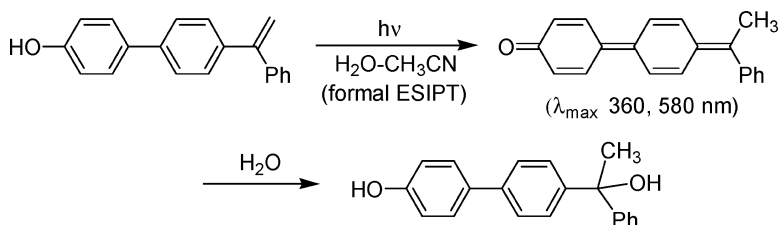Article

Photohydration and Photosolvolysis of Biphenyl Alkenes and Alcohols via Biphenyl Quinone Methide-type Intermediates and Diarylmethyl Carbocations

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Photohydration and Photosolvolysis of Biphenyl Alkenes and Alcohols via Biphenyl Quinone Methide-type Intermediates and Diarylmethyl Carbocations

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Abstract: Evidence is presented for the photochemical generation of novel biphenyl quinone methide (BQM)-type intermediates on photolysis of hydroxybiphenyl alkenes **7** and **8** and hydroxybiphenyl alcohols **9** and **10**. Mechanistic investigations utilizing product, fluorescence, and nanosecond laser flash photolysis (LFP) studies indicate two distinct pathways for the formation of these BQMs depending upon the functional groups of the progenitor. Formal excited-state intramolecular proton transfer (ESIPT) between the phenol and the alkene led to BQMs upon irradiation of the hydroxybiphenyl alkenes **7** and **8**, while excited-state proton transfer (ESPT) to solvent followed by dehydroxylation was responsible for BQM formation from the hydroxybiphenyl alcohols **9** and **10**. Photolysis of **7** and **8** in aqueous CH_3CN gave photohydration products via attack of water on the respective BQMs, while photolysis of the analogous methyl ethers (of the phenolic moiety) gave only carbocation intermediates. Hydroxybiphenyl alcohols **9** and **10** yielded the corresponding photomethanolysis products in aqueous methanol, through attack of CH_3OH on the respective BQMs. Although no evidence was found for BQM formation in LFP studies of **8** and **10**, due to its suspected short lifetime, the respective diaryl carbocation (λ_{max} 420 nm, $\tau = 8.5\ \mu s$) has been observed upon irradiation of **8** in 2,2,2-trifluoroethanol. A BQM (λ_{max} 580 nm) was observed for **9** but not for **10**, the latter having more complex chemistry on laser excitation, resulting in a transient that appears to mask any BQM absorption. Significant quenching of fluorescence from the hydroxybiphenyl alkenes at low water content implies that H_2O is directly involved in reaction from the singlet excited state. The decrease in fluorescence intensity of **8** was found to depend on $[H_2O]^3$; however, the distance required for ESIPT in these systems is too large to be bridged by a water trimer. The nonlinear quenching has been attributed to deprotonation of the phenol by two water molecules, with concerted protonation at the alkene by another molecule of water. Fluorescence quenching of the hydroxybiphenyl alcohols required much higher water content, implying a different mechanism of reaction, consistent with the proposal of ESPT (to solvent water) followed by dehydroxylation.

Introduction

Hydration and dehydration are well-known and commonly occurring reactions in organic chemistry. In general, acid catalysis (by strong acids such as H_2SO_4) is required to effect reasonable rates of reaction in the ground-state (thermal) process. The photohydration of aryl alkenes and acetylenes can occur in neutral water with significant quantum yields.[1] In addition, studies by Yates and co-workers[1,2] have shown that the photohydration of *o*-hydroxystyrenes and acetylenes (e.g., **1**) occurs via excited-state intramolecular proton transfer (ESIPT), through the intermediacy of *o*-quinone methide (QM) intermediates. Product studies provided evidence for ESIPT, as the yield of the photohydration product decreased significantly in alkaline solution, where there is no phenolic proton available for ESIPT. More recent studies by Foster et al.[3] have expanded upon this initial work by use of *o*-hydroxy-α-phenylstyrene (**2**). Product

studies of **2** in aqueous CH_3CN gave the respective photohydration product efficiently, consistent with an *o*-QM intermediate. This was confirmed by observation of a long-lived intermediate in nanosecond laser flash photolysis (LFP) experiments assigned to *o*-QM **3**. The fact that this transient was observed in both aqueous and neat CH_3CN indicates that water is not required for the proton transfer to occur in these ortho systems. Although the related methoxy compound **4** also gave photohydration, the reaction was much less efficient and has been attributed to formation of the respective diarylmethyl carbocation via simple photoprotonation from solvent water.


1 **2** **3** **4**
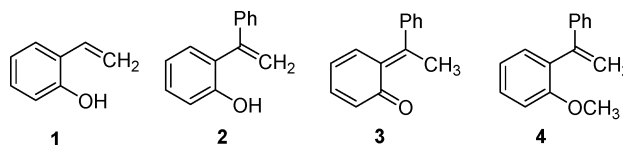
* To whom correspondence should be addressed: Tel (250) 721-8976.

