Photoaddition Reactions of Some Electron-Deficient Acyclic Olefins with Nucleophiles. Studies on the Scope and Mechanism[1]

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Abstract: The photochemical addition of alcohols, water, and ether to the acyclic olefinic bond of quaternary salts of pyridylethylenes is reported. These reactions are initiated by attack of the oxygen compound on the excited singlet state of the electron-deficient olefin. Decay of the excited state complex leads to alcohols or ethers when attack is by water or alcohols, respectively. The addition of ethers proceeds by a radical-type path (likely by electron transfer followed by proton transfer) to yield α-substituted ethers.

Photoaddition reactions of olefins and other conjugated compounds have recently received considerable attention. In addition to the well-studied cycloadditions, reactions involving addition of water, alcohols, ethers, amines, and aldehydes have been reported.[4-8] These reactions evidently involve many diverse mechanistic pathways. Several addition reactions of alcohols, thiols, carbonyl compounds, and ethers to olefins proceed by free-radical pathways in which olefin-excited states are not involved in the actual addition step.[4] The photochemical addition of water and alcohols to six- and seven-membered ring olefins is believed to proceed through initial protonation of a highly strained trans cycloalkene or orthogonal triplet.[5,6] Excited states of smaller cyclic olefins participate in radical addition reactions, probably *via* hydrogen abstraction,[5] while excited states of most larger cyclic and acyclic olefins are seldom involved in intermolecular addition reactions due to their rapid rates of radiationless decay *via* geometric relaxation.

Several electron-deficient molecules have been found to react photochemically with nucleophiles in reactions which can culminate either in addition or substitution. These reactions have been of interest since the excited state paths frequently are quite different from those followed by the corresponding ground states.[9,10] The photosubstitution of aromatic nitro compounds evidently involves initial nucleophilic attack on the excited state of the aromatic compound.[9,11] Similarly the photohydrolysis or solvolysis of aromatic phosphate, sulfate,[12] acetate,[10] and benzoate[13] esters appears to involve nucleophilic attack by water or alcohol on the excited state of the ester. The nucleophilic photoaddition of alcohols to olefins[7] in which the double bond is conjugated with a carbonyl group and to aromatic acetylenes[8] to yield ethers has been recently observed.

In a previous communication[1] we reported the photoaddition of water to quaternary salts of 1,2-bispyridylethylenes to yield salts of 1,2-bispyridylethanols. Fluorescence quenching studies indicate that the photohydration is initiated by attack of water on the excited singlet state of the acyclic olefin. Fluorescence quenching rates for a variety of quenchers show good correlation with quencher nucleophilicity as measured by the Edward's equation and other parameters.[14] In the present paper we report a detailed study of the photohydration of quaternary salts of the bispyridylethylenes as well as an extension of the reaction to other oxygen nucleophiles and aromatic amines. Interestingly we find that apparently similar excited state complexes between nucleophiles and these electron-deficient olefins can lead to remarkably different types of product. While alcohols and water react to give ethers and alcohols by the previously reported ionic paths, ethers and pyridine react with the olefin to yield adducts *via* radical intermediates.

Results

Photoaddition of Water. Direct irradiation of the dimethiodide of *trans*-1,2-bis(4-pyridyl)ethylene (**1a**) in aqueous solution at 3130 Å results in the spectral changes in the ultraviolet region shown in Figure 1; absorption of the olefin rapidly decreases with a concurrent increase in absorption at *ca.* 2650 Å. Product analyses from preparative scale irradiations indicate that the new absorption is due to the dimethiodide of 1,2-bis(4-pyridyl)ethanol (**2**) which is isolated in almost quantitative yield ($\phi_2 = 0.4$) (eq 1). A similar product
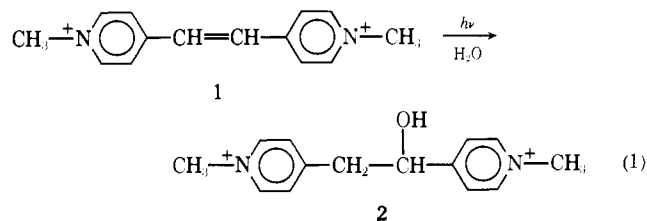
(1) A preliminary account of a portion of this work has appeared: M. T. McCall and D. G. Whitten, *J. Amer. Chem. Soc.*, **91**, 5681 (1969).
(2) National Aeronautics and Space Administration Predoctoral Fellow, 1966–1969.
(3) Alfred P. Sloan Foundation Fellow, 1970–1972.
(4) For a review see D. Elad in "Organic Photochemistry," Vol. 2, O. L. Chapman, Ed., Marcel Dekker, New York, N. Y., 1969, pp 193–195, 202–207.
(5) P. J. Kropp, *J. Amer. Chem. Soc.*, **91**, 5783 (1969); **89**, 3650, 5199 (1967); **88**, 4091 (1966).
(6) J. A. Marshall, *Accounts Chem. Res.*, **2**, 33 (1969), and references therein.
(7) S. F. Nelson and P. J. Hintz, *J. Amer. Chem. Soc.*, **91**, 6190 (1969).
(8) T. D. Roberts, L. Ardemagni, and H. Schechter, *ibid.*, **91**, 6185 (1969).
(9) E. Havinga and M. E. Kronenberg, *Pure Appl. Chem.*, **16**, 137 (1968), and references therein.
(10) H. E. Zimmerman and V. R. Sandel, *J. Amer. Chem. Soc.*, **85**, 915 (1963).
(11) R. L. Letsinger and J. H. McCain, *ibid.*, **91**, 6425 (1969).
(12) E. Havinga, "Reactivity of the Photoexcited Organic Molecule," Interscience, New York, N. Y., 1967, p 201.
(13) J. G. Pacifici, unpublished results.
(14) D. G. Whitten, J. W. Happ, G. L. B. Carlson, and M. T. McCall, *J. Amer. Chem. Soc.*, **92**, 3499 (1970).

