

Therefore, authentic phenylhydroxylamine was extracted from benzene in the same way and recovered again, after neutralizing the acid, as a solution in benzene. Workup gave a concentrated solution which by TLC was found to contain only phenylhydroxylamine. The phenylhydroxylamine used in these experiments was made from nitrobenzene.⁶⁸ Our procedure for preparing [4,4'-¹³C]**4**, therefore, was conveniently shortened by our not having to isolate and separate the [4-¹³C]aniline and [4-¹³C]phenylhydroxylamine before oxidation with MnO₂.

4,4'-Dideuterioazobenzene. To a stirred suspension of 10.7 g (45 mmol) of 4-nitrobenzenediazonium tetrafluoroborate⁶³ in 100 mL of CDCl₃ (99.6% D) cooled in ice was added 14.4 mL of D₃PO₂ (50% solution in D₂O, 99% D) and 100 mg of Cu₂O. The mixture was stirred for 5 min, and to it was added enough sodium carbonate to neutralize the acid. The chloroform layer was washed with D₂O and dried over sodium sulfate. Removal of the chloroform and distillation of the residue under vacuum gave 4.8 g (86.7%) of 4-deuterionitrobenzene with a satisfactory ¹H NMR spectrum. Earlier workers obtained a 99% yield (by GLC) of ordinary nitrobenzene.²⁹ The nitro[4-²H]benzene was converted into [4,4'-²H]**4** by reduction with zinc in aqueous methanolic sodium hydroxide solution,⁶⁹ in 64% yield.

Crystallization from aqueous ethanol gave a melting point of 67–67.5 °C. The product had an acceptable ¹H NMR spectrum and was found by mass spectrometry to contain 94% [²H₂]-, 5.8% [²H₁]-, and 0.1% [²H₀]**4**. This product was mixed with an equal weight of ordinary **4** and recrystallized for use in determining the secondary deuterium isotope effect.

Search for Ring-Deuterium Exchange during Rearrangement of 1. Two solutions were prepared and cooled to 0 °C before mixing. The first contained 105 mg (0.571 mmol) of ordinary **1** in 20 mL of 95% [O²H]ethanol (EtOD) and 6.7 mL of D₂O. The second was 26.7 mL of 0.2 N DCl in 75% EtOD in D₂O, containing 686 mg of lithium chloride. The mixture was allowed to stand for 97 min (50% conversion of **1**) and then treated with sodium hydroxide and air as described above. Workup gave 54.4 mg of **4** for mass spectrometric analysis. Two runs were made. The ratio of masses 182/183 were 6.665 ± 0.02 and 6.645 ± 0.04, as

compared with 6.652 ± 0.03 for the original **4**.

Mass Spectrometric KIE. The mass spectra of all compounds were obtained on a Hewlett-Packard instrument, Model 5930A, equipped with a data system, Model 5932. Introduction of a sample was effected with a direct insertion probe. The temperatures of the source and filter were adjusted for each compound so as to obtain sufficient volatility. An ionizing energy of 70 eV and ionizing current of 25 mA were used. The high-precision, isotope ratio measurement procedure used was as originally described by Kwart and Stanulonis⁷⁰ and as most recently applied by Reimschuessel and Paneth.⁷¹ Parent peaks of unlabeled or labeled substrate and/or product were scanned 20 000 times per sample to yield a mean ratio with a standard deviation of less than or equal to 0.2%.

The procedure which was used measured the relative change in isotope ratio in the samples as the reaction proceeded as compared with the ratio in the starting material or final product. For calculating k_H/k_L the data were treated according to the Bigeleisen equation⁷²

$$(k_H/k_L - 1) \ln [1 - f(x/y)] = \ln \left[1 + \frac{R_{A0} - R_{Af}}{R_{A0}} \frac{f(x/y)}{1 - f(x/y)} \right]$$

in which H and L designate the heavy and light isotope respectively, f = extent of reaction, R_{A0} = the AMU mass ratio at 100% reaction, R_{Af} = AMU mass ratio at f extent of reaction, $x = (1 + R_{A0})$, and $y = (1 + R_{Ad})$.

Acknowledgment. We wish to thank Dr. Frank W. Crow, Midwest Center for Mass Spectrometry, for help with mass spectrometric assays during the syntheses of labeled compounds.

Registry No. 1, 122-66-7; **2**, 92-87-5; **3**, 492-17-1; [4-¹⁴C]**4**, 81141-91-5; [4,4'-¹³C]**4**, 81141-92-6; [4,4'-²H]**4**, 35427-74-8; [¹⁵N]**4**, 35427-75-9; **5**, 81141-93-7; unlabeled **5**, 81141-94-8; 4-nitro[1-¹⁴C]aniline, 81141-95-9; nitro[4-¹⁴C]benzene, 81141-96-0; 4-nitro[1-¹³C]phenol, 3881-07-0; 4-deuterionitrobenzene, 13122-36-6; [¹⁵N]aniline, 7022-92-6; 5-chloro-1-phenyl-1H-tetrazole, 14210-25-4.

(68) Vogel, A. I. "Textbook of Practical Organic Chemistry", 4th ed.; Longman: London, 1978; p 722.

(69) Bigelow, H. E.; Robinson, D. B. "Organic Syntheses"; Wiley: New York, 1955, Coll. Vol. 3, p 103.

(70) Kwart, H.; Stanulonis, J. J. *J. Am. Chem. Soc.* **1976**, *98*, 4009.

(71) Reimschuessel, W.; Paneth, P. *Org. Mass Spectrom.* **1980**, *15*, 302.

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Photohydration of Aromatic Alkenes and Alkynes¹

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Contribution from the Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 1A1. Received April 21, 1980. Revised Manuscript Received July 28, 1981

Abstract: The photohydrations of aromatic alkenes and alkynes **2–12** have been studied in aqueous sulfuric acid. For the nonnitro-substituted substrates **2–8**, the products are the compounds obtained via Markovnikov addition of water to the alkene or alkyne moiety. Nitro-substituted styrenes **11** and **12** and phenylacetylenes **9** and **10** gave anti-Markovnikov addition products. Product quantum yields (Φ_{pd}) generally show a strongly sigmoidal dependence on the acidity of the medium, with the exception of the nitrostyrenes, where no such dependence was observed. For compounds **2–8**, quenching of fluorescence with increasing acidity was observed, and the proposed photohydration mechanism involves a rate-limiting protonation step on the first excited singlet state (S_1), while for the nitrostyrenes, a rate-limiting attack of water on T_1 is consistent with the available data. A mechanism involving a concerted addition of H_3O^+ to T_1 is proposed for the photohydration of (nitrophenyl)acetylenes **9** and **10**. The solvent isotope effect on the product quantum yield (Φ_H/Φ_D) is consistent with these proposals. Photoprotonation rate constants (k_H) have been obtained—via transient and steady-state measurements—for substrates **2**, **4–6**, and **8**. Alkenes are approximately one order of magnitude less reactive than alkynes to photoprotonation, both of which are 10^{11} – 10^{14} times more reactive than the corresponding ground-state molecules.