(1) Isaks, M.; Yates, K.; Kalanderopoulos, P. *J. Am. Chem. Soc.* **1984**, *106*, 2728−2730.

(2) Kalanderopoulos, P.; Yates, K. *J. Am. Chem. Soc.* **1986**, *108*, 6290−6295.

(3) Foster, K. L.; Baker, S.; Brousmiche, D. W.; Wan, P. *J. Photochem. Photobiol. A: Chem.* **1999**, *129*, 157−163.

Studies by Fischer and Wan[4] have shown that (formal) ESIPT can also occur over extended distances to yield QMs from the corresponding *m*- and *p*-hydroxystyrenes (e.g., **5**). Unlike **2**, however, LFP and fluorescence experiments have shown that water is required to mediate the ESIPT process. Stern−Volmer analysis of fluorescence quenching of **5** (by water in CH_3CN) showed a cubic dependence on water concentration, which was taken to indicate that a water trimer is necessary to mediate the proton transfer between the phenol and the alkene moiety in the excited state, to yield the *m*-QM **6a**, which is subequently trapped by water to give the net photohydration product **6b** (eq 1). Similar to previous studies,[1−3,5−8] only carbocation formation has been observed upon photolysis of the respective methoxy compounds.

(1)
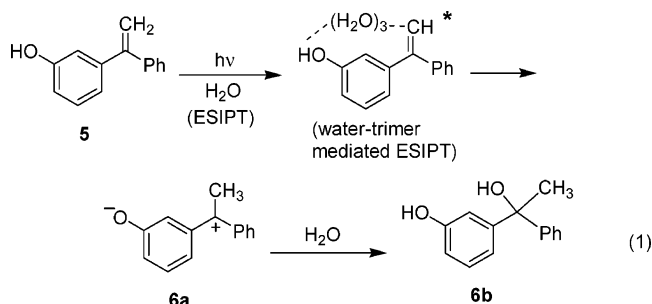
Wan and co-workers[9−20] have also shown a simple and efficient route to QMs through photolysis of hydroxybenzyl alcohols and related systems. Consistent with the formation of these intermediates, product studies on *o*-, *m*-, and *p*-hydroxy-benzyl alcohols and related compounds in H_2O/CH_3OH have shown formation of the respective methyl ethers through nucleophilic attack of methanol. Similarly, trapping studies with ethyl vinyl ether showed regioselective formation of the respective chroman product upon excitation of *o*-hydroxybenzyl alcohols, through reaction with the respective *o*-QM. Further evidence for the intermediacy of QMs upon photolysis of these systems was obtained from LFP studies on the related hydroxy-benzhydrols, which showed the formation of intermediates that were quenchable with nucleophiles and assignable to QMs. The proposed mechanism for this general reaction is ESPT from the phenol to solvent water, to yield the corresponding excited-state phenolate, followed by dehydroxylation (e.g., eq 2). Evidence for this pathway comes from the increased yield of photomethanolysis products and LFP transient signal at high

(4) Fischer, M.; Wan, P. *J. Am. Chem. Soc.* **1999**, *121*, 4555−4562.
(5) Wooldridge, T.; Roberts, T. D. *Tetrahedron Lett.* **1973**, *41*, 4007−4008.
(6) Wan, P.; Culshaw, S.; Yates, K. *J. Am. Chem. Soc.* **1982**, *104*, 2509−2515.
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(8) McEwen, J.; Yates, K. *J. Am. Chem. Soc.* **1987**, *109*, 5800−5808.
(9) Wan, P.; Chak, B. *J. Chem. Soc., Perkin Trans. 2* **1986**, 1751−1756.
(10) Wan, P.; Hennig, D. *J. Chem. Soc., Chem. Commun.* **1987**, 939−940.
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(12) Wan, P.; Barker, B.; Diao, L.; Fischer, M.; Shi, Y.; Yang, C. *Can. J. Chem.* **1996**, *74*, 465−475.
(13) Barker, B.; Diao, L.; Wan, P. *J. Photochem. Photobiol. A: Chem.* **1997**, *104*, 91−96.
(14) Huang, C.-G.; Shukla, D.; Wan, P. *J. Org. Chem.* **1991**, *56*, 5437−5442.
(15) Huang, C.-G.; Wan, P. *J. Org. Chem.* **1991**, *56*, 4846−4853.
(16) Huang, C.-G.; Beveridge, K. A.; Wan, P. *J. Am. Chem. Soc.* **1991**, *113*, 7676−7684.
(17) Shi, Y.; Wan, P. *J. Chem. Soc., Chem. Commun.* **1995**, 1217−1218.
(18) Shi, Y.; Wan, P. *J. Chem. Soc., Chem. Commun.* **1997**, 273−274.
(19) Fischer, M.; Shi, Y.; Zhao, B.; Snieckus, V.; Wan, P. *Can. J. Chem.* **1999**, *77*, 868−874.
(20) Shi, Y.; MacKinnon, A.; Howard, J. A. K.; Wan, P. *J. Photochem. Photobiol. A: Chem.* **1998**, *113*, 271−278.
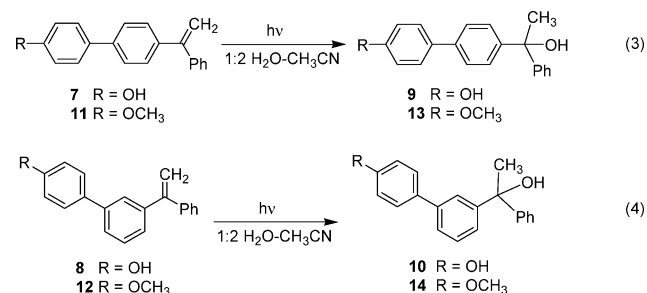
pH, where the phenolate is directly excited. At lower pH, the *o*-isomers may react via concerted loss of water, without the need for initial ESPT to solvent.