$$CH_3-{}^+N\underset{}{\bigcirc}-CH=CH-\bigcirc N^+-CH_3 \xrightarrow[H_2O]{h\nu}$$

1

$$CH_3-{}^+N\bigcirc-CH_2-\overset{OH}{\underset{}{CH}}-\bigcirc N^+-CH_3 \quad (1)$$

2

is obtained quantitatively, although less efficiently (ϕ = 0.04), from irradiation of the dimethiodide of *trans*-1,2-bis(3-pyridyl)ethylene (**3**) in water.

A number of similar olefins have been found to undergo efficient photohydration. For example, irradiation of the dihydrochloride of *trans*-1,2-bis(4-pyridyl)ethylene (**4**) in aqueous hydrochloric acid produces, after neutralization, good yields of 1,2-bis-(4-pyridyl)ethanol. The adduct loses water upon heating to yield a mixture of *cis*- and *trans*-1,2-bis-(4-pyridyl)ethylene.

No photoproduct other than the cis isomer was observed after irradiation of **4** in acetic acid or acetic acid containing a small amount of water. However, it is unlikely that the bispyridylethylene is protonated in this medium. The spectrum of **4** undergoes a large red shift when protonated by hydrochloric acid or trichloroacetic acid and also when the nitrogens are quaternized. No such shift was observed in the spectrum of **4** in acetic acid.

As data in Table I indicate, changing the anion from iodide **1a** to fluoroborate **1b** caused no detectable changes in the behavior of the quaternary salts on direct irradiation.

Table I. Quantum Yields for Adduct Formation from **1** and **3**

Solvent	1a	1b	3
Water–acetonitrile (1:1)	0.4	0.4	0.04
Deuterium oxide–acetonitrile (1:1)		0.25	
Ethanol–acetonitrile (1:1)		0.05	0.02
Ethyl ether–acetonitrile (1:1)		0.19	0.03
Tetrahydrofuran–acetonitrile (1:1)		0.20	
Pyridine–acetonitrile (1:1)		0.23[a]	

[a] Quantum yield for disappearance of starting olefin.

Qualitative experiments with the dimethiodide salts of *trans*-1,2-bis(2-pyridyl)ethylene and *trans*-1-(3-pyridyl)-2-(4-pyridyl)ethylene indicate that these salts also photohydrate efficiently when their dilute solutions are irradiated at 3130 Å.

Although photohydration of quaternary salts of pyridyl-substituted ethylenes appears to be fairly general, the reaction is complicated in several cases by concurrent photodimerization and isomerization. When a dilute aqueous solution of the methiodide of 4-stilbazole is irradiated, spectral changes are observed which are consistent with photohydration; the olefin absorption decreases with a new band appearing at approximately 2650 Å. In addition, trans–cis isomerization occurs. An nmr spectrum of the crude reaction mixture from preparative scale reactions indicates that some hydrate may be present; however, none could be isolated. Instead, the main product isolated appears to arise from photodimerization of the stilbazole salt. Formation of dimer at such low concentrations (10^{-3} M) where dimerization should be negligible was unexpected. A possible explanation is that due to the unique nature of this molecule, a long organic entity with a charge at one end, aggregates might be expected to form in aqueous solution and thus dimerization might result from reactions occurring within the aggregate.

The photochemical reactivity of the methiodide of 4-stilbazole contrasts with that of the methiodide of
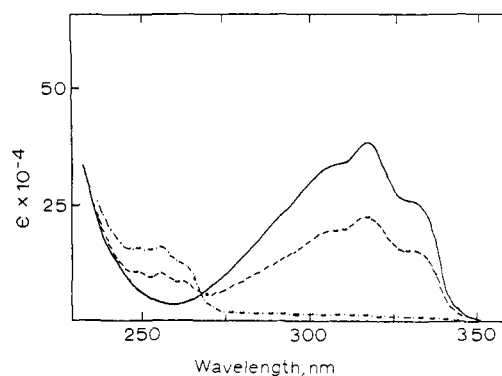

Figure 1. Photochemical conversion of **1** to **2**: ———, **1** before irradiation (3 × 10^{-5} M); – – –, aqueous solution after 10-min irradiation; —·—, same solution after prolonged irradiation.

1-(1-naphthyl)-2-(4-pyridyl)ethylene which readily undergoes photohydration when an aqueous solution of the salt is exposed to direct sunlight.[15]

For the methiodide of 3-stilbazole, trans–cis isomerization and photocyclization appear to be the predominant reactions upon irradiation in aqueous solution. A species having an absorption spectra similar to a phenanthrene derivative is rapidly formed. Likewise, trans–cis isomerization appears to be the chief reaction of *trans*-1,2-bis(2-pyridyl)ethylene which has been methylated in only one position.

Several other nucleophiles including alcohols, ethers, and pyridine, which do not react with **1**, **3**, and other quaternary salts in the ground state, were found to quench excited singlet states of these compounds at rates comparable to or exceeding that for water.[14] Adducts were formed in several cases; quantum yields for adduct formation with water, ethanol, tetrahydrofuran, and diethyl ether are listed in Table I.