The acid-catalyzed hydration of phenylacetylenes and styrenes in the ground state has been studied extensively.³ The products are, respectively, the acetophenones and 1-phenylethanols, both of which arise from Markovnikov addition of a proton in the rate-limiting step, followed by attack of water.³

(1) Part of this work was presented at the 64th Chemical Conference of the Chemical Institute of Canada, June, 1981, Halifax, Nova Scotia, Canada.

(2) To whom correspondence should be addressed.

(3) (a) Phenylacetylenes: Noyce, D. S.; Schiavelli, M. D. *J. Am. Chem. Soc.* **1968**, *90*, 1020. (b) Styrenes: Schubert, W. M.; Keefe, J. R. *Ibid.* **1972**, *94*, 559 and references therein.

At room temperature, these hydrations are very slow in the 0–25% (w/w) range of sulfuric acid concentrations, with half-lives of several hours or even days. A means by which the observed rate can be enhanced is by increasing the "basicity" of the substrate, thus making the protonation step more facile. This can, in principle, be achieved via photochemical excitation to the singlet or triplet excited states, since the enhanced basicity of numerous aromatic chromophores upon excitation is well-known.⁴

(4) For reviews, see: (a) Ireland, J. F.; Wyatt, P. A. H. *Adv. Phys. Org. Chem.* **1976**, *12*, 131. (b) Lahiri, S. C. *J. Sci. Ind. Res.* **1979**, *38*, 492.

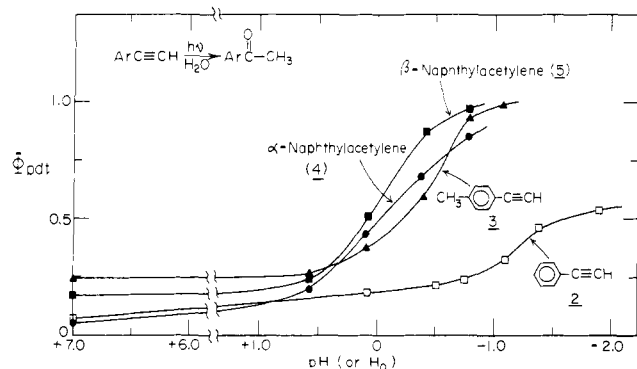
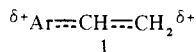


Figure 1. Φ_{pdt} as a function of acidity for aromatic alkynes 2-5.

An application of this principle is in the facile photohydration of several aromatic alkynes, either in water or in dilute aqueous acids, reported by Wooldridge and Roberts.^{5a} The products obtained were the corresponding ketones, as observed in the ground-state reaction. In addition, it was shown that the efficiency of the photoreaction increased with the acidity of the medium. This suggests a mechanism involving photoprotonation of the alkyne moiety, to give a vinyl cation which may be in an excited state.^{5a} Apart from the works of Roberts and co-workers,⁵ and two other groups,⁶ the photoprotonation of alkynes has not been studied extensively.

A related reaction is the photoprotonation of alkenes in hydroxylic solvents.⁷ For aliphatic alkenes that undergo photohydration, the mechanism is believed to involve nucleophilic trapping of the Rydberg state of the molecule by the solvent.⁷ For cyclic alkenes, both nucleophilic trapping of the Rydberg state and of the highly reactive *trans*-alkene intermediate are believed to be responsible for photohydration, the mechanism followed depends on the ring size.⁷ A number of aromatic alkenes (acyclic styryl systems) are also known to undergo photoprotonation,⁷ the reactive singlet states in these cases are believed to have a high degree of charge transfer character,^{7,8} as shown by **1**. However, additional study is necessary since the efficiency of the photoprotonation pathway is known to depend strongly on substitution on the side chain as well as on the aryl group.⁷



This paper presents results of our study of the photohydration of a number of aromatic alkenes and alkynes, which significantly extends our understanding of the photoprotonation of these compounds.

Results

Product Studies. Since photoreduction and other side reactions have been reported along with photoprotonation of alkenes and alkynes in hydroxylic solvents⁵⁻⁸ (alcohols or carboxylic acids), it was felt that aqueous sulfuric acid was a more suitable medium to study the photoprotonation process. This medium allows for the variation of the acidity in a quantitative fashion (at least in low acidities), as well as reduces the efficiency of photoreduction processes initiated by hydrogen abstraction from the solvent. Irradiation of 10^{-4} – 10^{-3} M solutions of compounds **2–8** in aqueous (5–10% H_2SO_4) acetonitrile at 254 or 300 nm in a Rayonet RPR-100 reactor gave only the corresponding Markovnikov hydration product—the methyl ketones in the case of the alkynes and the 1-arylethanol for the alkenes, as confirmed by comparison

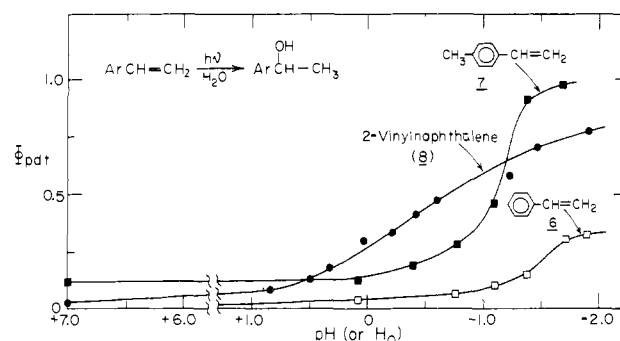
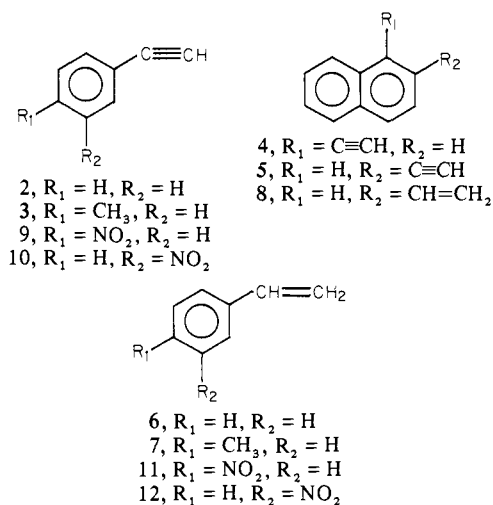
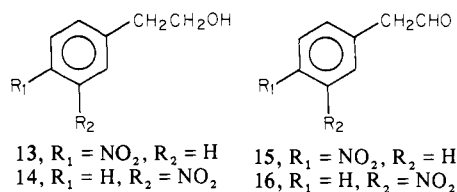


Figure 2. Φ_{pdt} as a function of acidity for aromatic alkenes 6-8.

with authentic samples of the products via ^1H NMR and GLC. Photohydration (hence photoprotonation) is a general reaction for these substrates.