(2)
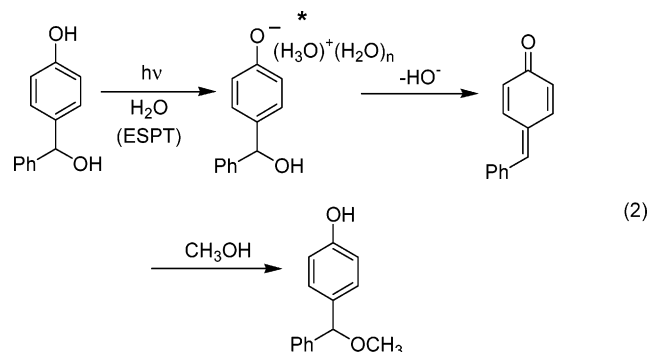
As a continuation of the studies on QM formation from hydroxystyrenes, and as a test of the proposed water mediation, it is important to investigate the (formal) ESIPT mechanism proposed for **5** over even longer distances. The demonstration of the generality of this phenomenon would have important implications in the design of light-activated supramolecular systems, currently of great interest in the chemical community. For these reasons, the first group of "extended" hydroxystyrenes (with a benzene ring as a conjugated "spacer"), viz., hydroxy-biphenyl alkenes **7** and **8**, have been synthesized and studied. The photochemistry of the related hydroxybiphenyl alcohols (**9** and **10**) has also been investigated, as the QMs generated upon photolysis of these molecules are identical to those arising from the hydroxybiphenyl alkenes, although they must arise via a different mechanism.

Results and Discussion

Product Studies. Photolysis of **7** and **8** (10^{-3} M, 254 or 300 nm, 1:2 $H_2O−CH_3CN$, 5 min) gave the corresponding hydration products **9** and **10** in 24% and 72% yield, respectively (eqs 3 and 4). The photohydration yields of both **7** and **8** gave a good linear dependence upon irradiation time up to ∼70% conversion for both systems, with no detectable side products. A slight deviation from linearity at conversions above 70% can be attributed to absorption by **9** or **10** becoming competitive. Irradiation of **7** to form **9** in a UV cuvette (in 1:1 $H_2O−CH_3CN$) yielded UV−vis traces with well-defined isosbestic points (Figure 1). Alkene **8** behaved similarly. In all cases, the yield of photoproducts was unchanged in runs purged with either O_2 or N_2.

(3)

(4)

Photolysis of the methoxy-substituted analogues **11** and **12** under the same conditions as **7** and **8** gave lower yields of the respective photohydration products (**13**, ∼6%; **14**, 47%) for the same (or longer) irradiation times. As the hydroxy and methoxy
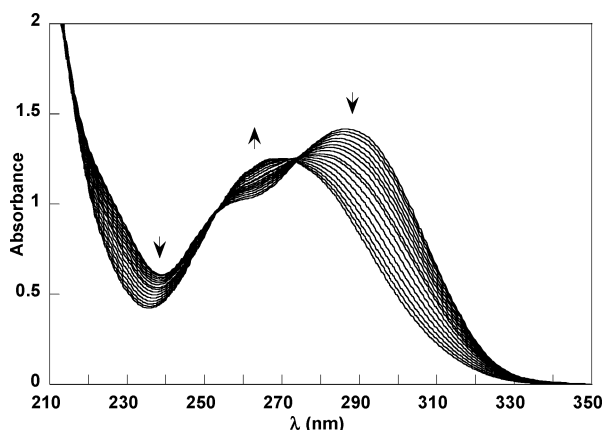
Figure 1. Photochemical UV−vis traces showing the conversion of biphenyl alkene **7** to the corresponding photohydration product **9** with irradiation at 300 nm in 1:1 H_2O−CH_3CN. Early traces were taken after 30 s photolysis intervals, increasing to 60 s photolysis with the later traces. The final spectrum is identical to that of authentic **9**.

groups have similar electronic effects (as measured by Hammett δ), the lower yield of products from **13** and **14** can be attributed to different reaction pathways for photohydration of the hydroxy- and methoxybiphenyl alkenes. Irradiation of the "parent" compound **15** resulted in complete lack of photohydration, indicating that the reaction requires an electron-donating group.

