even at the prolonged irradiation times required to obtain high ee. That is, apparently neither noxious energy transfers to BSA chromophores nor inhibition from photoproducts develop. This agrees well with the previous observation[5] that the protein recovered after irradiation is equivalent to the native BSA. Thus, each protein site represents a kind of microlaboratory which remains essentially undamaged by the chemical and photochemical operations performed on the substrates selected and worked-on by it. While it is difficult, on the basis of the present experimental evidence, to define with any certainty the position of these sites in the macromolecular sequence, there is no doubt that the SI site offers an environment for (−)-**1** comparable to basic CH_3CN, with a similar evolution of the lowest lying electronically-excited (−)-**1** state. It is worth noting that the inversion of excited (+)-**1** in its (basic?) site is not allowed by the protein.

It would be premature to extrapolate from the present case any general conclusion regarding other substrates. Most probably, photointerconversion remains a rare event in organic molecules.[10] Not so rare is the acid–base interaction between substrates and binding sites of biological macromolecules, or other forms of strong interaction: this, coupled to chiral discrimination, offers much latitude for explorations using the present technique.

Acknowledgment. We are grateful to ICQEM(CNR-Pisa) and to MURST(Rome) for financial support (40%–60% funds).

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(10) Photoracemization of diaryls: Zimmermann, H. E.; Crumrine, D. S,. *J. Am. Chem. Soc.* **1972**, *94*, 498–506. Irie, M.; Yoshida, K.; Hayashi, K. *J. Phys. Chem.* **1977**, *81*, 969–972. Yarozu, T.; Irie, M.; Hayashi, K. *J. Phys. Chem.* **1978**, *82*, 2301–2304. Photoinversion of cyclic ketones: Zandomeneghi, M.; Cavazza, M.; Pietra, F. *J. Am. Chem. Soc.* **1984**, *106*, 7261–7262.

Photoinduced Electron Transfer Reactions: Nitrogen–Oxygen Bond Cleavage in Reduced *N*-(Aryloxy)pyridinium and *N*,*N*′-Dialkoxy-4,4′-bipyridinium Salts

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Abstract: *N*-(Aryloxy)pyridinium cations and *N*,*N*′-dialkoxy-4,4′-bipyridinium dications form charge-transfer complexes with neutral hydrocarbons. Irradiation of these charge-transfer complexes leads to the cleavage of the nitrogen–oxygen bond and the formation of an aryloxy radical in the first case, but no reaction is observed for the second. In contrast, electron transfer to the dialkoxybipyridinium cation from the triplet state of 9-acetylanthracene leads to nitrogen–oxygen bond cleavage and the formation of an alkoxy radical. The rate constants for nitrogen–oxygen bond cleavage (k_{BC}) in the reduced pyridinium salts were estimated by time-resolved laser spectroscopy. For *N*-(4-cyanophenoxy)pyridinium tetrafluoroborate, $k_{BC} > 10^{11}$ s^{-1}, and for *N*,*N*′-diethoxy-4,4′-bipyridinium (bis)hexafluorophosphate), $k_{BC} = 1.4 \times 10^4$ s^{-1}. The effects of structure on the dynamics of the excited charge-transfer complexes and on k_{BC} are discussed.

Introduction

The study of single electron transfer reactions that result in bond cleavage is presently a field of active investigation.[1-8] The electron transfer may be thermally activated[9] or, more commonly, may be stimulated by light.[10,11] In the latter instance, irreversible chemical reactions must compete with the very exothermic back electron transfer which regenerates the ground-state reagents. The rates of back electron transfer in excited charge-transfer complexes and in solvent-separated ion pairs have recently been examined for several reaction classes.[12] It is clear from this work that the electronic coupling matrix element, which, in part, governs the rate of back electron transfer, is considerably larger in excited charge-transfer complexes (also known as contact ion pairs) than it is when the donor and the acceptor exist as a solvent-separated ion pair. Consequently, the rate of back electron transfer in contact ion pairs can be extraordinarily large. This postulate has been confirmed by direct measurement of electron transfer rates by spectroscopic means. Nevertheless, Kochi and co-workers discovered that some bond cleavage reactions initiated by irradiation of charge-transfer complexes can compete succesfully with energy-wasting back electron transfer.[10] Also, several recent reports describe bond cleavage reactions that compete with the back electron transfer in photogenerated solvent-separated ion pairs.[11]

The thermal chemistry of *N*-(aryloxy)pyridinium cations has been studied extensively,[13] but the photochemistry of these cations has not been reported. The absorption spectra of charge-transfer complexes of substituted *N*-alkylpyridinium salts are well known, since they form the basis of the widely used Kosower *Z*-value solvent microscopic polarity scale.[14] Similarly, *N*,*N*′-dimethyl-4,4′-bipyridinium dication (methyl viologen) has been extensively studied. Its reduction leads to a stable radical cation that does

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(1) Crivello, J. V.; Lam, J. H. W. *J. Org. Chem.* **1978**, *43*, 3055.

(2) Lee, L. Y. C.; Ci, X.; Giannotti, C.; Whitten, D. G. *J. Am. Chem. Soc.* **1986**, *108*, 175.

(3) Schweig, A.; Weidner, U.; Manuel, G. *J. Organomet. Chem.* **1974**, *67*, C4. Eaton, D. F. *J. Am. Chem. Soc.* **1981**, *103*, 7235.

(4) Borg, R. M.; Mariano, P. S. *Tetrahedron Lett.* **1986**, 2821.

(5) Chatterjee, S.; Gottschalk, P.; David, P. D.; Schuster, G. B. *J. Am. Chem. Soc.* **1988**, *110*, 2326.

(6) Kim, J. K.; Bunnett, J. F. *J. Am. Chem. Soc.* **1970**, *92*, 7643.

(7) (a) Saeva, F. D.; Morgan, B. P. *J. Am. Chem. Soc.* **1984**, *106*, 4121. (b) Breslin, D. T.; Saeva, F. D. *J. Org. Chem.* **1988**, *53*, 713. (c) Saeva, F. D.; Breslin, D. T.; Martic, P. A. *J. Am. Chem. Soc.* **1989**, *111*, 1328. (d) Saeva, F. D.; Breslin, D. T. *J. Org. Chem.* **1989**, *54*, 712. (e) Saeva, F. D.; Breslin, D. T.; Luss, H. R. *J. Am. Chem. Soc.* **1991**, *113*, 5333.