For the nitro-substituted compounds, *anti*-Markovnikov addition products are obtained; nitrostyrenes afforded 2-(nitrophenyl)ethanols **13** and **14** while phenylacetaldehydes **15** and **16** were obtained from the (nitrophenyl)acetylenes. These products were readily identified by comparison with authentic samples (^1H NMR and GLC). These anti-Markovnikov products observed in the photoprocess are in contrast to the Markovnikov products available from the corresponding ground state reaction. Thus, not all aromatic alkenes and alkynes undergo simple Markovnikov photoprotonation.⁹



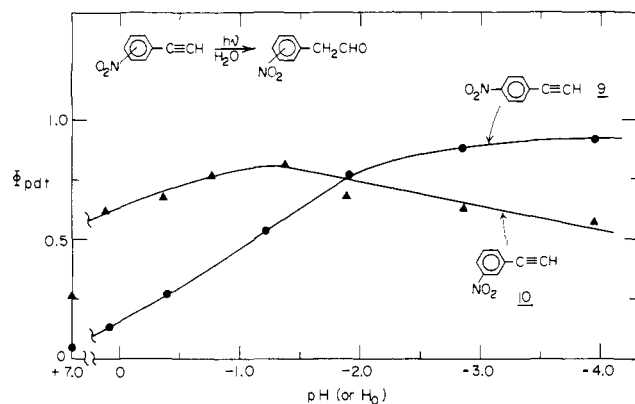
Product Quantum Yields. Photohydration product quantum yields (Φ_{pdt}) were measured as a function of medium acidity for compounds **2–12** at a substrate concentration of 10^{-5} M. This was done by following the course of the photohydration using UV spectrophotometry, since the substrate and product absorption characteristics were quite different (see Experimental Section). For alkynes **2–5**, product quantum yields depend strongly on medium acidity (Figure 1) and for most compounds reach an efficiency close to unity. These sigmoid-type quantum curves strongly suggest that protonation of the excited substrate is the

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(6) (a) Fujita, K.; Yamamoto, K.; Shono, T. *Tetrahedron Lett.* **1973**, 3865. (b) Ferris, J. P.; Antonucci, F. R. *Chem. Commun.* **1972**, 126. (c) For a review of alkyne photochemistry, see: Coyle, J. D. In "The Chemistry of the Carbon-Carbon Triple Bond"; Patai, S., Ed.; Wiley: New York, 1978; Part 2, Chapter 12.
(7) For a review of photoprotonation and other photoreactions of alkenes, see: Kropp, P. J. *Org. Photochem.* **1979**, *4*, 1, and references therein.
(8) Kropp, P. J. *J. Am. Chem. Soc.* **1973**, *95*, 4611.

(9) Photohydration is not an important pathway for (*p*-bromophenyl)-acetylene. When this compound was irradiated in aqueous acetonitrile, the major product is tentatively assigned as *p,p'*-diethynyl biphenyl. A trace of the hydration product was detected by GLC. In view of this result for (*p*-bromophenyl)acetylene, the photohydration of other halo-substituted compounds was not pursued.

Table I. Product Quantum Yields for Nitrostyrenes 11 and 12 as a Function of Medium Acidity

$-H_0$ (% H_2SO_4)	Φ_{pdt}	
	11	12
pH 7	0.15	0.43
-0.08 (5.08)		0.48
0.40 (10.54)	0.14	0.44
0.76 (15.50)		0.45
1.10 (20.35)	0.14	0.41
1.40 (24.90)	0.096	0.37
1.72 (29.76)	0.089	0.41
1.90 (32.74)		0.47


 Figure 3. Φ_{pdt} as a function of acidity for (nitrophenyl)acetylenes 9 and 10.

rate-limiting step in these photohydrations. In the range of pH 7–1, no enhancement in quantum yield is observed although the acidity of the medium is changed by 6 orders of magnitude. This is interpreted as being due to an uncatalyzed water addition pathway, in a region of acidity where the excited state is not yet significantly protonated.

For alkenes 6–8, a similar sigmoid dependence of Φ_{pdt} on medium acidity is observed (Figure 2), and a rate-limiting protonation step is also implicated.

Anomalous behavior of Φ_{pdt} is observed for both the nitrostyrenes 11 and 12 and (nitrophenyl)acetylenes 9 and 10. The efficiency of nitrostyrene photohydration (Table I) does not depend on medium acidity over an acidity range of 10 logarithmic units. On the other hand, Φ_{pdt} for the (nitrophenyl)acetylenes are strongly dependent on H_0 (Figure 3), with 10 exhibiting a maximum at $H_0 = -1.2$. It seems clear that different photohydration mechanisms are operative for these nitro-substituted styrenes and phenylacetylenes, all of which show quite different behavior from that observed for compounds 2–8.

Fluorescence Quenching Studies. Fluorescence quenching by added sulfuric acid was observed for substrates 2–8 (see Figure 4 for 2-vinylnaphthalene (8)). The nitro-substituted compounds exhibited no detectable fluorescence. Plots of the relative fluorescence quantum yields (Φ_f/Φ_f^0) (where Φ_f^0 is the fluorescence quantum yield in water at pH 7) vs. acidity show quenching of the singlet excited state (S_1) concurrent with the increase in photohydration efficiency, as shown in Figure 5 for 5 and 6. Fluorescence quenching experiments with β -naphthylacetylene (5) in aqueous perchloric and hydrochloric acids gave results which were superimposable on the sulfuric acid fluorescence quenching curve for this compound. This strongly suggests that the hydronium ion is the only important proton-transfer agent in these photoprotonations. From these observations, it is most probable that compounds 2–8 react via their S_1 states.