The photohydration of **7** and **8** is compatible with the reaction of electrophilic intermediates such as QMs or carbocations. However, it is impossible for either **11** or **12** to form a QM, due to the lack of a hydroxyl proton. The observed photohydration of these compounds must take place via another reactive intermediate, with the most likely candidates being the respective carbocations **16** and **17**. Formation of biphenyl quinone methides (BQMs) **18** and **19** (a non-Kekulé species) from the hydroxy-biphenyl alkenes **7** and **8**, respectively, would seem consistent with their apparent enhanced reactivity.
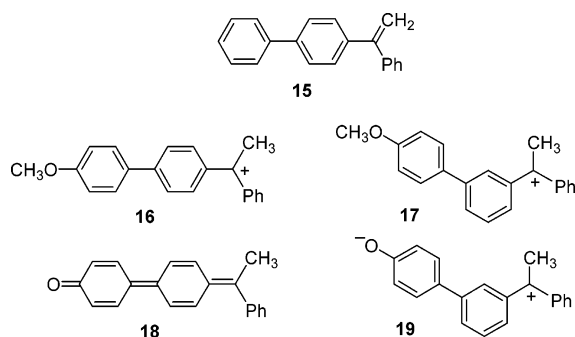

Irradiation of **9** (1:1 H_2O−CH_3OH, 10 min) gave **20** in 15% yield (eq 5). Similarly, photolysis of **10** under identical conditions gave 40% **21** (eq 6). Similar product studies carried out on **9** in 1:1 CH_3OH−CH_3CN also gave the methyl ether **20** but in much lower yield than the corresponding irradiation in 1:1 H_2O−CH_3OH (e.g., 12% vs 52%). This significant decrease in yield provides evidence for the suspected ESPT process, as it is consistent with studies that have shown that ESPT to methanol clusters is much less efficient than to water clusters.[21−23]

(21) Tolbert, L. M.; Haubrich, J. E. *J. Am. Chem. Soc.* **1994**, *116*, 10593−10600.
(22) Lee, J.; Robinson, G. W.; Webb, S. P.; Philips, L. A.; Clark, J. H. *J. Am. Chem. Soc.* **1986**, *108*, 6538−6542.
(23) Robinson, G. W. *J. Phys. Chem.* **1991**, *95*, 10386−10391.
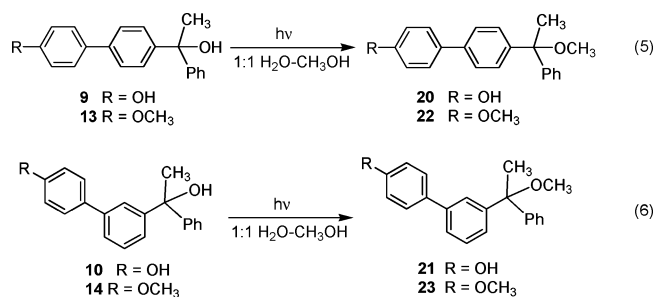
As with the product studies on the hydroxybiphenyl alkenes, formation of the photomethanolysis products (through nucleophilic attack by methanol) is consistent with formation of BQM intermediates **18** and **19**. Unlike the biphenyl alkene systems, however, formation of the respective carbocations **16** and **17** from irradiation of the methoxy compounds **13** and **14** is negligible. This is evidenced by product studies that showed little or no conversion to the corresponding methyl ethers (**22** and **23**) upon irradiation under identical conditions as the parent hydroxybiphenyl alcohols **9** and **10**. The yield of **22** from **13** was found to be ∼5% after 30 min of irradiation (compared to 26% **20** from irradiation of **9**), while photolysis of **14** gave no detectable amounts of **23** after 10 min (where **10** had conversions to **21** in excess of 40%). These results imply that the phenol moiety is vital in all of these biphenyl systems for formation of a reactive intermediate that eventually leads to the photohydration or photosolvolysis product.

Product quantum yields (Φ_p) for photohydration of biphenyl alkenes **7**, **8**, **11**, and **12** and photomethanolysis of biphenyl alcohols **9** and **10** (by use of potassium ferrioxalate actinometry and secondary reference compounds) are presented in Table 1. The relative quantum yields observed within a group (e.g., **7** vs **11**) are generally consistent with the isolated yields observed in the larger-scale product studies (vide supra). The significantly larger quantum yields observed for **8**, **10**, and **12** (pseudo meta isomers) compared to the corresponding **7**, **9**, and **11** (pseudo para isomers), respectively, may be thought of as another example of the "meta-effect" initially reported by Zimmerman and Sandel.[24]

Photolysis of hydroxybiphenyl alkenes **7** and **8** in solutions of varying water content gave no observable changes in quantum efficiency of photohydration over a wide range of water content (5−28 M H_2O, in CH_3CN). However, the photohydration quantum efficiency of methoxybiphenyl alkenes **11** and **12** depended greatly on water concentration, dropping rapidly to almost no observable reaction at about 6 M H_2O. These observations provide further evidence that these two classes of compounds (hydroxybiphenyls vs methoxybiphenyls) photohydrate via different pathways.