(8) (a) Maslak, P.; Guthrie, R. D. *J. Am. Chem. Soc.* **1986**, *108*, 2628, 2637. (b) Maslak, P.; Narvaez, J. N.; Kula, J.; Malinski, D. S. *J. Org. Chem.* **1990**, *55*, 4550. (c) Guthrie, R. D.; Shi, B. *J. Am. Chem. Soc.* **1990**, *112*, 3136.

(9) Koser, G. F.; Rebrovic, L. *J. Org. Chem.* **1981**, *46*, 4324.

(10) (a) Kim, E. K.; Lee, K. Y.; Kochi, J. K. *J. Am. Chem. Soc.* **1992**, *114*, 1756. (b) Saukaramua, S.; Kochi, J. K. *J. Chem. Soc., Chem. Commun.* **1989**, 1900. (c) Sankararamau, S.; Perrier, S.; Kochi, J. K. *J. Am. Chem. Soc.* **1989**, *111*, 6448.

(11) (a) Maslak, P.; Kula, J.; Chateaneuf, J. E. *J. Am. Chem. Soc.* **1991**, *113*, 2304. (b) Maslak, P.; Chapman, W. H., Jr. *Tetrahedron* **1990**, *46*, 2715. (c) Popielarz, R.; Arnold, D. R. *J. Am. Chem. Soc.* **1990**, *112*, 3068.

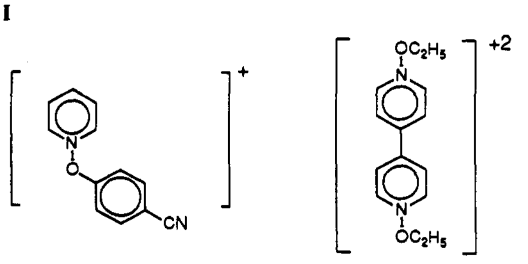
(12) (a) Gould, I. R.; Young, R. H.; Moody, R. E.; Farid, S. *J. Phys. Chem.* **1991**, *95*, 2068. (b) Gould, I. R.; Ege, D.; Moser, J. E.; Farid, S. *J. Am. Chem. Soc.* **1990**, *112*, 4290. Gould, I. R.; Moser, J. E.; Armiage, B.; Farid, S.; Goosman, J. L.; Herman, M. S. *J. Am. Chem. Soc.* **1989**, *111*, 1917.

(13) (a) Abramovitch, R. A.; Kato, S.; Singer, G. M. *J. Am. Chem. Soc.* **1971**, *93*, 3074. (b) Abramovitch, R. A.; Inbasekaran, M. N.; Kato, S.; Singer, G. M. *J. Org. Chem.* **1976**, *41*, 1717.

(14) Kosower, E. M. *An Introduction to Physical Organic Chemistry*; Wiley: New York, 1968; p 293.

0002-7863/92/1514-9304$03.00/0

Chart I



CPP$^+$ DEBP^{+2}

Table I. Redox Potentials, Molar Extinction Coefficients at 355 nm, and Equilibrium Constants for Formation of Charge-Transfer Complexes of CPP$^+$ and Electron Donors

donor	E_{ox} (V vs SCE)	ϵ_{355}	K_{CT}
hexamethylbenzene	1.66	3.5	5.8
pentamethylbenzene	1.72	100	0.8
1,3,5-trimethoxybenzene	1.48	16	6.2
2-methoxynaphthalene	1.40	200	0.4
1,2,3,5-trimethoxybenzene	1.03	100	0.8

not undergo carbon–nitrogen bond cleavage.[15] In contrast, the homolytic nitrogen–oxygen bond cleavage that follows electron transfer to *N*-alkoxypyridinium cations forms the basis for their important practical application in the photoinitiation of polymerization.[16] Similarly, in a related process, Kochi and co-workers have recently uncovered evidence for electron transfer and bond cleavage in aromatic nitrations with *N*-nitropyridinium cations.[10a]

Irradiation of the charge-transfer complexes formed from a cationic acceptor and a neutral donor shifts one electron and converts the acceptor to a radical and the donor to a radical cation. Similarly, excitation of complexes formed from a dication and a neutral donor gives two radical cations. These processes are classified as charge-shift electron transfer reactions since there is no difference in net charge between the initial and the final states. We describe herein experiments which show that the excited charge-transfer complexes of *N*-(aryloxy)pyridinium cations and neutral electron donors undergo nitrogen–oxygen bond cleavage with rates that compete successfully with energy-wasting back electron transfer. Time-resolved spectroscopic measurements reveal that the bond cleavage reaction is complete in less than 20 ps after the excitation of the complex. In contrast, nitrogen–oxygen bond cleavage in excited *N,N'*-diethoxy-4,4'-bipyridinium charge-transfer complexes is too slow to overcome energy-wasting back electron transfer. For this case, time-resolved spectroscopic measurements show that nitrogen–oxygen bond cleavage occurs from the reduced *N,N'*-diethoxybipyridinium dication with a lifetime of ca. 70 μs.

Results

(1) Charge-Transfer Complexes of *N*-(4-Cyanophenoxy)pyridinium Tetrafluoroborate [CPP$^+$BF$_4^-$] and *N,N'*-Diethoxy-4,4'-bipyridinium Bis(hexafluorophosphate) [DEBP^{2+} (PF$_6^-$)$_2$]. The absorption spectra of CPP$^+$BF$_4^-$, hexamethylbenzene, and a mixture containing CPP$^+$BF$_4^-$ and hexamethylbenzene in acetonitrile solution are shown in Figure 1. Formation of a charge-transfer complex in the mixture is apparent from the appearance of the broad, low-energy absorption band in these spectra. Related complexes with CPP$^+$ are observed with 2-methoxynaphthalene, 1,3,5-trimethoxybenzene, and the other donors listed in Table I and also when the DEBP^{2+} is used as the electron acceptor. In each case examined, the complexes yield linear Benesi–Hildebrand plots[17] that give association constants in the range of 0.5–1.5 M^{-1} and extinction coefficients at 355 nm from 50 to 200 M^{-1} cm^{-1}. These values are typical of relatively weak charge-transfer complexes.