Triplet Sensitization and Quenching Studies. To investigate the possibility of a triplet pathway in the photohydration of 2–12, triplet sensitization experiments employing three water-soluble triplet sensitizers (Table II) were carried out. In a typical experiment, 20–50 mg of substrate was dissolved in aqueous acetonitrile and enough sensitizer was added (10–20 g) to ensure that

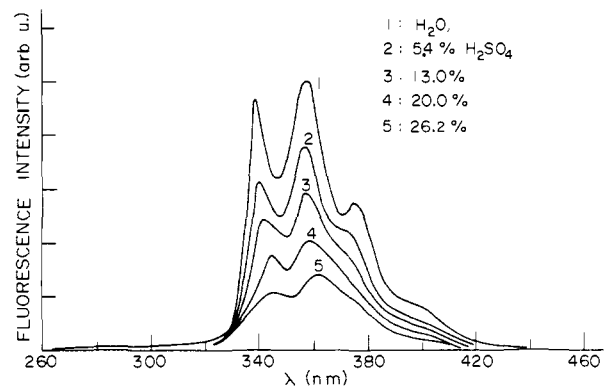
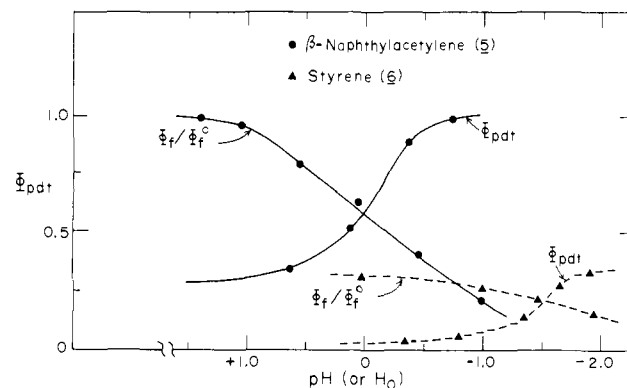
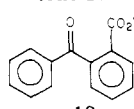
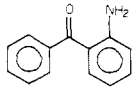

 Figure 4. Quenching of fluorescence in aqueous H_2SO_4 for 2-vinylnaphthalene (8) (exciting wavelength 250 nm).

 Figure 5. Complementary product quantum yield (Φ_{pdt}) and fluorescence quenching (Φ_f/Φ_f^0) curves for styrene (6) and β -naphthylacetylene (5). The initial Φ_f/Φ_f^0 value has been set arbitrarily at the maximum observed product quantum yield.

Table II. Triplet Sensitizers

sensitizer	E_t^a , kcal mol $^{-1}$	exciting wavelength, b nm
acetone 17	~79	300
 18	~68	350
 19	~68	350

^a From published sources¹⁰ or as estimated based on benzophenone. ^b The lamps of the specified wavelength were purchased from the Southern New England Ultraviolet Co. and employed in a Rayonet RPR-100 reactor.

the sensitizer absorbed at least 95% of the exciting light. It was found that the photohydration of 5, 6, and 8, all of which have triplet energies of approximately 60 kcal mol $^{-1}$,^{10,11} could not be sensitized by 17 or 18. Sensitizer 19 was employed in 15% H_2SO_4 -acetonitrile mixtures and failed to sensitize the photohydration of 8. For 8, the mass spectrum of the product mixture indicated predominantly dimeric products, while 1H NMR showed complete disappearance of starting material. Thus the triplet state (T_1) of these compounds are not inert in aqueous acid, but the evidence shows that they do not undergo photoprotonation. This

(10) (a) Murov, S. L. "Handbook of Photochemistry"; Marcel Dekker: New York, 1973. (b) Gordon, A. J.; Ford, R. A. "The Chemist's Companion"; Wiley: New York, 1972.

(11) Zimmerman, H. E.; Bender, C. O. *J. Am. Chem. Soc.* 1970, 92, 4366.

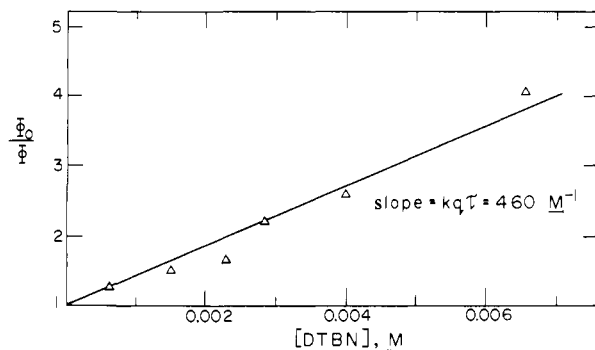


Figure 6. Quenching of *m*-nitrostyrene (12) photohydration by DTBN.

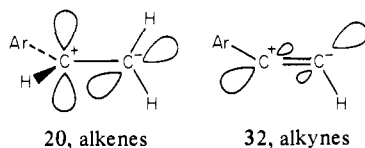
is fully consistent with these states possessing diradicaloid character hence not being able to react in a zwitterionic manner.

The photohydration of nitrostyrenes **11** and **12** could be sensitized by both **17** and **18**, while for (nitrophenyl)acetylenes **9** and **10**, only **17** could sensitize the reaction. On the basis of this latter observation, the triplet energy of **9** and **10** is between 68 and 80 kcal mol⁻¹, which is similar to the known T₁ energy of phenylacetylene (ca. 72 kcal mol⁻¹)¹⁰ than that of nitrobenzene (ca. 60 kcal mol⁻¹).¹⁰

Quenching of *m*-nitrostyrene (**12**) photohydration could be effected by di-*tert*-butyl nitroxide (DTBN), a known quencher of triplet states of energy greater than ca. 55 kcal mol⁻¹.¹² The resulting linear Stern-Volmer plot (Figure 6) gave a triplet lifetime of 0.46 μs (a value of 10⁹ M⁻¹ s⁻¹ for *k_q* was employed)¹² in 30% CH₃CN-H₂O. The reaction is essentially completely quenched at 0.01 M DTBN. Similarly for (*m*-nitrophenyl)acetylene (**10**), quenching with DTBN in 30% CH₃CN-H₂O gave a triplet lifetime of 2.8 μs.

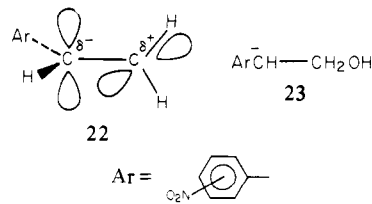
With the above results at hand, the following conclusions can be made. The photohydration of compounds **2-8** occurs via a reactive singlet state, the triplet state leading only to dimers and other unidentified products. On the other hand, for the nitro-substituted compounds **9-12**, the triplet state undergoes photohydration.