The yields of photohydration from **7** and **8** decreased in solutions of pH > 9 where the phenol moiety is deprotonated (Figure 2). An apparent acid-catalyzed pathway was observed for **7** at pH < 4. The observed decrease in photohydration products at high pH for both systems is consistent with the requirement of a formal ESIPT process between the phenol and the alkene moiety, to yield BQMs **18** and **19**, respectively. The observed increase in product yield at low pH for **7** is believed to result from direct protonation of the alkene by hydronium

(24) Zimmerman, H. E.; Sandel, V. R. *J. Am. Chem. Soc.* **1963**, *85*, 915−922.

Table 1. Quantum Yields of Photohydration and Photomethanolysis

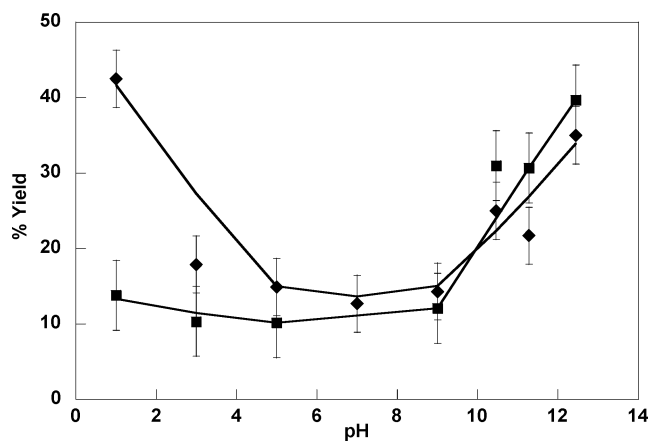| compound	Φ_p	compound	Φ_p
	Photohydration		
7	0.013 ± 0.005^a	**8**	0.10 ± 0.02^b
11	$\sim 0.008^c$	**12**	0.05 ± 0.01^a
	Photomethanolysis		
9	$\sim 0.04^d$	**10**	0.22 ± 0.02^e

a In 1:1 H_2O-CH_3CN, by potassium ferrioxalate actinometry (monitored by UV–Vis). *b* Measured against **12** as secondary reference standard, in 1:1 H_2O-CH_3CN (monitored by ^1H NMR). *c* Measured against **7** as secondary reference standard, in 1:1 H_2O-CH_3CN (monitored by ^1H NMR). *d* Measured in 1:1 H_2O-CH_3OH by the photomethanolysis of *p*-hydroxybenzhydrol ($\Phi_p = 0.19$)[11] as secondary standard (monitored by ^1H NMR). *e* Measured in 1:1 H_2O-CH_3OH by the photomethanolysis of *m*-hydroxybenzhydrol ($\Phi_p = 0.40$)[11] as secondary standard (monitored by ^1H NMR).
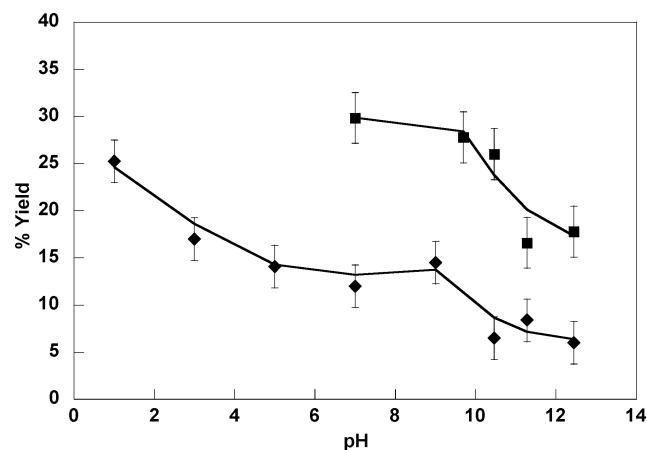
Figure 2. pH Dependence of photohydration yield observed on photolysis of **7** (♦) and **8** (■) in 1:2 H_2O-CH_3CN ($\lambda_{ex} = 300$ nm). The quoted pH is of the aqueous portion of the solvent system. Yields were calculated by ^1H NMR.

Figure 3. pH Dependence of methyl ether yield observed on photolysis of **9** (♦) and **10** (■) in 1:1 H_2O-CH_3OH ($\lambda_{ex} = 254$ nm). The quoted pH is of the aqueous portion of the solvent system. Yields were calculated by ^1H NMR.