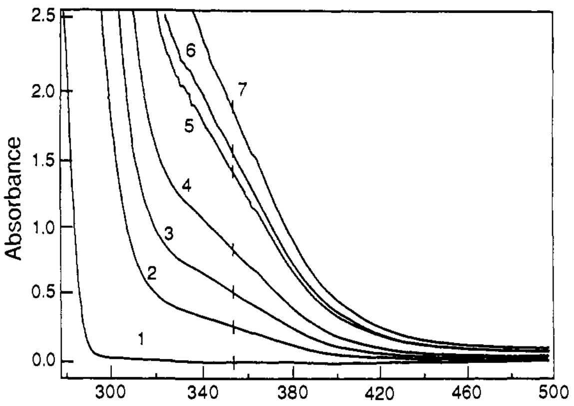
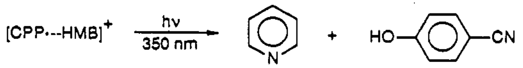


Figure 1. Absorption spectra of CPP$^+$BF$_4^-$ (0.055 M) and hexamethylbenzene in acetonitrile solution. The curves are at different hexamethylbenzene concentrations: (1) 0 M, (2) 0.024 M, (3) 0.05 M, (4) 0.083 M, (5) 0.14 M, (6) 0.16 M, and (7) 0.20 M.

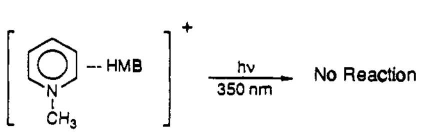
(2) Electrochemical Reduction of Pyridinium Salts. The electrochemical behavior of *N*-alkylpyridinium salts[18] and *N,N'*-dialkylpyridinium salts[15] has been extensively studied. In both cases, cyclic voltammetric measurements yield waves characteristic of reversible one-electron reductions. In contrast, cyclic voltammetry of CPP$^+$ in CH$_3$CN reveals an irreversible reduction wave with peak potential at ca. −0.5 V vs Ag/Ag$^+$ (sweep rate = 50 V/s; the reduction remains irreversible when the sweep rate is increased to 21 kV/s). Similarly, reduction of DEBP^{2+} reveals only an irreversible wave with a peak at −0.3 V. These findings are taken as evidence for rapid (on the timescale of the electrochemical experiments) reactions of the reduced pyridinium cations.

(3) Photochemistry of CPP$^+$ and DEBP^{2+}. Irradiation of an acetonitrile solution containing CPP$^+$ and hexamethylbenzene at 350 nm, a wavelength at which only the charge-transfer complex absorbs, converts the pyridinium cation to pyridine and 4-cyanophenol in high yield (eq 1). Similar results are obtained when the charge-transfer complexes formed from CPP$^+$ and the other donors listed in Table I are irradiated. For comparison, irradiation of the charge-transfer complex formed from *N*-methylpyridinium tetrafluoroborate and hexamethylbenzene does not lead to consumption of the cation (eq 2). In contrast to the high reactivity of CPP$^+$, irradiation of the charge-transfer complex



(1)

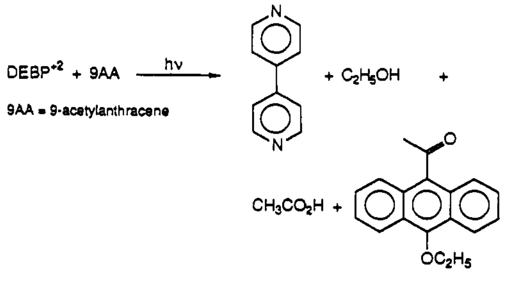
HMB = hexamethylbenzene



(2)

$$[\mathrm{DEBP}\text{---}\mathrm{DMB}]^{+2} \xrightarrow[350\ \mathrm{nm}]{h\nu} \text{No Reaction} \qquad (3)$$

DMB = dimethoxybiphenyl



(4)

9AA = 9-acetylanthracene

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[15] (a) Hünig, S.; Schenk, W. *Liebigs Ann. Chem.* **1979**, 1523. (b) Bird, C. L.; Kuhn, A. T. *Chem. Soc. Rev.* **1981**, *10*, 49.

[16] Specht, D. P.; Farid, S. Y. U.S. Patent Appl. 185,854, 1980. *Chem. Abstr.* **1982**, *97*, 82722b.

[17] Benesi, H. A.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1949**, *71*, 2703.

[18] Menon, R. K.; Brown, T. L. *Inorg. Chem.* **1989**, *28*, 1371.

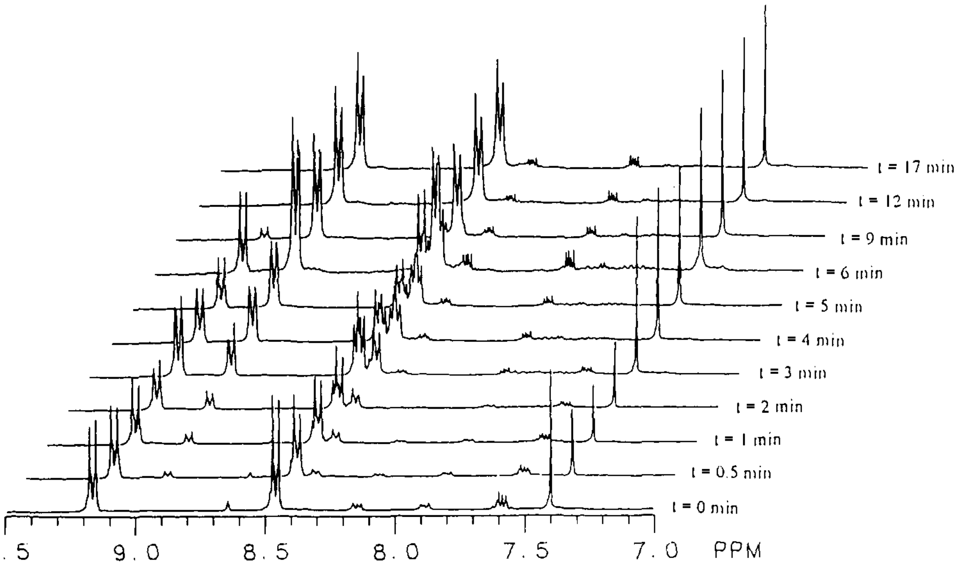
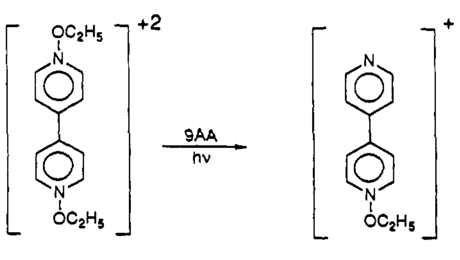