Photohydration Mechanisms. For aromatic alkenes and alkynes **2-8**, a rate-limiting protonation step on S₁ is consistent with the available data. The S₁ states of these molecules probably possess a high degree of charge-transfer character (as shown by **1** for the alkenes). This was also postulated by a number of previous workers in their study of the photoprotonation of aromatic alkenes.^{7,8,13} Since alkenes are known to undergo a stabilizing twisting motion on excitation,¹⁴ and acetylene itself is known to have a bent excited state geometry,¹⁵ the S₁ states of these compounds probably resemble structures **20** and **21**. Trapping of the



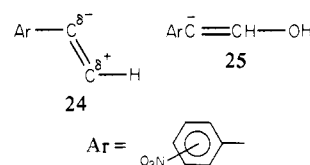
protonated species (vinyl cations or carbocations depending on the substrate) in a subsequent fast step by water molecules from the solvation shell leads to the hydration products.

The nondependence of Φ_{pd} on medium acidity for the photohydration of nitrostyrenes **11** and **12** (Table I) can best be explained in terms of a rate-limiting attack of water (at the β-carbon) on a highly polarized triplet state, as depicted by **22**, resulting in overall anti-Markovnikov addition of water. The reversal of polarity in the excited state of these nitro aromatic alkenes is fully consistent with the enhanced electron-withdrawing character of



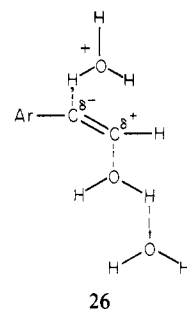
aromatic nitro groups in the excited state.¹⁶ Simple photo-protonation does not take place. The protonation of carbanion **23**, obtained after nucleophilic attack of water, is most likely a ground-state process. This mechanism explains the observed dependence of Φ_{pd} on acidity since the efficiency of this reaction would depend only on the availability of water, which does not vary significantly in the region of acidity studied.

The photohydration behavior of (nitrophenyl)acetylenes **9** and **10** is more complicated than for the compounds discussed so far. The observation of anti-Markovnikov addition and acid catalysis (Figure 3) suggests a mechanism involving a proton transfer in the rate-limiting step. The reactive triplet state is assumed to be polarized as shown by **24**.



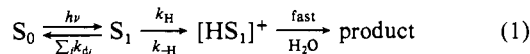
The suggested mechanism involves nucleophilic attack of water (at the β-carbon) synchronous with proton transfer to **24**. Direct nucleophilic attack on **24** does not take place. Possibly **24** is not sufficiently polarized (cf. **22**) to facilitate such an attack, and proton transfer concerted with water addition is required. An alternate rationalization is that the formation of **25** (obtained by direct nucleophilic attack on **24**) has such a high activation energy that its formation is avoided in the reaction pathway.

It remains to explain the decrease in Φ_{pd} observed for (*m*-nitrophenyl)acetylene (**9**) above H₀ = -1.2 and the leveling off in efficiency observed for (*p*-nitrophenyl)acetylene (**10**) above H₀ = -2. A synchronous addition of H₃O⁺ to the excited acetylene moiety **24** would require not one but at least two or more water molecules to mediate the process, as crudely shown by **26**. A



mechanism of this sort would be expected to have a strong dependence on medium acidity, as well as on the availability of water. Thus, the decrease or leveling off in photohydration efficiency is most likely due to the depletion of water on going to strongly acidic media, the onset of which would depend on the reactivity and lifetime of the excited-state species.

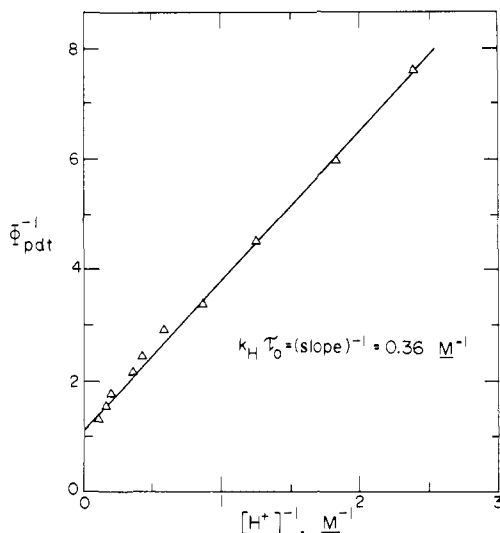
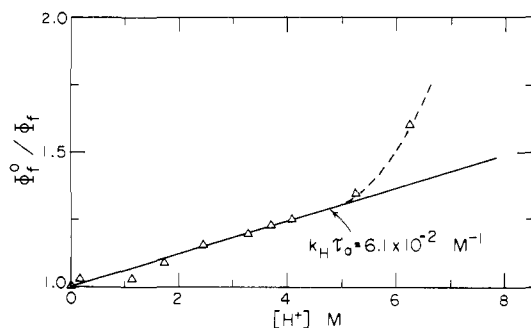
Photoprotonation Rate Constants, *k_H*. The proposed mechanism for the photohydration of compounds **2-8** (eq 1) allows the



calculation of the photoprotonation rate constants (*k_H*) via

(12) Schwerzel, R. E.; Caldwell, R. A. *J. Am. Chem. Soc.* **1973**, *95*, 1382.
 (13) Hixon, S. S. *Tetrahedron Lett.* **1973**, 277.
 (14) (a) Salem, L.; Rowland, C. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92. (b) Salem, L.; Stohrer, W.-D. *J. Chem. Soc., Chem. Commun.* **1975**, 140.
 (c) Dauben, W. G.; Salem, L.; Turro, N. J. *Acc. Chem. Res.* **1975**, *8*, 41.
 (15) Ingold, C. K. *J. Chem. Soc.* **1954**, 2991.

(16) (a) Zimmerman, H. E.; Somasekhara, S. *J. Am. Chem. Soc.* **1963**, *85*, 922. (b) Havinga, E.; Kronenberg, M. E. *Pure Appl. Chem.* **1968**, *16*, 137. (c) Döpp, D. *Top. Curr. Chem.* **1975**, *55*, 49.


 Figure 7. Plot of Φ_{pdt}^{-1} vs. $[H^+]$ for 2-vinylnaphthalene (8).