Table 2. Summary of Fluorescence Data for **7**–**14**[a]

compound	λ_{max} (nm)[b]	$\Phi_f{}^c$	$\tau_f{}^d$ (ns)
8	281, 377	0.17 ± 0.05	6.9 ± 0.2
			13.9 ± 0.5
12	281, 359	0.15 ± 0.05	6.9 ± 0.2
			13.9 ± 0.5
7	295, 365	0.61 ± 0.05	1.6 ± 0.2
11	290, 359	0.65 ± 0.05	~ 1.3
9	280, 332	0.16 ± 0.05	6.5 ± 0.2
13	280, 330	0.25 ± 0.05	6.4 ± 0.5
10	274, 330	0.17 ± 0.05	7.5 ± 0.2
14	277, 328	0.14 ± 0.05	6.8 ± 0.2

a Measured in neat CH_3CN. *b* Excitation and emission wavelength maxima, quoted in that order. *c* Measured with 2-aminopyridine in 0.1 M H_2SO_4 as a secondary emission standard.[25] *d* Measured by single photon counting. Decays of **8** and **12** were best fitted to two single-exponential decays, with a relative weighting of 60:40 for the short vs long lifetime components.

ion. Similar studies of the methoxybiphenyl alkenes **11** and **12** showed no change in yield in the pH 7–12 range, consistent with the proposed involvement of the phenol proton in a formal ESIPT process.

Unlike the respective hydroxybiphenyl alkenes **7** and **8**, where the yield of photohydration decreased in alkaline solution, photolysis of **9** and **10** (in 1:1 H_2O-CH_3OH) at pH > 9 resulted in an *increase* in the respective yields of **20** and **21** (Figure 3). This is consistent with past proposals[10–12] that the excited-state phenolate is required for QM formation in the benzenoid versions of these compounds. Direct photolysis of the phenols in alkaline solution results in more efficient formation of the corresponding excited-state phenolate and hence overall quantum efficiency of reaction. The importance of the phenolate in these biphenyl alcohols is further emphasized by the product studies at pH 7 on **13** and **14** (vide supra). In these systems, where the phenolate cannot be formed, photodehydroxylation to yield the respective carbocations (and hence methanolysis) does not occur. Presumably the electron-donating ability of the methoxy group is not enough to allow for efficient reaction.

The observation that the photomethanolysis yield of **21** from **10** does not significantly change in acidic medium (Figure 3) indicates that formation of the QM is occurring by the same mechanism as in pH 7 (i.e., via BQM **19**) or that any acid-catalyzed mechanism for photohydration does not compete well with one involving formation of BQM **19**. The apparent strong acid catalysis observed for reaction of **9** was subsequently

explained as due to thermal dehydration of **9** to form **7**, which adds methanol with a much higher quantum efficiency than **9**.

Fluorescence Studies. Selected fluorescence data (Φ_f, τ_f, excitation and emission spectra λ_{max}) of **7**–**14** have been measured in neat CH_3CN and are summarized in Table 2. The fluorescence emission spectra arising from **9**, **10**, **13,** and **14** are readily attributed to that of the biphenyl chromophore, whereas the emissions from **7**, **8**, **11,** and **12**, which are red-shifted by 30–40 nm, are due to a more conjugated chromophore (viz., a biphenyl alkene). No aggregation effects were detected, as evidenced by the consistent Φ_f values obtained for all of **7**–**11** over a range of concentrations. In all cases, the fluorescence lifetimes of the respective hydroxy and methoxy compounds (e.g., **9** and **13**) were identical (in neat CH_3CN). Interestingly, both **8** and **12** (both "meta" compounds) exhibited two monoexponential decays for fluorescence emission decay (in neat CH_3CN, in a 60:40 relative ratio of the short and long lifetimes, respectively). These more complex decays were observed even on samples that were repurified several times, which therefore suggests that two fluorescent forms are available for these compounds on the excited-state surface. This may arise via a more substantial barrier to twisting of the biphenyl in these meta compounds, although this needs further substantiation. The corresponding "para" isomers (**7** and **11**) gave good single-exponential decays. These observations suggest that there are two emissive chromophores in **8** and **12** (a " biphenyl" and a
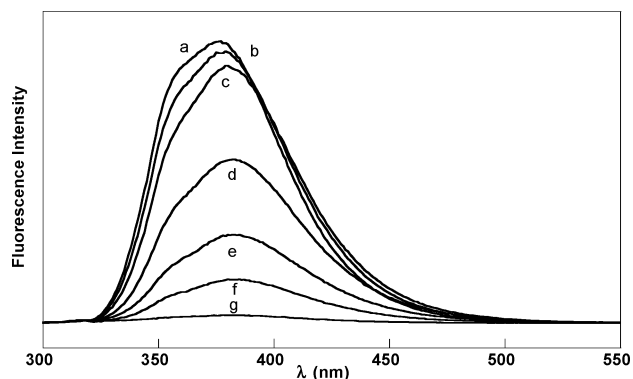
Figure 4. Quenching of fluorescence of **8** (λ_{ex} = 285 nm) in CH$_3$CN by added H$_2$O: (a) 0 M; (b) 0.19 M; (c) 0.47 M; (d) 0.94 M; (e) 1.4 M; (f) 1.9 M; (g) 4.7 M.