Figure 2. A portion of the ^{1}H NMR spectrum of the N_2-saturated acetonitrile solution of acetylanthracene and $DEBP^{2+}$, recorded during the photochemical sensitization of $DEBP^{2+}$ with acetylanthracene in CD_3CN solution.

formed from $DEBP^{2+}$ and 4,4′-dimethoxybiphenyl, for example, does not initiate a reaction (eq 3). The difference between these systems must be related to the competition between bond cleavage and back electron transfer in their excited charge-transfer complexes. Significantly, sensitization of $DEBP^{2+}$ with 9-acetylanthracene does lead to its efficient consumption with formation of 4,4′-bipyridine, ethyl alcohol, acetic acid, and 9-acetyl-10-ethoxyanthracene (eq 4). For comparison purposes, we examined the acetylanthracene-sensitized reaction of *N,N*′-diethyl-4,4′-bipyridinium (ethyl viologen, EV^{2+}) bis(hexafluorophosphate). In contrast to the rapid disappearance of $DEBP^{2+}$, there is no detectable consumption of the EV^{2+} under these conditions.

The photochemistry of excited charge-transfer complexes of CPP^+ appears to be dominated by rapid cleavage of the nitrogen–oxygen bond. This view is supported by the time-resolved absorption experiments that are described later. On the other hand, the photochemistry of $DEBP^{2+}$, particularly in the sensitization experiments, appears to be more complex. We examined this reaction in some detail.

Visible-light irradiation of a N_2-saturated acetonitrile solution of acetylanthracene and $DEBP^{2+}$ (only the anthracene absorbs light) leads to consumption of both the dication and the sensitizer with formation of the products shown in eq 4. The ^{1}H NMR spectra of the reaction mixture were recorded at various times during the course of the irradiation. These spectra, shown in Figure 2, indicate the intermediate formation of the singly-substituted *N*-ethoxy-4,4′-bipyridinium cation (eq 5). Interestingly,



(5)

the chemical shifts of the protons on the α-carbons of the monocation are the same as those of their counterparts on 4,4-bipyridine and $DEBP^{2+}$. However, the intermediacy of the monocation is revealed by analysis of the proton splitting pattern. At intermediate irradiation times, the resonance at δ 8.43, assigned to hydrogen on the β-carbons, forms a doublet of apparent triplets, indicating the presence of the unsymmetrical structure.

The stoichiometry of the acetylanthracene-sensitized reaction was determined by analysis of the NMR spectra. Each equivalent of $DEBP^{2+}$ consumed yields 1 equiv of bipyridine and 0.5 equiv of ethyl alcohol. The other ethoxy group of $DEBP^{2+}$ is converted to acetic acid and the ethoxy-substituted anthracene. These product studies indicate that nitrogen–oxygen bond cleavage to form an ethoxy radical is the dominant path in the sensitized photoreaction of $DEBP^{2+}$. This view is supported by time-resolved spectroscopic experiments.

(4) Time-Resolved Absorption Spectroscopy. Differences in the behavior of the charge-transfer complexes formed from CPP^+ and from $DEBP^{2+}$ are observed also by means of time-resolved absorption experiments. Laser flash photolysis (355 nm, 18 ps, 250 μJ) of a solution containing trimethoxybenzene and CPP^+ gives the transient spectrum, recorded 450 ps after the pulse, shown in Figure 3. Irradiation of either component alone under these conditions does not give a detectable absorption change. The spectrum in Figure 3 shows two features with apparent maxima at 436 and 595 nm. On the timescale of this experiment, both peaks rise immediately and then decay over a period of several hundred microseconds. Similar irradiations of the charge-transfer complexes formed from CPP^+ and the other donors listed in Table I also give the 4-cyanophenoxy radical ($CPO^•$) and the respective donor radical cation. For comparison purposes, we showed that laser flash photolysis of the charge-transfer complex formed from hexamethylbenzene and the *N*-methylpyridinium cation does not give any detectable transient absorptions under these conditions.

The identities of the transient species formed from photolysis of CPP^+ charge-transfer complexes were determined by comparison with independently generated spectra. The transient compound with an apparent absorption maximum at 595 nm is determined to be the trimethoxybenzene radical cation by comparison with its spectrum obtained at low temperature[19] and by its independent generation with fumaronitrile under the conditions of the laser flash photolysis experiment. Similarly, the absorption band at 436 nm is assigned to the 4-cyanophenoxy radical by its independent generation from 4-cyanophenol and triplet benzophenone[20] and by irradiation of CPP^+ in the presence of tetraphenylborate anion.

The photochemistry of the trimethoxybenzene–CPP^+ charge-transfer complex was also examined by means of picosecond timescale spectroscopic methods. Pulsed irradiation of an acetonitrile solution of the complex shows immediate formation of the trimethoxybenzene radical cation and a similarly rapid appearance of $CPO^•$. All of the charge-transfer complexes of CPP^+ examined behave similarly, except those formed with hexamethylbenzene and methoxynaphthalene. In these cases there

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(19) Shida, T. *Electronic Absorption Spectra of Radical Ions*; Elsevier: Amsterdam, 1988; p 238.

(20) Das, P. K.; Encinas, M. V.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 4154.

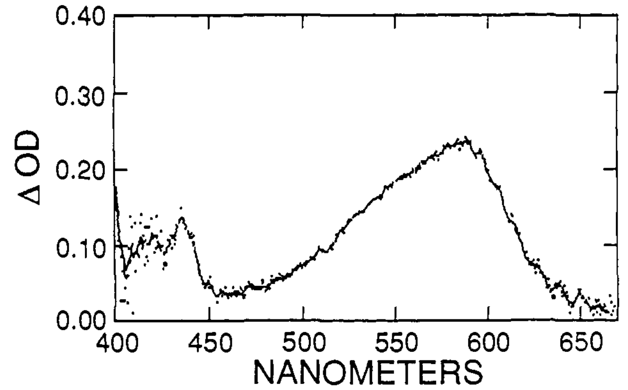


Figure 3. Transient absorption spectrum recorded 450 ps after irradiation of the charge-transfer complex of CPP^+ and trimethoxybenzene. The apparent peak at 436 nm is assigned to the 4-cyanophenoxy radical. The peak at 595 nm is assigned to the trimethoxybenzene radical cation.

are slight changes in the absorption spectra of the radical cations during the first nanosecond following irradiation.

