (Aldrich) was purified by sequential reflux and distillation over phosphorus pentoxide and calcium hydride and stored over 3A molecular sieves. Spectrograde benzene (Aldrich) was washed with concentrated sulfuric acid and refluxed and distilled over sodium foil with benzophenone under an N_2 atmosphere. Methylene chloride was dried over calcium chloride, distilled from phosphorus pentoxide, and stored over 4A molecular sieves. Toluene was distilled prior to use. Diethyl ether was distilled from sodium benzophenone ketyl under a nitrogen atmosphere prior to use. CD_3CN, C_6D_6, $CDCl_3$, and D_2O were used as received.

The TI was a gift from Dr. A. Braun of Ciba-Geigy. It was purified through recrystallization from chloroform followed by vacuum sublimation to yield dark purple crystals. Purified 9,10-dicyanoanthracene, 1,4-dicyanonaphthalene, and 2,6,9,10-tetracyanoanthracene were gifts from Dr. S. Farid of Eastman Kodak Co. Potassium ferrioxalate (Pfaltz & Bauer) was recrystallized twice from warm water in a darkroom and dried in a vacuum oven overnight.

General Experimental Condition. All irradiations were carried out in vacuum degasable sample tubes (degassed through 6–8 freeze–pump–thaw cycles until the pressure was 3×10^{-6} Torr or less and sealed with a torch). An apparatus used for these purposes was designed by fusing an NMR tube (or a quartz cuvette, or quartz or Pyrex test tube) onto the reservoir cell (5- or 10-mL round-bottom flask). Different reaction cells were selected, depending on the detection methods, e.g., NMR, fluorescence, or absorption spectra. The entire process including vacuum degassing, photolysis, and detection was performed in a dark room with dim red lights since several of the electron acceptors used in these studies strongly absorb in the visible range.

UV–vis absorbance spectra were measured on a Hewlett-Packard 8451A diode array spectrometer. Fluorescence spectra were measured on a SPEX 111CM Fluorolog fluorimeter with a 150W Xenon lamp and a photon counting thermoelectrically cooled detector. The routine ^1H NMR analysis was conducted at room temperature and recorded at 300 MHz on a General Electric/Nicolet QE-300 spectrometer. All NMR samples were prepared in Wilmad 527-pp 5 mm O.D. tubes. Proton chemical shifts are recorded in ppm downfield from tetramethylsilane. NMR spectra from FT instruments were calibrated against the residual proton resonance of the deuterium lock solvent: i.e. ($CDCl_3$), 7.24, (C_6D_6), 7.13, (CD_3CN), 1.93. High-pressure liquid chromatography (HPLC) was carried out by using an IBM LC 9633; the detector was an ISCO UV–vis variable wavelength detector. Fluorescence lifetimes were measured on a Photochemical Research Associates single photon counting fluorescence lifetime instrument with a hydrogen flash lamp. The lifetime analysis was conducted with software written by PRA. Analytical gas chromatography was performed on a Shimadzu GC-9A chromatography with a flame ionization detector, using a capillary column. Mass spectra were measured on a VG Analytical LTD 7035 mass spectrometer. Inert atmosphere manipulations were performed under nitrogen atmosphere in an HE-43-2, DRI-LAB glovebox equipped with an HE-493 DRI-TRAIN. Elemental analyses were performed by Galbraith Laboratories, Inc., P.O. Box 51610, Knoxville, TN 37950-1610.

Electrochemical Measurements. Redox potentials were determined by cyclic voltammetry with use of a three-electrode cell (platinum disk as working electrode, a platinum grid as counterelectrode, and a saturated calomel electrode or a silver/silver nitrate 0.1 M solution as reference electrode) fitted with a scintered glass frit made from a regular pipet, through which argon was introduced for degassing the solution prior to measurement. Tetrabutylammonium fluoroborate was used as electrolyte and was dried in a vacuum oven overnight prior to use. Solutions were typically prepared by dissolving amine donors (1–3 mM) and electrolyte 0.1 M into purified acetonitrile which was argon degassed for 20 min with stirring prior to measurement, and an argon atmosphere was maintained above the solution during the measurement. The peak potentials were measured with a 200 mV/s sweep rate. No cathodic wave was detected following the anodic sweep.

Electrochemical oxidation of **1** was conducted at the peak potential of *erythro*-**1** (which was set by scanning the oxidation wave to its maximum and was held constant during continuous electrolysis). Such electrochemical oxidation was monitored by a continuous change of current which dropped gradually to reach the static state.