Figure 5. Quenching of fluorescence of **10** (λ_{ex} = 275 nm) in CH$_3$CN by added H$_2$O: (a) 0 M; (b) 18.5 M; (c) 27.8 M; (d) 37.1 M; (e) 46.3 M; (f) 55.6 M.

"diphenyl ethylene") and that the anticipated twisting to a more planar biphenyl system (leading to a more conjugated system) may result in a nonfluorescent state.

Addition of small amounts of water was found to cause significant decreases in the fluorescence of **8** (Figure 4). Following a small initial red shift (probably due to hydrogen bonding of the phenol proton with water molecules), the fluorescence decreased uniformly with increasing concentration of added water up to 4.7 M, where it was entirely quenched. Similar results were obtained upon the addition of water to CH$_3$CN solutions of **7** except that higher [H$_2$O] was required to effect the same fractional quenching, with residual fluorescence still being observed even in 9.3 M water. Overall photohydration of these compounds (as monitored by UV−vis) also display a similar sensitivity to the water content, consistent with the direct link of fluorescence quenching by added water and the photohydration process. In addition, the relative fluorescence quenching efficiency observed for **7** and **8** (by H$_2$O) is consistent with the higher Φ_p for photohydration found for **7** compared to **8** in 1:1 H$_2$O−CH$_3$CN (Table 1). Much higher water concentrations were required to effect observable fluorescence quenching for the respective methoxy compounds **11** and **12**. In the case of **12**, the fluorescence was quenched by less than 50% in solutions of >18 M water, while **11** exhibited no quenching at all in solutions of up to 27 M water. These results are consistent with the notion that photohydration of the methoxybiphenyl alkenes and the hydroxybiphenyl alkenes proceeds via different pathways. Interestingly, studies of **24** (which lacks a reactive alkene moiety but in other respects resembles **7**) showed no quenching at all across a range of water concentrations from 0 to 15 M. This suggests that the quenching observed must be linked to the alkene moiety, in addition to the phenol.

Small concentrations of water (<2 M) had no effect on the fluorescence from either **9** or **10** (except for an initial red shift). No quenching was observed for either compound in solutions of up to 18.5 M water (Figure 5), although a small (<10%) increase in the fluorescence was observed between 2 and 18.5 M. Beyond this water concentration the fluorescence decreased uniformly but was still not fully quenched in either case, even in neat water. Given the large amounts of water required for quenching, these studies indicate a different reaction pathway than that of the hydroxybiphenyl alkenes that does not rely on relatively low concentrations of water. Similar fluorescence
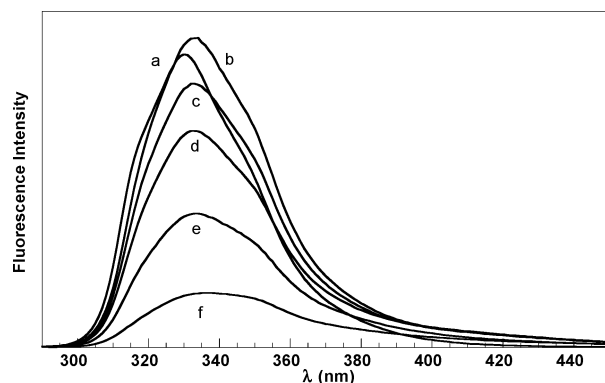
results were observed for the methoxybiphenyl alcohols **13** and **14**, i.e., no fluorescence quenching in CH$_3$CN solutions containing up to ∼46 M water. This is consistent with the lack of reactivity observed upon photolysis of either **13** or **14** in 1:1 H$_2$O/CH$_3$OH and was attributed to the inability of these compounds to form the phenolate in the excited state.

Quenching studies of **7** and **8** with D$_2$O (in CH$_3$CN) showed that higher [D$_2$O] was required to effect the same amount of quenching observed for H$_2$O. For example, fluorescence from **8** was quenched by 70% in 1.4 M H$_2$O solution but only by 55% in the same concentration of D$_2$O. This may be regarded as a primary solvent isotope effect for ESIPT or photohydration and is consistent with proton transfer from H$_2$O (or D$_2$O) being intrinsically linked in the quenching process. The question arises as to why the quenching is less efficient in D$_2$O. If we assume that some sort of (formal) ESIPT process is occurring, at least two proton transfers are required: one from the phenol to a cluster of water molecules and one from the water cluster to the alkene. If these two processes are very fast (if not concerted), they would compete with fluorescence of the molecule. The phenol moiety of **8** (or **7**) is expected to be quite acidic in the excited state [pK_a(S$_1$) ≤ 1, on the basis of 4-phenylphenol (**25**), which has a pK_a(S$_1$) of 1.8].[26] Thus, it is possible that initial proton transfer from the phenol occurs very quickly with an early transition state and thus exhibits little or no isotope effect. This would imply that protonation of the alkene is "rate-determining" and that the observed isotope effect on quenching by H$_2$O vs D$_2$O arises mainly from this process. A detailed understanding of this type of isotope effect would require time-resolved fluorescence data at the picosecond or shorter time scale, which is beyond the scope of this work.