Laser flash photolyses of the charge-transfer complexes formed with $DEBP^{2+}$ do not give meaningful transient spectra on a nanosecond timescale. This is consistent with our observation that there is no reaction from irradiation of these complexes. However, transient species are detected on the nanosecond timescale from the acetylanthracene-sensitized photolysis of $DEBP^{2+}$.

Irradiation of acetylanthracene in acetonitrile solution (388 nm, 20 ns, 4 mJ) leads to rapid (less than 0.5 ns) formation of its triplet state, which is characterized by a strong absorption at 440 nm.[21] The acetylanthracene triplet is quenched at a diffusion-limited rate by $DEBP^{2+}$, and two new transient species with absorption maxima at 410, 440, and 600 nm are simultaneously formed. The species absorbing at 440 nm is determined to be the acetylanthracene radical cation by comparison with a spectrum generated at low temperature and by independent generation of this species under the laser photolysis conditions. The intermediate absorbing at 410 and 600 nm is determined to be $DEBP^{\bullet+}$ by analogy with the well-known spectrum of the methyl viologen radical cation[22] and by comparison of its spectroscopic and kinetic behavior with $EV^{\bullet+}$.

The time-dependent behaviors of the acetylanthracene radical cation, $EV^{\bullet+}$ and $DEBP^{\bullet+}$ formed under laser irradiation conditions were analyzed. In all cases examined, the acetylanthracene radical cation decays by a kinetically second-order pathway. In contrast, the decay of $DEBP^{\bullet+}$ shows both first- and second-order components. For comparison (Figure 4), the decay of $EV^{\bullet+}$, where no irreversible chemical reaction is observed, obeys a simple second-order rate law. The first-order component uniquely observed in the decay of $DEBP^{\bullet+}$ is assigned to cleavage of the nitrogen–oxygen bond with formation of the ethoxy radical and the *N*-ethoxy-4,4′-bipyridinium cation. The rate constant obtained for this reaction by least-squares analysis of the decay is $(1.4 \pm 0.3) \times 10^4\ s^{-1}$.

Discussion

(1) Direct Irradiation of the Charge-Transfer Complexes. Absorption of light by the charge-transfer band of a complex leads to instantaneous transfer of an electron from the donor component to the acceptor moiety. In the present case, excitation of the charge-transfer complex formed from a neutral hydrocarbon and a pyridinium cation (or a bipyridinium dication) can be considered to form the donor radical cation and the pyridinyl radical (or the bipyridinyl radical cation). This process is shown as eq 6 in Scheme I. Initially, the donor radical cation and the pyridinyl radical are in contact within a "solvent cage" and the nitrogen–oxygen bond is intact. We consider three reactions that originate from this caged pair: (i) energy-wasting back electron transfer (k_{bet}) to reform the ground-state complex; (ii) solvation (k_{solv}) (eq 7), an essentially irreversible separation of the caged pair, and (iii) cleavage of the nitrogen–oxygen bond (k_{BC}) of the pyridinyl radical (or the bipyridinyl radical cation) to form pyridine (or a bipyridium cation) and an oxygen-centered free radical (eq 8). The result of irradiating these charge-transfer complexes is controlled by the relative magnitudes of these rate constants.

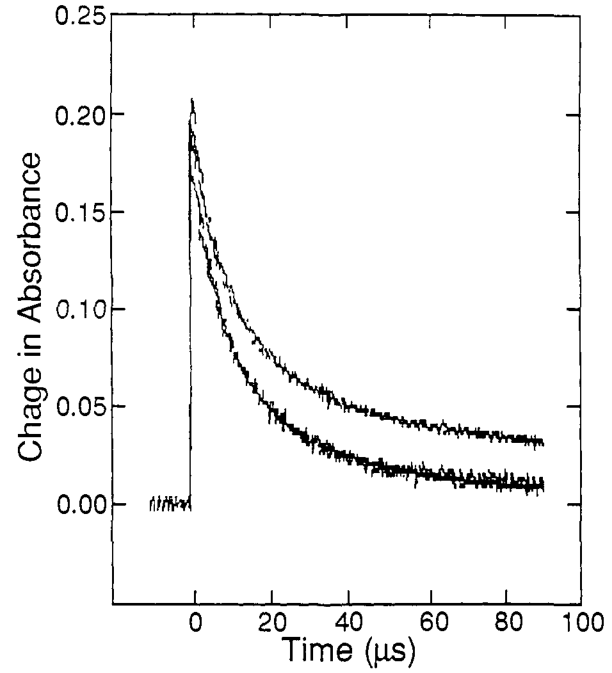
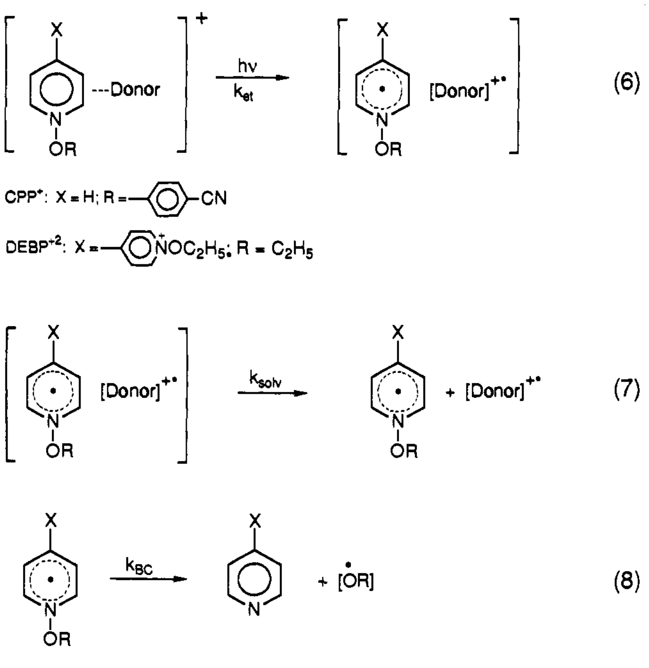


Figure 4. Time dependence of the absorption of the ethyl viologen radical cation ($EV^{\bullet+}$, upper trace) and the $DEBP^{\bullet+}$ radical cation (lower trace) following laser irradiation of the acetylanthracene sensitizer. The data are the individual points; the (barely visible) solid line is the least-squares fit according to the kinetic model described in the text.