Photolysis. Irradiations by visible light were carried out on a 200-W Hg lamp or a 100-W tungsten lamp with the monochromator set at a wavelength where the excited acceptor has its maximum absorbance. Alternatively, the exciting light was purified with Corning glass filters. A combination of a cut-off filter and a band-pass filter was used to isolate the band for selective excitation of electron acceptors. Comparative photolysis of solutions was carried out on an Hanovia 450-W medium-pressure Hg lamp with Corning glass filters in a merry-go-round reactor. Photolyses at the low-temperature range were performed inside a dewar with four quartz windows. The thermometer, sample, and stirbar were all mounted on a plastic foam support. A low-temperature bath was prepared by pouring liquid nitrogen into organic solvent[78] while stirring until a slush was formed. Photoreactions above room temperature were conducted in a water bath set at the desired temperature. Irradiation times were controlled to achieve ca. 10–20% conversion.

Kinetics and Quantum Yield Determinations. Solutions containing 1×10^{-5} to 5×10^{-5} M of the light-absorbing electron acceptor to give optical densities of approximately 1.0 at the wavelength of maximum absorbance were prepared. Concentrations of donor are in the range 0.01–0.1 M.

Quantum yields were obtained by irradiating samples with various light sources as described above. Incident light intensities were measured by using either Reinecke's salt or potassium ferrioxlate as the actinometer, depending on the irradiation wavelength. In cases where thioindigo was used as the electron acceptor, samples were irradiated in parallel with a secondary actinometer (which is a deaerated solution of benzene containing 5×10^{-5} M TI and 0.02 M TEA; and the quantum yield for bleaching of TI in this solution was measured relative to Reineckes salt). Quantum yields of other samples were determined relative to a secondary actinometer irradiated in parallel with solutions (0.0027).[31] Reaction was monitored by periodically measuring absorbances on a UV–vis spectrometer, until approximately 15% conversion was reached. Plots of absorbance λ_{max} vs irradiation time usually give a straight line within a range of less than 10–15% conversion, where only the primary photoreaction can be observed. The slopes of the plots are proportional to the quantum yields for the reaction after correction for incomplete light absorption. High conversion percentage, on the other hand, led to curvature of this plot, and this may be attributed to secondary reactions from the photoproducts.

Fluorescence quenching experiments were done with solutions containing 1×10^{-5} to 5×10^{-5} M of dye in either benzene or acetonitrile (OD 0.1–0.5 at $\lambda_{excitation}$). Samples were either vacuum degassed by freeze–pump–thaw or by bubbling with argon for 20 min.

Photo-ESR Experiments. Samples for the photo-ESR experiment were prepared in a 0.1-mm quartz ESR flat cell for acetonitrile solution or Pyrex glass tubes (O.D. 3 mm) for benzene, methylene chloride, and isopropyl alcohol solutions. Solutions were argon degassed for 20 min prior to irradiation. The cell was then put into an ESR-400X-RL cavity of a Bruker ER-420 spectrometer equipped with B-ST 100/700, BHN12, and B16 accessories for variable-temperature controls, magnetic field calibration, and frequency measurements. The samples were irradiated in the cavity with an Hanovia 977B0090 1000-W mercury–xenon arc lamp in a Model LH 15 1H Scheffel lamp housing. The light was focused through quartz lenses and filtered through a 15-cm flowing water filter and a combination of corning glass filters to isolate the absorption band of electron acceptors. ESR experiments were carried out both during and after photolysis at different temperatures (−90 °C or room temperature).

Infrared Experiment. IR experiments were conducted for diastereomers of MDBOH and relevant amino alcohols in both solution and solid state. Solid samples were prepared by the complete mixing of predried potassium bromide powder with 1–3-mg substrates to make a uniformly thin pellet. The measurement immediately followed the preparation. Dried nitrogen gas was slowly blown into the sample compartment to prevent condensation of moisture (which could strongly affect the region of the O–H stretch). Solution samples were prepared by dissolving the donor in purified methylene chloride solvent. IR spectra of the substrates were taken at different concentrations of the substrates (0.01–0.1 M).

Product Analysis. Photooxidation products of donors were analyzed with HPLC with either reverse phase column on octadecyl (C18) bonded-silica (partisil ODS/25, IBM) or a silica gel normal phase column (partisil 5/25, Whatman). When photoreactions were conducted in NMR tubes, photoproducts were also characterized by NMR spectra. Quantitative measurements were achieved by including an internal standard, methylcyclohexane. Reduction products were characterized by absorption spectra.