Photoaddition of Alcohols. When **1a** is irradiated in ethanol, the isolated product has an absorption spectrum which corresponds to a saturated bispyridyl-ethane salt. The elemental analysis is consistent with either adduct **5**, which is formed by addition at the hydroxyl group of ethanol, or adduct **6**, which is formed by addition at the carbon atom adjacent to the hydroxyl group. However, the structure is unambiguously as-

5

6
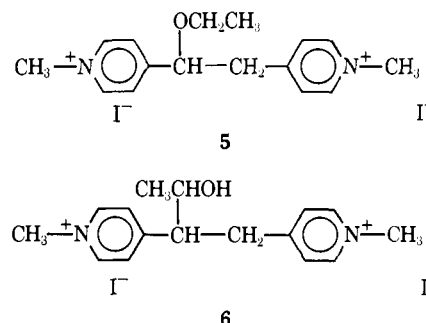
signed to ether **5** by analysis of the nmr spectrum which shows triplet splitting by the methyl protons. The yields of **5** are low in preparative scale reactions, however, perhaps due to secondary reactions. Prolonged irradiation of **1b** results in products having visible spectra which are identical with those produced from zinc reduction of **1a** or **1b** to the radical cation **7** in

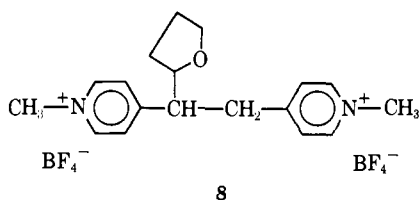(15) C. J. Cavallito, private communication.

$$CH_3-\overset{+}{N}\langle\bigcirc\rangle-CH=CH-\langle\bigcirc\rangle\overset{+}{N}-CH_3$$

$$BF_4^-$$

7
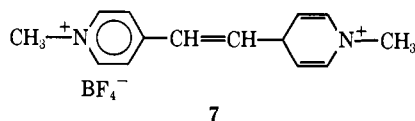
acetonitrile.[16] Since irradiation of 1,1'-dimethyl-4,4'-bipyridinium dichloride and related compounds has been found to lead to photoreduction to the cation radical *via* electron transfer from ethanol or other alcohols,[17,18] we examined crude reaction mixtures for products of the possible redox reaction. While traces of acetaldehyde[18,19] could be detected by vpc in long-irradiated solutions of **1b** in ethanol, none of the anticipated quaternary salt of 1,2-bis(4-pyridyl)ethane could be detected in the nmr of the crude product. In addition, solutions of **1b** in ethanol containing phenyl *tert*-butylnitrone as a free-radical trap[20] were irradiated in the cavity of an electron spin resonance spectrometer. However, no free radicals resulting from the possible oxidation of ethanol could be detected.

Like the dimethiodide or dimethylfluoroborate salts of 1,2-bis(4-pyridyl)ethylene, the dihydrochloride salt reacts photochemically with ethanol to produce, after neutralization, 1,2-bis(4-pyridyl)-1-ethoxyethane in good yield. On heating, the product undergoes decomposition to predominantly *cis*-1,2-bis(4-pyridyl)ethylene.

Photoaddition of methanol to **1** was also attempted. Spectral analysis indicated that some saturated product was formed; however, side reactions also occur as indicated by the appearance of a strong uv absorption at approximately 3500 Å. This product could not be isolated.[21]

Photoaddition of Ethers. Irradiation of **1b** at 3130 Å in tetrahydrofuran–acetonitrile mixtures results in spectral changes which are typical of photoreactions previously mentioned; the olefin rapidly disappears with the concurrent increase in absorption at 2650 Å. The reaction is evidently clean since an isobestic point is observed in the uv spectra, and product formation is rather efficient ($\phi = 0.20$). From preparative scale irradiations, a high yield of product **8** is

$$CH_3-\overset{+}{N}\langle\bigcirc\rangle-\overset{\overset{\displaystyle\langle\ \rangle}{|}O}{CH}-CH_2-\langle\bigcirc\rangle\overset{+}{N}-CH_3$$

$$BF_4^- \qquad\qquad BF_4^-$$

8

isolated which appears to result from the free-radical addition of tetrahydrofuran to **1b**. This contrasts with the photoaddition of water and alcohols which appears to occur predominantly by ionic nucleophilic addition. Apparently the photoaddition of tetrahydrofuran to **1** proceeds *via* a free-radical cage rather than chain

(16) J. W. Happ and D. G. Whitten, to be published.

(17) C. S. Johnson, Jr., and H. S. Gutowsky, *J. Chem. Phys.*, **39**, 58 (1963).

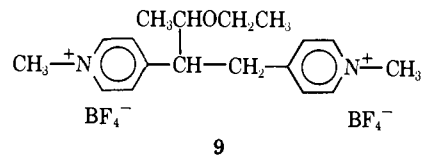(18) A. S. Hopkins, A. Ledwith, and M. G. Stam, *Chem. Commun.*, 494 (1970).

(19) We suspect the acetaldehyde arises from secondary processes and is not a direct product.

(20) E. G. Janzen and B. L. Blackburn, *J. Amer. Chem. Soc.*, **91**, 4481 (1969); E. G. Janzen and J. L. Gerlock, *ibid.*, **91**, 3108 (1969).