Scheme I



The magnitude of k_{bet} in contact radical pairs has been extensively studied by Farid and co-workers, who found that semiclassical Marcus theory provides an accurate estimate of the rate.[12a] In this formulation, k_{bet} is determined by three parameters: *V*, an electronic matrix element; λ, the reorganization energy; and ΔG_{bet}, the free energy change for the reaction. It is reasonable to presume for particular pyridinium compounds that k_{BC} and k_{solv} will be essentially independent of the identity of the aromatic hydrocarbon donor. Thus, irradiation of the charge-transfer

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(21) Carmiachel, I.; Hug, G. L. *J. Phys. Chem. Ref. Data* **1986**, *15*, 1.
(22) Rodgers, M. A. J. *Photochem. Photobiol.* **1979**, *29*, 1031.

complex should be controlled primarily by variations in k_{bet}. Experimentally, two limiting behaviors were observed. For CPP^+, the cyanophenoxy radical is observed instantaneously in the picosecond timescale experiment, which indicates that k_{BC} is fast and competitive with k_{bet} and k_{solv}. For $DEBP^{2+}$, the radical cation is not observed, which indicates that k_{bet} is larger than k_{BC} or k_{solv}.

Analysis of the chemical and spectroscopic results indicates that cleavage of the nitrogen–oxygen bond in reduced CPP^+ is very rapid. We selected CPP^+ for examination because cleavage of the nitrogen–oxygen bond yields the 4-cyanophenoxy radical and a donor radical cation; both species may be monitored spectroscopically. Irradiation of these charge-transfer complexes with an 18-ps laser pulse results in the instantaneous appearance of both $CPO^\bullet$ and the donor radical cation. In most cases studied, there is a slight decrease in both the absorptions of $CPO^\bullet$ and the donor radical cation in the 800 ps following excitation of the complex, and then no additional changes in the transient absorption spectra are observed over the next 5 ns. If k_{BC} were comparable to k_{bet}, then the donor radical cation spectrum would appear instantaneously and then decay simultaneously with the appearance of $CPO^\bullet$. If k_{BC} and k_{solv} were of the same magnitude, then the donor radical cation spectrum would appear instantaneously but would not change as the $CPO^\bullet$ absorption later grew into the spectrum. We attribute the slight decrease in absorption of both $CPO^\bullet$ and the donor radical cation to reaction of these intermediates within the solvent cage. On the basis of these observations, we estimate that k_{BC} is greater than ca. 10^{11} s^{-1} and cannot exclude the possibility that the nitrogen–oxygen bond is dissociative in reduced *N*-(aryloxy)pyridinium cations.

The nitrogen–oxygen bond is certainly not dissociative in reduced *N,N'*-dialkoxybipyridinium dications. We selected $DEBP^{2+}$ for examination because, by analogy with methyl viologen, its reduction can be monitored spectroscopically since the radical cation generated will absorb strongly at ca. 600 nm. Both the product and the spectroscopic experiments we carried out reveal that in this case k_{BC} is much smaller than k_{bet} and k_{solv}. Irradiation of these charge-transfer complexes does not effectively initiate bond cleavage, and the laser spectroscopic results show no evidence for formation of the donor radical cation or the bipyridinium radical cation. Triplet sensitization experiments provide an estimate for k_{BC} in this case.

(2) Acetylanthracene-Sensitized Electron Transfer to $DEBP^{2+}$. The rate of back electron transfer in a radical pair usually depends on spin multiplicity. If the radical pair is an "overall singlet" state, then back electron transfer can generate a ground state and there is no spin prohibition. If the radical pair is an overall triplet, then back electron transfer must generate a triplet state, which usually is energetically impossible and, therefore, not observed. Thus, processes that are too slow to compete with back electron transfer from singlet radical pairs can often be observed when the radical pair is formed in a triplet state. We took advantage of this difference to measure k_{BC} for reduced $DEBP^{2+}$.

Direct absorption by acetylanthracene in the presence of $DEBP^{2+}$ generates the anthracene singlet and then its triplet state by intersystem crossing. The subnanosecond lifetime of the singlet means that there is little likelihood of its diffusive encounter with $DEBP^{2+}$. In contrast, triplet acetylanthracene has a lifetime of ca. 100 μs and is efficiently quenched by $DEBP^{2+}$ by electron transfer to give the acetylanthracene–$DEBP^{\bullet+}$ radical cation pair in an overall triplet state. The absorption of $DEBP^{\bullet+}$ at 600 nm can be readily monitored by time-resolved spectroscopy. It decays with mixed first- and second-order kinetics. By comparison with the behavior of EV^{2+}, which shows only a second-order decay, we attribute the first-order rate process in $DEBP^{2+}$ to cleavage of the oxygen–nitrogen bond: $k_{BC} = (1.4 \pm 0.3) \times 10^4$ s^{-1}.

Comparison of the nitrogen–oxygen bond cleavage rates for the two reduced pyridinium salts examined shows that the limiting value obtained for $DEBP^{2+}$ is at least one million times slower than that for CPP^+. It is reasonable to attribute this rate difference to stabilization of the transition state for nitrogen–oxygen bond cleavage by resonance of reduced CPP^+ that is absent in $DEBP^{2+}$. A related effect is apparent also from the absence of reaction in reduced EV^{2+}. In this case, repulsion by electrons on adjacent heteroatoms does not weaken the bond to the substituent.

Conclusions

Our examination of the charge-shift electron transfer reactions of complexes formed from CPP^+ and $DEBP^{2+}$ with neutral donors shows that for the former, nitrogen–oxygen bond cleavage of the initially formed radical pair competes successfully with back electron transfer and solvation, but back electron transfer is much faster than bond cleavage and solvation for the latter. This difference in reactivity is attributed to weakening of the nitrogen–oxygen bond in reduced CPP^+ due to the resonance stabilization of the cyanophenoxy radical. When the radical pair formed from reduction of $DEBP^{2+}$ by a neutral donor is in an overall triplet spin state, back electron transfer cannot occur and solvation and nitrogen–oxygen bond cleavage to form an ethoxy radical are competitive.