 Figure 8. Plot of Φ_f^0/Φ_f vs. $[H^+]$ for styrene (6).

transient and steady-state methods. $\sum_i k_{di}$ in eq 1 is the sum of the rate constants of all deactivational processes leading back to S_0 . If one assumes that protonation of S_1 is irreversible (i.e., $k_{-H} \approx 0$), the expression for the inverse of the product quantum yield (Φ_{pdt}^{-1}) and fluorescence quenching (Φ_f^0/Φ_f) is given by eq 2 and 3, respectively, where τ_0 is the fluorescence lifetime in water.

$$\Phi_{\text{pdt}}^{-1} = 1 + \frac{1}{\tau_0 k_H [H^+]} \quad (2)$$

$$\Phi_f^0/\Phi_f = 1 + \tau_0 k_H [H^+] \quad (3)$$

Plots of Φ_{pdt}^{-1} vs. $[H^+]^{-1}$ are linear, as shown in Figure 7 for 2-vinylnaphthalene (8). The photoprotonation rate constant (k_H) can thus be obtained if τ_0 is known. Plots of Φ_f^0/Φ_f vs. $[H^+]$ are linear up to ca. 4 M proton concentration but curve upward at higher acidities (see Figure 8 for styrene (6)). This suggests that hydronium ion becomes a much more effective quencher than indicated by its stoichiometric concentration (i.e., $a_{H^+} \gg C_{H^+}$). For these plots, the reasonably long linear portions were employed to give estimates of k_H .

Fluorescence lifetimes (τ_{obsd}) of a number of substrates have been measured by using the single photon counting technique, as a function of medium acidity. The relationship between τ_{obsd} and k_H is given by eq 4. As observed for fluorescence quenching, plots

$$\tau_{\text{obsd}}^{-1} = \tau_0^{-1} + k_H [H^+] \quad (4)$$

of eq 4 are linear up to ca. 4 M $[H^+]$. Estimates of k_H for a number of substrates calculated via the above three methods are tabulated in Table III. The good to reasonable agreement of k_H obtained by these independent methods is additional support for irreversible rate-limiting protonation in the photohydration mechanism proposed in eq 1.

Solvent Isotope Effect on Φ_{pdt} . As an additional probe into the photohydration process, the solvent isotope effect on product quantum yield (Φ_H/Φ_D) has been measured for substrates 2, 6,

Table III. Protonation Rate Constants

substrate	$k_H, M^{-1} s^{-1}$			$\tau_0,$ ns
	product quantum yield	fluorescence quenching	lifetime measure- ments	
phenylacetylene (2)	1.2×10^7	0.84×10^7	<i>a</i>	4.5
α -naphthylacetylene (4)	4.3×10^7	5.7×10^7	3.7×10^7	10.5
β -naphthylacetylene (5)	1.5×10^7	1.6×10^7	1.5×10^7	49.5
styrene (6)	2.3×10^6	8.1×10^6	<i>a</i>	7.5
2-vinylnaphthalene (8)	6.2×10^6	4.6×10^6	4.5×10^6	58.2

^a Lifetimes were too short in aqueous acids to give a reliable estimate of k_H .

Table IV. Solvent Isotope Effect on Product Quantum Yields

substrate	Φ_H	Φ_D	k_H/k_D^a
2	0.18 ^b	0.14 ^b	1.35 ^b
6	0.045 ^b	0.028 ^b	1.62 ^b
	0.025	0.019	1.32
9	0.047	0.031	1.54
10	0.26	0.19	1.49
11	0.14 ^b	0.13 ^b	1.08 ^b
	0.15	0.15	1.00
12	0.47 ^b	0.46 ^b	1.04 ^b
	0.43	0.43	1.00

^a Unless otherwise quoted, conditions employed were pure H_2O and D_2O . ^b Conditions employed were 6.3% ($H_0 = -0.056$) H_2SO_4 and D_2SO_4 .

and 9–12. If one assumes that deactivational processes not leading to product are identical in the two solvent systems, then it can be shown that the relationship between Φ_H/Φ_D and the solvent kinetic isotope effect for photoprotonation (k_H/k_D) is given by eq 5. Thus measurement of Φ_H and Φ_D allows for the calculation

$$\frac{k_H}{k_D} = \frac{\Phi_H}{\Phi_D} \frac{1 - \Phi_D}{1 - \Phi_H} \quad (5)$$

of k_H/k_D . The results are given in Table IV. The magnitudes of k_H/k_D observed for these substrates is fully consistent with their proposed photohydration mechanisms. For substrates 2, 6, 9, and 10, k_H/k_D is greater than unity and is consistent with a mechanism involving a proton transfer in the rate-limiting step. On the other hand, for substrate 11 and 12, k_H/k_D is essentially unity and is consistent with a rate-limiting attack of water on the excited state since the difference in the rate of nucleophilic attack between H_2O and D_2O is expected to be negligible.

Discussion

Photohydration appears to be a general reaction for nonhalo-substituted aromatic alkenes and alkynes. From the results of this work, three photohydration mechanisms are operative. This is in contrast to the ground-state reaction in which all aromatic alkenes and alkynes hydrate via rate-limiting proton transfer to give Markovnikov addition products.³ The complexities observed in the excited-state process are not unexpected since molecules in the excited state are high-energy species, and a number of different routes are usually available along the reaction pathway.

The study of the photohydration of aromatic alkenes and alkynes has given us insight into the electronic distribution of the excited states of these substrates. The singlet state of nonnitro-substituted aromatic alkenes and alkynes 2–8 most likely possess a high degree of charge-transfer character (as depicted by 20 and 21), thus facilitating protonation at the β -carbon and hence hydration. The triplet states of these molecules do not possess charge-transfer character but are probably of a diradicaloid nature. On the other hand, the triplet state of nitro-substituted aromatic alkenes and alkynes are highly polarized (as depicted by 22 and 24), resulting in complex photohydration behavior. The degree of this reverse polarization due to the nitro group appears to be greater for the alkenes than the alkynes.

It is unlikely that the photohydration is adiabatic over the whole reaction coordinate (see Figure 9 for phenylacetylene (2)), i.e.,

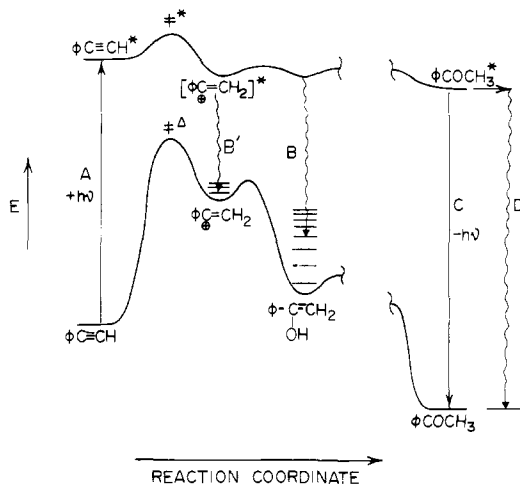


Figure 9. Excited-state vs. ground-state reaction coordinates in the hydration of phenylacetylene (**2**). Relative energy levels are not drawn to scale.

to give an excited ketone (or alcohol from the alkenes) from which the ground-state molecule can be obtained via either fluorescence (process C) or internal conversion (process D). The attack of water on the excited vinyl cation probably also deactivates the molecule to a vibrationally excited ground state (process B), and the reaction subsequently follows the ground-state energy surface. Similarly, deactivation via process B' will also lead to product. Thus the initial excitation with light (process A) is a means by which the initial energy barrier (the rate-limiting step in the ground-state reaction) can be overcome without having to resort to strong acids or high temperature.