(21) Spectral evidence suggests that the new product observed in methanol arises from a nucleophilic attack by methanol on one of the methyl groups yielding dimethyl ether and monomethylated 1,2-bis(4-pyridyl)ethylene.

reaction since electron paramagnetic resonance spin trapping experiments[20] fail to detect free tetrahydrofuranyl radicals. These radicals are readily trapped by phenyl *tert*-butylnitrone during the photolysis of benzophenone in tetrahydrofuran.[20]

Ethyl ether also undergoes free-radical photoaddition to **1b** with approximately the same efficiency ($\phi = 0.19$) to produce the ether adduct **9**. However, side reactions complicate isolation of the product.

$$CH_3CHOCH_2CH_3$$
$$CH_3-\overset{+}{N}\langle\bigcirc\rangle-\overset{|}{CH}-CH_2-\langle\bigcirc\rangle\overset{+}{N}-CH_3$$

$$BF_4^- \qquad\qquad BF_4^-$$

9

Reactivity with Amines. Pyridine reacts efficiently with excited singlets of **1b** to yield cation radical **7** and subsequently a mixture of products.[16] Spectral evidence (nmr and uv) indicates that these products are substituted 1,2-bis(4-pyridyl)ethanes. Attempts to add other amines to the double bond of **1** were unsuccessful. No product could be isolated when this olefin was irradiated in the presence of aniline. More reactive amines such as *n*-butylamine, di- and triethylamine, pyrolidine, piperidine, 2,6-lutidine, and dimethylformamide react with the ground states of **1** or **3**; the olefinic absorption disappears with the concurrent appearance of strong absorption bands at about 3500–4500 Å depending on the particular type of donor.[16] Interestingly, conjugated systems such as benzene, naphthalene, and acridine also form colored complexes with **1**.

Effect of Sensitizers. Photohydration of the dimethiodide or fluoroborate salts of **1** could not be sensitized by triplet energy sensitizers such as benzophenone or Michler's ketone in acetonitrile–water mixtures. After irradiation spectral analysis indicated that no hydrate had been formed, nor did trans–cis isomerization occur. Concentrations were such that the ketones absorbed all of the light. Relatively dilute solutions were used due to solubility problems. In each case, stilbene and the ketone were irradiated in parallel with the solutions of the salts as a monitor to ensure that at the concentrations used energy transfer would indeed occur. Under these conditions, trans–cis isomerization of stilbene did occur. The total time of irradiation of the stilbene- and nitrogen-containing olefin solutions was much longer than that required to reach a photostationary state in stilbene. Quenching of triplet ketone by salts of **1** evidently did occur, at least from benzophenone, since **1** quenched the photopinacolization of benzophenone in methanol. However, the possibility of quenching by nonenergy transfer routes has not been eliminated.[22]

Results from Flash Photolysis Experiments. Flash photolysis of *trans*-**1b** in water and ethanol has revealed transients absorbing at 4400 Å which appear to be intermediates of photoaddition. The lifetimes of the

$$CH_3-\overset{+}{N}\langle\bigcirc\rangle-\overset{\overset{\displaystyle R}{|}}{CH}-CH=\langle\bigcirc\rangle N-CH_3$$

$$BF_4^-$$

$$R = HO,\ CH_3CH_2O$$
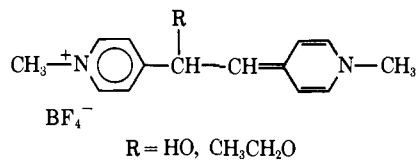
(22) See, for example, I. G. Lopp, R. W. Hendren, P. D. Wildes, and D. G. Whitten, *J. Amer. Chem. Soc.*, **92**, 6440 (1970); A. Weller, *Pure Appl. Chem.*, **16**, 115 (1968), and references therein.

Table II. Lifetimes of Intermediates by Flash Photolysis of 1[a]

Solvent	τ	λ_{max}, Å
H₂O–acetonitrile (1:1)	3.6 msec	4400
D₂O–acetonitrile (1:1)	18 msec	4400
Ethanol–acetonitrile (1:1)	70 msec	4400
Ethyl ether–acetonitrile (1:1)	4 min	5150
Pyridine–acetonitrile (1:1)	2 days	5150

[a] 1×10^{-4} M.

transients are shown in Table II; these are longer than would be expected if the transients were in excited states. Flash photolysis of *cis*-**1b** in water leads to a transient having the same lifetime and absorption spectrum as that from *trans*-**1b**. Replacement of water by deuterium oxide results in a significant isotope effect on the lifetime of the transient.

Flash photolysis of **3** in water or ethanol mixed with acetonitrile produces intermediate olefin–nucleophile adducts having lifetimes much shorter than those observed from **1b** in the same solvents. The adducts from **1b** should be considerably stabilized relative to those from **3**.

R = HO, CH₃CH₂O
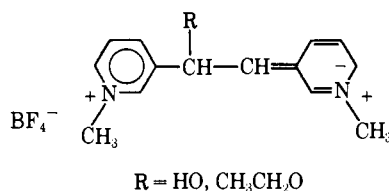
A different transient which absorbs at higher wavelengths (5150 Å) is observed from flash photolysis of ether and pyridine solutions of **1b**. The visible spectrum of this transient is clearly different from that observed from photolysis of **1b** in water or ethanol and is identical with that produced by zinc reduction of **1b** to its radical cation in acetonitrile.