Experimental Section

General. Unless otherwise noted, materials obtained from commercial suppliers were purified by recrystallization and checked by melting point. The synthesis of CPP^+ followed that reported previously.[13a] ^{1}H and ^{13}C NMR spectra were recorded on a Varian XL-200 or GE 300 spectrometer in CD_3CN, $CDCl_3$, or DMSO-d_6 solution. UV-vis spectra were recorded on a Perkin-Elmer 552 spectrometer. Elemental analyses were performed at the University of Illinois Microanalytical Laboratory.

The oxidation and reduction potentials were measured on a BAS 100A potentiostat equipped with a BAS PA-1 preamplifier. The working electrode employed was a platinum ultramicroelectrode (diameter = 10 μm), and the counter electrode was a platinum wire. The reference electrode was a silver wire (Ag) in tetraethylammonium perchlorate in CH_3CN solution. The solutions of the sample in CH_3CN (5–10 mM) with supporting electrolyte tetraethylammonium perchlorate (0.15–0.17 M) were degassed just before the measurements were carried out.

***N,N'*-Diethoxy-4,4'-bipyridinium Bis(hexafluorophosphate).** 4,4'-Bipyridinium *N,N'*-dioxide was prepared by modification of the procedure reported by Fielden and Summers.[23] 4,4'-Bipyridine (25 g, 0.16 mol) in glacial acetic acid (125 mL) was heated to 70 °C. After complete dissolution of the bipyridine, a 30% solution of H_2O_2 in H_2O (18.2 g, 0.16 mol) was added dropwise, and the mixture was stirred at 70 °C for 6 h. After dropwise addition of a second equivalent of H_2O_2, the mixture was stirred at 70 °C for another 24 h. The solvent was then removed, and the remainder was neutralized with saturated aqueous $NaHCO_3$. Recrystallization from water afforded the product as the hemihydrate as yellow needles (21.4 g, 65%), mp 305 °C (lit.[24] mp 305–306 °C). ^{1}H NMR (D_2O): δ 7.93 (d, 2 H, *J* = 9 Hz), 8.38 (d, 2 H, *J* = 6 Hz). Anal. Calcd for $C_{10}H_8N_2O_2{\cdot}H_2O$: C, 58.25; H, 4.89; N, 13.58. Found: C, 58.50; H, 4.75; N, 13.64.

N,N'-Diethoxy-4,4'-bipyridinium hexafluorophosphate was prepared by heating a solution of 4,4'-bipyridinium *N,N'*-dioxide (5 g, 24 mmol) and triethyloxonium hexafluorophosphate (13.2 g, 54 mmol) in CH_3CN (30 mL) at reflux under N_2 for 5 h. The reaction mixture was kept at room temperature overnight, and the bipyridinium salt was precipitated by addition of $CHCl_3$ (300 mL). The resulting solid was recrystallized twice from methanol to give the product as fluffy white crystals; mp 216 °C. Anal. Calcd for $C_{14}H_{18}N_2O_2P_2F_{12}$: C, 31.36; H, 3.38; N, 5.22; P, 11.55. Found: C, 31.38; H, 3.41; N, 5.14; P, 11.47. ^{1}H NMR (CD_3CN): δ 1.53 (t, 6 H, *J* = 6.9 Hz), 4.77 (q, 4 H, *J* = 6.9 Hz), 8.47 (d, 4 H, *J* = 6.9 Hz), 9.17 (d, 4 H, *J* = 6.9 Hz). ^{13}C NMR (CD_3CN): δ 12.37, 80.89, 128.62, 142.45, 149.14. UV–vis λ_{max} (CH_3CN): 197 nm (ϵ = 25 000 M^{-1} cm^{-1}), 269 nm (ϵ = 28 000 M^{-1} cm^{-1}), 360 nm (ϵ = 10 M^{-1} cm^{-1}). Fluorescence λ_{max} (CH_3CN): 350 nm, 435 (excitation 320 nm), 440 (excitation 355 nm). τ_{fl} (CH_3CN) = 0.5 ns (320 nm excitation). E_{red}(irr) = −0.3 V vs Ag/AgCl (CH_3CN).

***N,N'*-Diethyl-4,4'-bipyridinium Bis(hexafluorophosphate).** A solution of 4,4'-bipyridine (2 g, 12.8 mmol) and triethyloxonium bis(hexafluorophosphate) (7 g, 28.2 mmol) in CH_3CN (20 mL) was heated at reflux under N_2 for 5 h and then kept at room temperature overnight. The product was precipitated with $CHCl_3$ (200 mL), filtered, and recrystallized from methanol to give colorless needles; mp 236 °C. ^{1}H NMR (CD_3CN): δ 1.68 (t, 6 H, *J* = 7.5 Hz), 4.66 (q, 4 H, *J* = 7.2 Hz), 8.42 (d, 4 H, *J* = 6.3 Hz), 8.95 (d, 4 H, *J* = 6.9 Hz). ^{13}C NMR (CD_3CN): δ 15.55, 57.71, 127.15, 145.27, 149.94. Anal. Calcd for $C_{12}H_{18}N_2P_2F_{12}$: C, 33.35; H, 3.60; N, 5.56. Found: C, 33.39; H, 3.65; N, 5.54.

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(23) Fielden, R.; Summers, L. A. *J. Heterocycl. Chem.* **1974**, *11*, 299.

(24) Tolstikov, G. A.; Jemilev, U. M.; Jurjev, V. P.; Gershanov, F. B.; Rafikov, S. R. *Tetrahedron Lett.* **1971**, 2807.

Steady-State Photolyses. Typically, nitrogen-saturated acetonitrile-d_3 solutions (ca. 10^{-2} M) in a Pyrex NMR tube were irradiated through an appropriate filter. The photolyses were monitored by ^{1}H NMR spectroscopy. Product yields were calculated from integrations of unique peaks in the spectrum with 1,4-dichlorobenzene as internal standard.