From the photoprotonation rate constants (k_H) for substrates **2**, **4–6**, and **8** presented in Table III, it would appear that *aromatic alkynes are approximately one order of magnitude less reactive to photoprotonation than aromatic alkenes*. This is in contrast to the ground-state hydration reaction in which aromatic alkenes and alkynes are approximately of the same reactivity.¹⁷ The possible reasons for the enhanced difference in reactivity of the excited state of these functional groups is a subject for further investigation.

The ground-state protonation rate constants for substrates **2–8** are in the range of 10^{-5} – $10^{-7} \text{ M}^{-1} \text{ s}^{-1}$.³ Thus the excited state is approximately 10^{11} – 10^{14} times more reactive to protonation than the ground state. In the ground state, proton transfer to a neutral carbon is generally slow.¹⁸ This is due mainly to the ground-state electronic configurations and geometries involved and the need for rehybridization on protonation.^{4a} Since the excited-state electronic distribution is quite different, the activation barrier to proton transfer may be reduced significantly. If the excited states are assumed to have twisted (or bent) geometries, with charge-transfer character (as proposed above), then the need for rehybridization on protonation is avoided.

For substrates **2**, **6**, **9**, and **10**, the magnitudes of the solvent kinetic isotope effect for photoprotonation (k_H/k_D) are similar to the solvent isotope effects observed for carbon protonation of enolate anions (typically $k_H/k_D \approx 1$ – 2) in the ground state;¹⁹ the second-order protonation rate constants of these anions are also in the order of 10^6 – $10^7 \text{ M}^{-1} \text{ s}^{-1}$ and is believed to be essentially encounter controlled.²⁰ Although these protonation rate constants are 3–4 orders of magnitude below the encounter-controlled limit of $10^{10} \text{ M}^{-1} \text{ s}^{-1}$, carbon protonations in general seem to give limiting

rate constants well below this limit.²⁰ In other words, the proton-transfer part of the overall process has become so rapid that formation of the reaction complex, i.e., encounter of the reactants plus desolvation of the proton donor, is now the slow step.^{19,20} This suggests that *the photoprotonation of aromatic alkenes and alkynes is essentially an encounter plus desolvation controlled process*.

For the nonnitro-substituted aromatic alkenes and alkynes studied in this work, the dependence of Φ_{pt} and Φ_f/Φ_f^0 on pH (or H_0) is sigmoid, and the inflection points of the two curves coincide reasonably well for all these compounds. The inflection points occur around pH (or H_0) values of +1 to -2 (corresponding roughly to 1–20% H_2SO_4), suggesting that the excited states involved have $\text{p}K^*$ values far from the expected ground-state basicities. Although ground-state $\text{p}K$ s cannot be measured for alkenes and alkynes, it is reasonable to assume that they are weaker bases than benzonitrile ($\text{p}K_{\text{BH}^+} \approx -10$).²¹ Therefore, the $\text{p}K$ shifts on excitation ($\Delta\text{p}K = \text{p}K^* - \text{p}K$) must be of the order of 8 logarithmic units or more. Such large shifts in basicity are not unusual for conjugated aromatic systems of this type.⁴

From the results of this study and those reported previously by other workers,^{5–7} it would appear that for those compounds that hydrate or react in the ground state by rate-limiting protonation at carbon, an analogous photochemical pathway exists. The photoaddition of acetic acid, alcohols, and water to aromatic cyclopropanes has been reported.²² In light of our findings, this is not unexpected since cyclopropanes are known to hydrate in the ground state via a mechanism similar to that of the styrenes.²³ These and other photoinitiated hydrolyses and hydration reactions are presently under study in this laboratory.

Experimental Section

General Remarks. ^1H NMR spectra were recorded on a Varian T-60 spectrometer in CDCl_3 with Me_4Si as internal standard. UV spectra were recorded on a Cary 14 or a Unicam SP 1800 instrument. Optical density measurements for product quantum yield (Φ_{pt}) determinations were measured on a Cary 16 UV-vis spectrophotometer. GLC analyses were performed on a Varian Aerograph series 2700 instrument on either a 3% OV17 on Chromosorb W/HP or a 5% Carbowax 20M column. Integrated peak areas were calculated by using a Varian CDS 111 processor. Fluorescence spectra were recorded on a Perkin-Elmer MPF-44B fluorescence spectrophotometer at 20 °C. Mass spectra were obtained on a Du Pont Model 21-490 instrument.

Materials. The alkenes studied in this work were obtained from commercial sources and distilled or sublimed before use. Phenylacetylene (**2**) was purchased from Aldrich and double distilled before use. The remaining alkynes were gifts from Dr. T. A. Go and Professor J. Powell of this department. Di-*tert*-butyl nitroxide (DTBN) was purchased from Eastman Kodak and fractionally distilled under reduced pressure prior to use. Sensitizers **18** and **19** were purchased from Aldrich and were used without purification. All the ketones employed for the product determinations were commercially available. The corresponding alcohols were obtained by lithium aluminum hydride reduction. Phenylacetaldehydes **15** and **16** were synthesized according to the method of Norman and co-workers.²⁴

Irradiations. Preparatory irradiations were carried out on a Rayonet RPR-100 reactor at 254, 300, or 350 nm. Solutions were purged with argon for 30 min before irradiation. Stirring during irradiation was accomplished by a magnetic stirring bar. For quantum yield determinations, a GE 250-W medium-pressure lamp (General Electric, England) was employed. Monochromatic light was obtained by using a Bausch and Lomb high intensity monochromator (blaze 250 nm; dispersion 3.2 nm/mm) with variable entrance and exit slit widths. A Corning 7-54 band-pass filter (240–420 nm) was also employed to filter out scattered light from the monochromator.