Discussion

Both from the structure of the isolated products as well as from the different intermediates detected in flash experiments, it is evident that the present photoaddition reactions involve at least two distinct pathways. Addition of water and ethanol proceeds by nucleophilic addition to the olefinic bond and subsequent protonation of the adduct to yield alcohols and ethers. In contrast, photoaddition of diethyl ether, tetrahydrofuran, and probably pyridine follows a radical path in which electron transfer to the electron-deficient olefin to yield the radical cation[23] is the critical step. Formation of the ether and tetrahydrofuran adducts probably proceeds by an electron transfer–proton transfer–radical coupling path as outlined in Scheme I for reaction of **1b** with diethyl ether. This reaction sequence is quite analogous to the photoreduction of ketones and aromatic hydrocarbons by amines and related reactions proceeding through charge-transfer exciplexes.[24–29]

(23) This is a radical cation in the case of **7**; since it results from electron addition to unfilled orbitals of the olefin it is appealing to regard it as a radical anion.

(24) S. G. Cohen and B. Green, *J. Amer. Chem. Soc.*, **91**, 6824 (1969); S. G. Cohen and J. B. Guttenplan, *Tetrahedron Lett.*, 2125 (1969); S. G. Cohen and R. J. Baumgarten, *J. Amer. Chem. Soc.*, **89**, 3471 (1967), and references therein.

(25) R. S. Davidson, *Chem. Commun.*, 1450 (1969); R. S. Davidson and P. F. Lambeth, *ibid.*, 511 (1968); 1265 (1967).

Scheme I
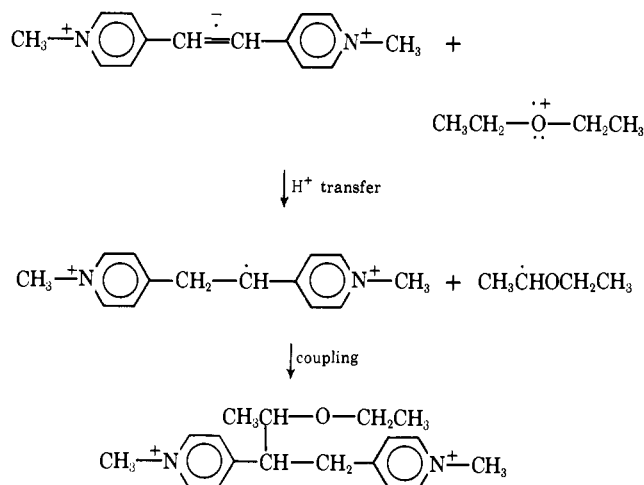
It is possible that the products arise from two entirely separate reactions, one involving initiation by nucleophilic attack on the excited olefin singlet and the other involving excited state electron transfer. A more economical path involves formation of similar exciplexes (**11**) in each case, with paths for exciplex decay determining the type of product formed (Scheme II, which compares the reaction of ether and ethanol). Path 1 would involve decay of the exciplex to a ground-state nucleophile olefin adduct **10**, perhaps with proton loss. Path 2 would involve decay of the exciplex with electron transfer while path 3 would simply provide a mechanism for radiationless decay.[14] That path 2 would be preferred for diethyl ether, tetrahydrofuran, and pyridine is reasonable since the ionization potentials of these three compounds (9.6, 9.5, and 9.2 eV, respectively)[30] are lower than those for water (12.6 eV)[30] and ethanol (10.5 eV).[30] Since its ionization potential is only slightly higher than that of the ethers, it would be conceivable that ethanol (and other alcohols) might form exciplexes that could decay by either path 1 or path 2. This could explain the observation that ethanol reduces photoexcited 1,1′-dimethyl-4,4′-bis-pyridinium dichloride by electron transfer[17,18] but adds to **1** and other olefins. The former salt lacks a convenient path 1.

The structure of the exciplex **11** proposed in Scheme II remains uncertain; the exciplexes have not been detected spectrally. However, that simple attack on the excited olefin leading directly to a ground-state adduct as shown in Scheme III is probably not the case is shown by comparison of experiments with H₂O and D₂O. If **12** were the only species formed (or if an exciplex, perhaps an encounter complex, which decayed exclusively to **12** were an intermediate), the quantum efficiency of product formation (Table I) at high (H₂O) would reflect the ratio: $\Phi_{prod} = k_{prod}/(k_{prod} + k_{decay})$.

(26) R. A. Caldwell, *Tetrahedron Lett.*, 2121 (1969).

(27) P. J. Wagner and A. Kemppainen, *J. Amer. Chem. Soc.*, **91**, 3085 (1969).

(28) J. G. Pacifici, G. Irick, Jr., and C. G. Anderson, *ibid.*, **91**, 5654 (1969).

(29) C. C. Wamser, G. S. Hammond, C. T. Chang, and C. Baylor, Jr., *ibid.*, **92**, 6362 (1970).

(30) J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, "Ionization Potentials, Appearance Potentials and Heats of Formation of Gaseous Positive Ions," U. S. Government Printing Office Publication NSRDS-NBS-26, Washington, D. C., 1969.