9-Acetyl-10-ethoxyanthracene was isolated and characterized after photolysis on a larger scale in CH_3CN with a 1000-W Hg–Xe lamp with a 420-nm cutoff filter for 2 h. Evaporation of the solvent and elution of the residue through a silica gel column with 10% ethyl acetate in hexane afforded the product as a yellow solid along with a small amount of 9-acetylanthracene. ^{1}H NMR (CD_3CN): δ 1.64 (t, 3 H, $J = 6.9$ Hz), 2.80 (s, 3 H), 4.30 (q, 2 H, $J = 6.9$ Hz), 7.56 (m, 4 H), 7.87–7.90 (m, 2 H), 8.38–8.41 (m, 2 H). GC/MS m/e (rel intensity): 264 (100), 235 (92), 221 (98), 207 (74), 163 (43), HRMS (EI, 70 eV) calcd for $C_{18}H_{16}O_2$: 264.1150, found 264.1135.

General Procedure for Transient Absorption Spectra. The solution to be irradiated was placed in a 1-cm path length stopcock-fitted quartz or Pyrex cell equipped with a Teflon-coated magnetic stir bar. The solution, in most cases, was air-saturated and stirred during the irradiation. The concentration of the electron acceptor was kept constant (0.16–0.17 M), but the concentration of the electron donor was adjusted in such a way that an optical density of 2 (±5%) across the cell was achieved. Transient absorption spectra were generated by monitoring the change in absorption at various wavelengths. To avoid the photolysis of sample with probe light, a cutoff filter (WG-345; <400 nm) was placed in the probe beam. The analysis of the mixed-order kinetic decay for acetylanthracene-sensitized irradiation of DEBP^{2+} was made with the assumption that the second-order component arises from annihilation of the acetylanthracene radical cation and the DEBP radical cation, which are formed in identical initial concentration.

Study of Formation of Charge-Transfer Complexes. In a typical procedure, 2 mL of a 0.16–0.17 M solution of *N*-(4-cyanophenoxy)-pyridinium tetrafluoroborate in CH_3CN was prepared, and the UV absorption spectrum was recorded. To this solution were added electron donors in small increments, and the UV absorption spectra of the mixtures recorded. These data were analyzed according to the Benesi–Hildebrand equation.[17]

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Enantioselective Catalysis of the Triplex Diels–Alder Reaction: A Study of Scope and Mechanism

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Abstract: Irradiation of the chiral sensitizers 1,1′-bis(2,4-dicyanonaphthalene) and 1,1′-bis(2,10-dicyanoanthracene) catalyzes the triplex Diels–Alder reaction of *trans*-β-methylstyrene with 1,3-cyclohexadiene to form the [4 + 2] cycloadducts *endo-trans*-6-methyl-5-phenylbicyclo[2.2.2]oct-2-ene. When the sensitizer is optically active and the irradiation is performed at low temperature in ether or toluene solution, the [4 + 2] cycloadducts are formed enantioselectively. The mechanism of the enantioselective triplex Diels–Alder reaction was examined by chemical and spectroscopic means. Interaction of the chiral sensitizer with the prochiral styrene forms diastereomeric exciplexes. The equilibration of these exciplexes is fast at room temperature but not at low temperature. The exciplexes react with diene to form a triplex. This reaction leads to cycloadduct formation. Enantioselection is a consequence of different trapping efficiencies for the diastereomeric exciplexes by diene.

Introduction

The predictable regiochemistry and stereochemistry of the Diels–Alder reaction are two factors that make it an important process for synthesis of compounds having six-membered rings.[1] The rate and regiochemical outcome of normal Diels–Alder reactions are thought to be determined by the interaction of frontier orbitals: the LUMO of the dienophile and the HOMO of the diene. Consequently, the reaction proceeds rapidly when an electron-poor dienophile reacts with an electron-rich diene. Correspondingly, the reaction of electron-rich dienes and electron-rich dienophiles normally proceeds slowly if at all. Attempts to overcome this limitation have focused on the discovery of catalysts. Chief among these are Lewis acids which are believed to function by forming a complex with the dienophile.[1] Transfer of electron density from the dienophile to the Lewis acid in the complex is thought to play the key role in the catalysis. In addition to the rate enhancement, the use of chiral Lewis acids as catalysts in the Diels–Alder reaction provides a means for controlling the stereochemistry of the adducts formed.

Excited states have unique electronic properties that may be used to influence reactions. In particular, singlet excited states of electron-deficient arenes often form exciplexes with electron-rich alkenes. Exciplex formation results in a transfer of electron density from the alkene to the excited arene. This fact suggests the possibility that exciplexes and Lewis acid complexes of dienophiles may undergo similar reactions. This similarity was demonstrated experimentally with the discovery of the triplex Diels–Alder reaction.[2]

The triplex Diels–Alder reaction is the photocatalyzed [4 + 2] cycloaddition of an electron-rich diene and an electron-rich dienophile carried out in a nonpolar solvent initiated by irradiation of an electron-deficient arene. For example, irradiation of a benzene solution containing tetracyanoanthracene (TCA), 1,3-cyclohexadiene (CHD), and *trans*-β-methylstyrene (tBMS) leads to the efficient formation of *endo-trans*-6-methyl-5-phenylbicyclo[2.2.2]oct-2-ene (**1**), eq 1.[3] Other examples of the triplex Diels–Alder reaction that have been investigated provide evidence for its scope, utility, and mechanism.[3]

The mechanism of the triplex Diels–Alder reaction has been examined by chemical, stereochemical, and spectroscopic means.[2,3] These experiments are consistent with a two-step reaction se-

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(1) Narasaka, K. *Synthesis* **1991**, 1.

(2) Calhoun, G. C.; Schuster, G. B. *Tetrahedron Lett.* **1986**, *27*, 911. Calhoun, G. C.; Schuster, G. B. *J. Am. Chem. Soc.* **1986**, *108*, 8021. Calhoun, G. C.; Schuster, G. B. *J. Am. Chem. Soc.* **1984**, *106*, 6870.

(3) Akbulut, N.; Hartsough, D.; Kim, J.-I.; Schuster, G. B. *J. Org. Chem.* **1989**, *54*, 2549. Hartsough, D.; Schuster, G. B. *J. Org. Chem.* **1989**, *54*, 3. Akbulut, N.; Schuster, G. B. *Tetrahedron Lett.* **1988**, *29*, 5125. Wölfle, I.; Chan, S.; Schuster, G. B. *J. Org. Chem.* **1990**, *55*, 7313.

0002-7863/92/1514-9309$03.00/0