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Chemical Oxidation of α,β-Amino Alcohols with Dioxygen Hexafluoroantimonate in CH_2Cl_2. α,β-Amino alcohols were weighed in a glovebox and transferred into a 5-mL Pyrex test tube which was sealed with a septum cap and parafilm. A molar equivalent amount of dioxygen hexafluoroantimonate was weighed separately and placed into a test tube with a T14/20 adaptor (microflask) containing a stirbar, which was capped with a high-vacuum T-switch stopcock. After the sample was removed from the glovebox, 1 mL of purified methylene chloride solvent was added to the α,β-amino alcohol solid by injection through the septum cap. The microflask was connected to the nitrogen gas line and cooled in a temperature bath to below −110 °C. The methylene chloride solution of amino alcohol was added to the cold O_2SbF_6 solid with a syringe under a nitrogen atmosphere. The solution immediately froze on the wall of the reaction cell. The cell was isolated from the N_2 line and thawed in a temperature bath (T = ca. −90 °C) with stirring. The reaction was performed at −85 °C for 2 h. After reaction the solvent was removed under vacuum at T = 30 °C. The vacuum was then released by slowly blowing nitrogen gas into the sample until atmospheric pressure was reached. CD_3CN or C_6D_6 was added to the reaction tube to dissolve the oxidation products, and the resulting solution was carefully pipeted into a NMR tube. An NMR spectrum was taken immediately after the sample was prepared.

Acknowledgment. We are grateful to the U.S. Department of Energy (Grant DE-FG02-86ER13504) for support of this research.

Novel [3 + 2] Photocycloadditions of 3-(1-Alkynyl)-2-cycloalken-1-ones with Alkenes†

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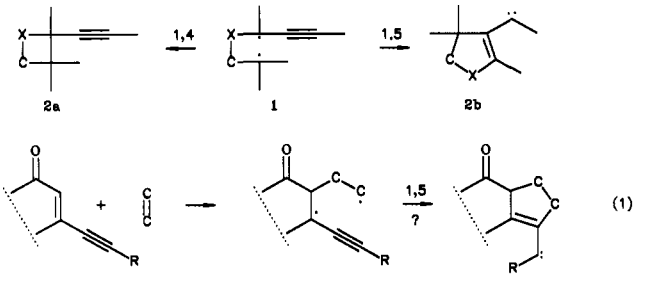
Received December 17, 1990

Abstract: Photochemical cycloaddition of 3-alkynylcycloalkenones **3a,b,c** and **4** with tetramethylethylene (**8**) at ~40 °C leads to mixtures of 1:1 adducts that arise largely from 1,5 closure of the biradical intermediate (eq 1), providing examples of a novel [3 + 2] cycloaddition reaction. Similar reactions occur between these same ketones and 1,1-dimethoxy-2-methylpropene (**9**) and 1,1-dimethoxyethylene (**10**). In several cases, these reactions lead in a single step to complex and otherwise difficultly accessible systems such as **21** and **30**. In contrast, at −60 °C, normal 1,4 closure is favored in addition of **4** with **8**. This and previously observed temperature effects on related rearrangements of triplet biradicals suggest that such biradical rearrangements occur prior to and in competition with intersystem crossing to the singlet.

Investigations over the past decade have demonstrated that alkyl propargyl 1,4-biradicals of general structure **1** (X = C, O), which may be created photochemically in several different ways, can either close 1,4 to form alkynyl-substituted four-membered rings **2a** or close 1,5 to form vinyl carbenes **2b**.[4,5] There are examples of each type of cyclization where X is either oxygen or carbon. When the initial product is **2b**, this intermediate stabilizes itself through some characteristic carbene reaction, with the particular products dependent upon structure and reaction conditions in each case. There is some evidence suggesting that 1,5 closure occurs specifically from triplet **1**,[5] and we believe that direct cyclization of triplet biradical to triplet carbene **2b** competes with the intersystem crossing that must accompany collapse of the biradical to a four-membered ring (**2a**). In several instances, formation of **2b** is the major or even sole pathway observed. With these findings in hand, we were interested in examining the photochemical cycloaddition of 3-alkynyl-2-cycloalken-1-ones with alkenes. Such reactions might offer a new route to alkyl propargyl 1,4-biradicals that could provide a novel type of [3 + 2] cycloaddition (eq 1). To the best of our knowledge, the only previously reported example of photocycloaddition in such a β-alkynyl α,β-unsaturated ketone involves simple solid state [2 + 2] dimerization of an open chain dienynone at one of the carbon–carbon double bonds.[6] There are also known photocycloadditions of alkenes with β-cyano α,β-unsaturated ketones and analogous 6-cyanouracils[7] that are at least formally akin to the reaction of eq 1, and these are discussed in more detail below, along with related intramolecular processes.[8] We have now explored such reactions with alkynylcycloalkenones and found that [3 + 2] addition does occur, furnishing in several instances a simple approach to complex systems. In this paper, we describe our examination of this process in the reactions of four substrates with four alkenes.[9]



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† For our friend and colleague, Professor Kurt Schaffner, Max-Planck-Institut für Strahlenchemie, Mülheim a.d. Ruhr, on the occasion of his 60th birthday.

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