Scheme II

BPE = bispyridylethylene
R = H, CH$_3$CH$_2$
R' = CH$_3$CH$_2$
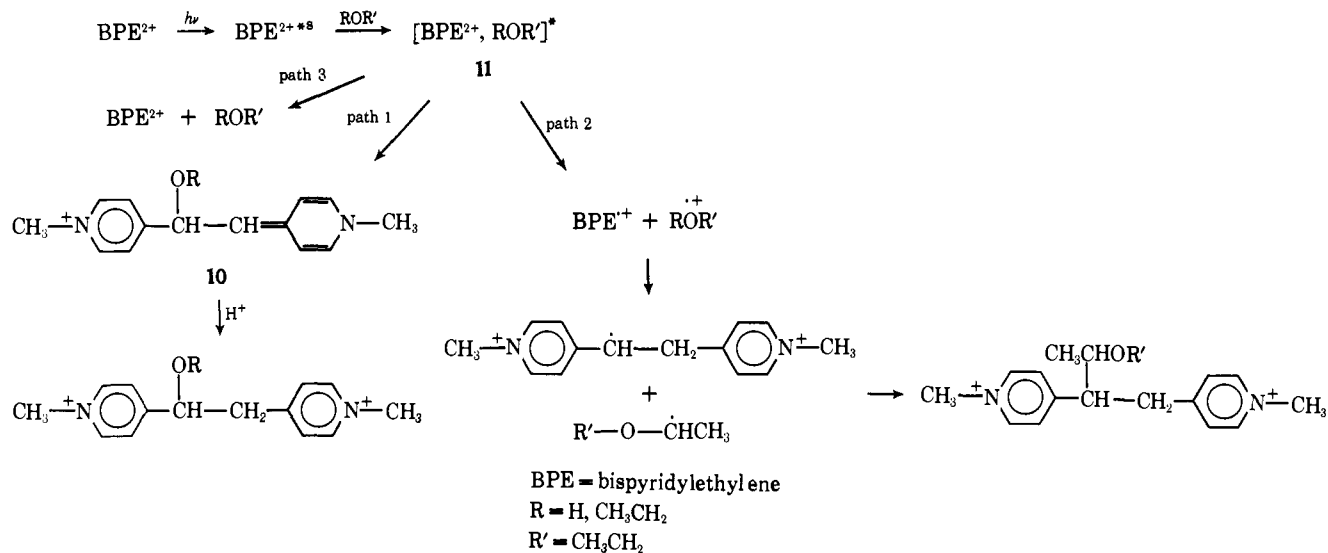
Scheme III
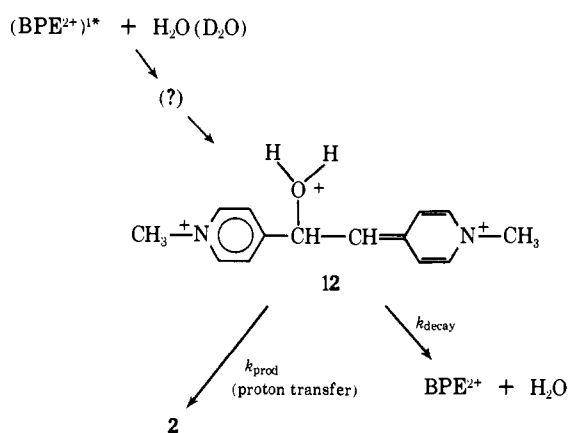
From the quantum yield ($\phi = 0.4$) and the flash results ($k_{prod} + k_{decay} = 280$ sec^{-1}) we calculate $k_{prod} = 112$ sec^{-1} and $k_{decay} = 168$ sec^{-1}. It appears that there should be a primary isotope effect on k_{prod} but not on k_{decay}. However, from the increased lifetime of the transients in D$_2$O it can be calculated that the sum, $k_{prod} + k_{decay} = 56$ sec^{-1} in D$_2$O, is a value much less than k_{decay}. Therefore, these results do not support the direct formation of adduct **12** by attack of water on the excited olefin as shown in Scheme III. Although the isotopic experiments could be interpreted in several ways, the results are consistent with the isotope effect on product formation being due to competition between decay of the exciplex to starting materials (path 3, probably no primary isotope effect) and exciplex decay with proton loss (path 1) to give **10**, the transient observed in the flash experiments. The isotope effect on the transient lifetime would then be merely a rate phenomenon ($k_H/k_D = 5.1$) unrelated to product formation.

A suggestion as to why excited states of **1** and **3** are susceptible to nucleophilic attack and electron transfer in the excited state is found in the results of INDO and CNDO[31] molecular orbital calculations on these compounds.[32] The calculations suggest considerable

(31) J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **44**, 3289 (1966).
(32) L. Pedersen, J. W. Happ, and D. G. Whitten, unpublished results.

positive charge on the ethylene carbons in the ground state. However, the excitation of **1** and **3** involves promotion of an electron to an orbital which has very little contribution at the ethylene carbon; consequently there is a large increase in the positive charge at these sites. That the antibonding orbital has such small contributions on the ethylene carbons in these compounds probably explains the reluctance of these acyclic olefins to undergo cis–trans isomerization.[16]

Experimental Section

Materials. Methods of preparation and purification of free-base stilbazoles and bispyridylethylenes have been described in a previous publication.[33] Methiodide salts of the nitrogen-containing olefins were prepared by adding a 2–4 M excess of methyl iodide to a solution containing 1 g of olefin in approximately 10 ml of ethyl alcohol or acetonitrile. After stirring at reflux for 4–6 hr, the reaction mixture was cooled and the colored salts were filtered. Purification was achieved by several recrystallizations from isopropyl alcohol–water mixtures. Salts prepared by this method included: 1,2-bis(4-pyridyl)ethylene dimethiodide (orange-red crystals; mp > 310° dec; uv max 317 nm (ϵ 38,200); nmr (D$_2$O) δ 4.55 (s, 6, CH_3), 8.00 (s, 2, CH=CH), 8.37 (d, 4, aromatic), and 8.93 ppm (d, 4, aromatic)); 1,2-bis(3-pyridyl)ethylene dimethiodide (yellow crystals, mp 298–302°; uv max 275 nm (ϵ 22,000)); 1,2-bis(4-pyridyl)ethylene dimethiodide (red crystals; mp 220–225°; uv max 317 nm (ϵ 24,000)); 4-stilbazole methiodide (yellow crystals; mp 211–220° dec; uv max 342 (ϵ 30,000)); 3-stilbazole methiodide (pale yellow crystals, mp 211–217° dec; uv max 296 nm (ϵ 23,000)).