Product Studies. The following experiment was typical of the procedure employed. A solution of 2-vinylnaphthalene (**8**) (30 mg in 250 mL of CH_3CN and 400 mL of 10% H_2SO_4) was outgassed with argon for 30 min and then irradiated at 254 nm in a quartz vessel. The progress

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of the reaction was followed by UV spectroscopy. After 6 h, the solution was saturated with NaCl and extracted with 2 × 150 mL CH₂Cl₂. Subsequent drying over MgSO₄ and solvent removal on a rotary evaporator afforded 22 mg of a yellow-orange solid. ¹H NMR and GLC analysis indicated ca. 80% 1-naphthylethanol (by comparison with an authentic sample) and 20% starting material.

Product Quantum Yields. The general method is described as follows. Solutions of the substrates (10⁻⁵ M) in the appropriate acid²⁵ were prepared in quartz cuvettes (Hellma, 1.00 cm) equipped with micro stirring bars. After the solutions were purged with argon, the optical density (OD) at the exciting wavelength (λ_{excit}) (between 238 and 280 nm, depending on the substrate) and λ_{max} were measured on the Cary 16 spectrophotometer. After irradiation (typically 1–5 min) on the optical bench, OD's were re-measured (conversion 5–10%), and product quantum yields were calculated via

$$\Phi_{\text{pdt}} = \Delta A_{\lambda} / (10^3 \epsilon_{\lambda} \Delta I_a)$$

where ΔA_λ is the loss of OD at λ_{max} of the substrate (or increase in OD if product formation was followed, which was possible for all the alkynes and alkenes **8**, **11**, and **12**), ε_λ is the extinction coefficient at this wavelength, and ΔI_a is the number of photons absorbed per unit volume during the irradiation. Φ_{pdt} calculated by either following the loss of substrate or product formation (where possible) gave identical values.

For determination of whether the ground-state hydration reaction was significant or not during the irradiation, identical "blank" solutions were made and kept in the dark. Employing this technique, we found that for all the nitro-substituted compounds **9–12**, the ground-state reaction is negligible over the acidity range studied. For the other substrates, the ground-state hydration becomes significant only at higher acidities (e.g., for styrene (**6**), at -H₀ > 1.4). In these cases, quantum yields were calculated after subtracting out the ground-state contribution.

Malachite green leucocyanide²⁶ (MGL) in acidic ethanol was employed for chemical actinometry. We found this actinometer to be more appropriate than potassium ferrioxalate because of the low light intensities employed (10⁻⁸–10⁻⁹ einsteins min⁻¹ cm⁻²), MGL being ca. 10 times more sensitive than the ferrioxalate actinometer. The compound was synthesized according to the method of Calvert and Rechen,²⁷ mp 174–176 °C (lit.²⁷ 176–177 °C). The actinometer solution was prepared by mixing 0.5 mL of acidic aqueous ethanol (ca. 10⁻³ M HCl) with 2.5 mL of a 10⁻³ M stock solution of MGL in ethanol in a quartz cuvette. The OD at 622 nm was measured before and after irradiation, and the change in OD (ΔA) was then used to calculate the light intensity of the source via

$$I(\text{einsteins min}^{-1} \text{ cm}^{-2}) = 10^3 \Delta A / (\epsilon_{622} \Phi_{\text{MGL}} \Delta t)$$

where ε₆₂₂ is the extinction coefficient of the blue dye produced at 622 nm (1.063 × 10⁵ cm⁻¹ M⁻¹),²⁶ Φ_{MGL} is the quantum yield for dye formation (0.91),²⁶ and Δt is the elapsed irradiation time in minutes. Light intensities were found not to fluctuate by more than 5% over a 4-h period. Since the OD at λ_{excit} for the substrates were kept ≥ 1, ΔI_a can be calculated and employed in the expression for Φ_{pdt}.

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Steady-State and Transient Fluorescence Studies. Solutions for fluorescence studies were prepared by injecting a stock solution of the substrate (in CH₃CN) into the appropriate acid via a microlitre syringe. After the solutions were purged with argon, fluorescence spectra were recorded under identical conditions. The fraction of fluorescence quenching (Φ_f/Φ_f⁰) was obtained via

$$\Phi_f / \Phi_f^0 = (I_f / I_f^0)_{\lambda_{\text{max}}}$$

where I_f and I_f⁰ are the fluorescence intensity at λ_{max} in the aqueous acid and water, respectively.

Fluorescence lifetimes were measured by single photon counting.²⁸ Excitation was through a Jarrell-Ash monochromator (230–290 nm) and the emission was isolated by a combination of band-pass and cutoff filters. Solutions of the substrates (10⁻⁵ M) in quartz vessels were degassed by five freeze-pump-thaw cycles prior to use.

Sensitization and Quenching Studies. The following experiment was typical of the procedure employed for the sensitization experiments. A solution of 2-vinylnaphthalene (**8**) (30 mg) and sensitizer **18** (15 g, 200 mL of CH₃CN and 800 mL of H₂O) was purged with argon for 30 min and subsequently irradiated in a Pyrex vessel for 12 h at 350 nm. The solution was then saturated with NaCl and extracted with 2 × 150 mL of CH₂Cl₂. Subsequent drying over MgSO₄ and solvent removal afforded a white solid. The ¹H NMR spectrum showed the presence of no starting material but only broad signals between δ 7–7.5 and δ 1–3. GLC analysis of the product mixture showed no hydration product while the mass spectrum gave peaks at m/e (relative intensity) 308 (10), 226 (10), 155 (30), 154 (100), and 153 (30), implicating the presence of dimers.

Triplet quenching experiments were accomplished by dissolving the appropriate substrate and a known amount of DTBN in 50% CH₃CN–H₂O in Pyrex vessels (15-mm o.d.). After being degassed by three freeze-pump-thaw cycles, the samples were irradiated at 350 nm on a merry-go-round apparatus for 30–45 min. After workup (CH₂Cl₂ extraction), the product mixtures were analyzed on a 3% OV 17 on Chromosorb W/HP column, with m-nitrobenzaldehyde as internal standard.

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Registry No. **2**, 536-74-3; **3**, 766-97-2; **4**, 15727-65-8; **5**, 2949-26-0; **6**, 100-42-5; **7**, 622-97-9; **8**, 827-54-3; **9**, 937-31-5; **10**, 3034-94-4; **11**, 100-13-0; **12**, 586-39-0; (*p*-bromophenyl)acetylene, 766-96-1.

Supplementary Material Available: Table of product quantum yields as a function of medium acidity for the photohydration of substrates **2–10** (1 page). Ordering information is given on any current masthead page.

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