Conversion of methiodide salts to methylfluoroborate salts was accomplished by treating 10 mmol of silver fluoroborate with a 5 mM aqueous solution of the dimethiodide salt followed by removal of silver iodide by filtration. Evaporation of the solvent under vacuum yielded 1,2-bis(4-pyridyl)ethylene dimethylfluoroborate which was purified by several recrystallizations from ethanol–water mixtures.

Anal. Calcd for C$_{14}$H$_{16}$N$_2$B$_2$F$_8$: C, 43.57; H, 4.18. Found: C, 43.38; H, 4.25.

The dimethylfluoroborate of 1,2-bis(3-pyridyl)ethylene was prepared in the same manner.

Anal. Calcd for C$_{14}$H$_{16}$N$_2$B$_2$F$_8$: C, 43.57; H, 4.18. Found: C, 43.31; H, 3.94.

The preparation of phenyl-*N-tert*-butylnitrone has been reported previously in the literature.[20,34]

Reagent grade absolute ethanol from U. S. Industrial Chemical Co. was used as received. Other solvents were of spectral quality and were distilled before use.

(33) D. G. Whitten and M. T. McCall, *J. Amer. Chem. Soc.*, **91**, 5097 (1969).
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Preparative scale irradiations were carried out in a cylindrical, three-necked reaction vessel. Through the center neck was immersed a quartz lamp well containing a high-pressure Hanovia mercury lamp surrounded by a Pyrex sleeve. Oxygen was removed from the solutions by purging with oxygen-free nitrogen before and during irradiation.

Photohydration of 1,2-Bis(4-pyridyl)ethylene Dimethiodide (1a). A solution containing 1.4 g (0.01 M) of **1a** in 300 ml of distilled water was irradiated under nitrogen for approximately 2 hr. The photoreaction could be conveniently followed by uv by removing aliquots and monitoring the decrease in absorption of the olefin and concurrent increase in intensity of absorption of the hydrate. After concentrating the reaction mixture under vacuum, a small amount of 95% ethanol was added to the residue causing brown crystals to form. The crude compound **2** was recrystallized several times from isopropyl alcohol–water to obtain an analytical sample: mp 235–240° dec; nmr (D$_2$O) δ 3.50 (d, 2 ArCH(OH)CH_2Ar), 4.37 (s, 3, NCH_3), 4.40 (s, 3, NCH_3), 5.42 (t, 1, ArCH(OH)CH$_2$Ar), and 8.33 ppm (m, 8, aromatic).

Anal. Calcd for C$_{14}$H$_{18}$N$_2$I$_2$O: C, 34.19; H, 3.78. Found: C, 34.32; H, 3.79.

Photohydration of 1,2-Bis(4-pyridyl)ethylene Dihydrochloride. 1,2-Bis(4-pyridyl)ethylene (1 g) and 1 ml of concentrated HCl dissolved in 300 ml of distilled water were irradiated under nitrogen for approximately 1 hr. A uv spectrum indicated that the hydrated product comprised greater than 90% of the reaction mixture although small amounts of unreacted cis and trans olefin also appeared to be present. The solution was neutralized with aqueous NH$_3$ and concentrated on a rotary evaporator to approximately 20 ml. Crystals precipitated after cooling. Analytical samples of white flaky crystals were obtained after several recrystallizations from benzene: mp 128–129°; nmr (CDCl$_3$) δ 3.0 (d, J = 6 Hz, 2, ArCH_2CH(OH)Ar), 4.4 (broad singlet, 1, OH), 5.0 (t, J = 6 Hz, 1, ArCH$_2$CH(OH)Ar), and 7.8 ppm (m, 8, aromatic).

Anal. Calcd for C$_{12}$H$_{12}$N$_2$O: C, 72.00; H, 6.00. Found: C, 71.92; H, 6.10.

Photohydration of 1,2-Bis(3-pyridyl)ethylene Dimethiodide (3). This reaction was much more difficult than the photohydration of **1a**. The hydrate was isolated from a reaction in which 200 mg of **3** was dissolved in 350 ml of water. After 3 hr of irradiation under nitrogen, the photolysis was stopped and the solvent was reduced to *ca.* 20 ml on a rotary evaporator. Upon cooling, unreacted **3** precipitated. The filtrate was further concentrated, ethanol was added, and the solution was cooled. The hydrate precipitated as a fine powder: mp 244–258° dec. Three recrystallizations from isopropyl alcohol–water produced an analytical sample.

Anal. Calcd for C$_{14}$H$_{18}$N$_2$I$_2$O: C, 34.19; H, 3.78. Found: C, 34.35; H, 3.62.

Photoaddition of Ethanol to Bispyridylethylene Salts. A solution of 100 mg of **1a** in 350 ml of absolute ethanol was irradiated for 4 hr. The reaction was stopped because the solution was becoming deeply colored. A uv spectrum indicated that only about 50% of the starting material had disappeared. Upon concentrating the reaction mixture to about 75 ml and cooling, unreacted starting material crystallized. The filtrate was concentrated further and crystals formed. This compound was not identified; its uv spectrum had an absorption maximum at 350 nm. The filtrate was further concentrated and crystals formed which had a uv consistent with the expected ether: mp 220–240° dec. Several recrystallizations from isopropyl alcohol–water produced an analytical sample.

Anal. Calcd for C$_{16}$H$_{22}$N$_2$OI$_2$: C, 37.50; H, 4.30. Found: C, 37.65; H, 4.18.

The dimethylfluoroborate salt (**1b**) gave a similar product upon irradiation in absolute ethanol: nmr (D$_2$O) δ 1.29 (t, J = 6.8 Hz, 3, CH$_2$CH_3), 3.3–3.7 (m, 4, OCH_2CH$_3$, ArCH(R)CH_2Ar), 4.39 (s, 3, NCH_3), 4.46 (s, 3, NCH_3), 5.03 (s, 1, ArCH(R)CH$_2$Ar), 7.93 (t, 4, aromatic), and 8.67 ppm (t, 4, aromatic).

Irradiation of 500 mg of 1,2-bis(4-pyridyl)ethylene and 1 ml of concentrated HCl in 1250 ml of absolute ethanol resulted in a decrease in absorption at 313 nm with a concurrent increase in absorption at 258 nm. After 7 hr, irradiation was stopped and the volume of the solvent was reduced under vacuum to 100 ml. The solution was diluted with 200 ml of water, neutralized with aqueous

NH$_3$, and extracted with chloroform. Evaporation of the chloroform layer gave the corresponding ether: nmr (CDCl$_3$) δ 1.06 (t, J = 6.8 Hz, 3, CH$_2$CH_3), 2.82 (s, 2, ArCH(R)CH_2Ar), 3.23 (q, J = 7.0 Hz, 2, OCH_2CH$_3$), and 4.35 ppm (t, J = 7.5 Hz, 1, ArCH(R)CH$_2$Ar).

Photoaddition of Ethers to 1,2-Bis(4-pyridyl)ethylene Dimethylfluoroborate (1b). A solution of 100 mg of **1b** in 300 ml of acetonitrile and 100 ml of tetrahydrofuran was irradiated under nitrogen for 40 min. During that time, an isosbestic point was observed in the uv spectra of the reaction mixture. Absorption due to the olefin quickly decreased with the concurrent increase in absorption at 258 nm. After evaporation of the solvent, the semisolid was chromatographed through a column containing Bio-Rex 70 cation exchange resin (20–50 mesh). The product was eluted with an aqueous solution of sodium fluoroborate. Fractional recrystallization from ethanol–water mixtures gave the saturated bispyridylethane derivative: nmr (D$_2$O) δ 1.5–2.2 (m, 4, C$H_2 \beta$ to O), 3.1–4.1 (m, 5, CH_2OCH, ArCH(R)CH_2Ar), 4.36 (s, 3, NCH_3), 4.40 (s, 3, NCH_3), 4.72 (s, 1, ArCH(R)CH$_2$Ar), 7.87 (t, 4, aromatic), and 8.65 ppm (t, 4, aromatic). Similar spectra for alkylated tetrahydrofuran derivatives have been reported.[35]

When 200 mg of **1b** was irradiated in 300 ml of acetonitrile and 100 ml of ethyl ether, the uv absorption due to olefin **1b** disappeared in *ca.* 1 hr with a concurrent increase in absorption in the uv region. After evaporating the solution to dryness, the brown oil was chromatographed through the above-mentioned ion exchange column. Elution with an aqueous solution of sodium fluoroborate yielded first a saturated bispyridylethane derivative and secondly, a product whose uv spectrum was similar to that of a phenanthrolinium salt. The crude bispyridylethane derivative was fractionally recrystallized from ethanol–water mixtures: nmr (D$_2$O) δ 1.08 (t, 3, CH_3CH$_2$), 1.26 (d, 3, CH_3CH), 3.4–3.8 (m, 5, CHOCH_2, ArCH(R)CH_2Ar), 4.27 (s, 3, NCH_3), 4.32 (s, 3, NCH_3), 5.08 (s, 1, ArCH(R)CH$_2$Ar), 7.83 (t, 4, aromatic), and 8.53 ppm (t, 4, aromatic).

Methods. Quantum yields for photoaddition reactions were obtained by irradiating samples in Pyrex ampoules degassed by three cycles of freeze–pump–thaw. The ampoules were irradiated in a merry-go-round apparatus[36] with light from a medium-pressure mercury lamp. Ferric oxalate actinometry was used to measure light intensities.[37] To isolate the mercury emission lines of 313 and 366 nm, the following filters were used: 313 nm, 7-54 Corning glass filter and a 0.7-cm path, 0.0025 M K$_2$CrO$_4$ in 1% Na$_2$CO$_3$; 366 nm, Corning glass filters 0-52 and 7-37. Samples were analyzed by measuring changes in absorption spectra recorded on a Unicam SP800B spectrophotometer. In the benzophenone sensitization experiments, benzophenone was extracted from the solutions with ether, and then the absorption spectrum of the charged species was recorded.

The apparatus for flash spectroscopic studies has been described.[22a] Samples for flash photolysis were 1 × 10^{-4} M and were degassed by four–five cycles of the freeze–pump–thaw method. Corning glass filters 0-53 and 7-54 were placed between the sample cavity and the flash tube.

Spin trapping experiments were performed by the method of Janzen, Blackburn, and Gerlock.[20] Samples containing phenyl-N-*tert*-butylnitrone and olefin **1b** in either 1:1 ethanol–acetonitrile or 1:1 tetrahydrofuran–acetonitrile were irradiated at 335 nm, in the cavity of a Varian E-3 electron spin resonance spectrometer. The light from a high-pressure mercury lamp was passed through a high-intensity Bausch and Lomb mónochromator and focused on the sample with a quartz condensing lens.

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