The relatively large fluorescence quenching effect observed with small amounts of added H$_2$O for **7** and **8** indicates that water is intrinsically linked to reaction from the singlet excited state for both of these compounds. Indeed, similar observations for the "parent" compound, *m*-hydroxystyrene (**5**), were proposed[4] to arise from a mechanism involving an ESIPT process with three water molecules bridging the phenol and alkene moieties. In the present systems, three molecules cannot span the distance between the phenol and alkene moieties, so a modified version of the mechanism in which water molecules are required to solvate the two reactive sites individually during

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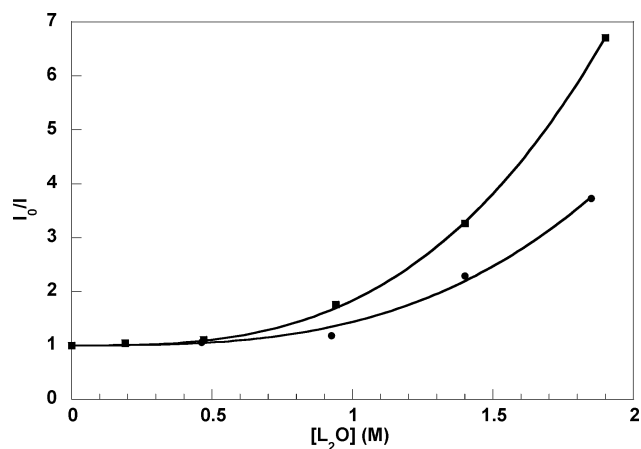(26) Townsend, R.; Schulman, S. G. *Chim. Oggi.* **1992**, *10*, 49−52.

Figure 6. Modified Stern–Volmer plots of fluorescence intensity quenching I_0/I for **8** by H_2O and D_2O in CH_3CN (■, H_2O; ●, D_2O) fitted to $y = 1 + k_q[H_2O]^3$.

Figure 7. Transient absorption spectra observed for **7** (♦) and **9** (■) in 1:1 H_2O/CH_3CN and **7** (●) in neat CH_3CN, 9 μs (♦, ●) and 6 μs (■) after 266 nm laser excitation excitation (all O_2 purged).

the proton transfer is probably operative. To probe the order of water required to mediate the formal ESIPT, a modified Stern–Volmer plot of relative fluorescence emission intensity vs $[H_2O]$ and $[D_2O]$ for **8** was carried out, which gave a nonlinear plot that was best fitted to a cubic dependence on water concentration (Figure 6). Interestingly, a similar plot for **7** required a squared dependence on water concentration. These results suggest that 2–3 water molecules are required to effect the overall formal ESIPT, leading to BQMs **18** and **19**, which subsequently react with water to give the overall photohydration products.

Laser Flash Photolysis. Nanosecond LFP was employed to probe for the first observable reactive intermediates formed in the photohydration/photosolvolysis of these biphenyl systems. The formal ESIPT required for reaction (and excited-state proton transfers in general) of **7** and **8** is believed to be very fast; hence nanosecond LFP is useful only for identifying those intermediates formed after the initial proton transfer, viz., BQMs or diarylmethyl carbocations (**16**–**19**) that are longer-lived than the laser pulse (∼15 ns). BQM **18** would be expected to be the longest-lived (least reactive in water) of the group of relevant reactive intermediates **16**–**19**. Hence, we started with LFP studies of their potential precursors, viz., **7** and **9**. LFP of **9** (λ_{ex} 266, 308 nm, 1:1 H_2O–CH_3CN, oxygen-purged solutions) gave a transient that absorbs over a wide spectral range (300–700 nm), with two maxima [360 and 580 (broad) nm, relative ratio 4:1, respectively] (Figure 7). Both bands decay to baseline (first-order kinetics), with the same rate constant of $k_{obs} = (4.3 \pm 0.1) \times 10^3$ s^{-1} ($\tau = 230$ μs). In nitrogen-purged solutions, an additional transient at 420 nm was observed, which decayed with first kinetics to baseline [$k_{obs} = (1.3 \pm 0.1) \times 10^6$ s^{-1}; $\tau = 0.80$ μs] and was assigned to the triplet state of **9**. When this transient has completely decayed, the resulting spectrum is identical to that observed under oxygen, which is much longer-lived.

The observed transient for **9** in 1:1 H_2O–CH_3CN is similar in spectral width to that reported for the parent BQM **26** ($\tau = 67$ μs in 100% H_2O), which was photogenerated from the corresponding biphenyl alcohol **27**.[17] As additional confirming evidence that the 360 and 580 nm transients observed for **9** are assignable to BQM **18**, LFP and product studies were carried out in 1:1 H_2O–CH_3CN in the presence of added ethanolamine, a much better nucleophile than H_2O. Addition of up to 0.5 M
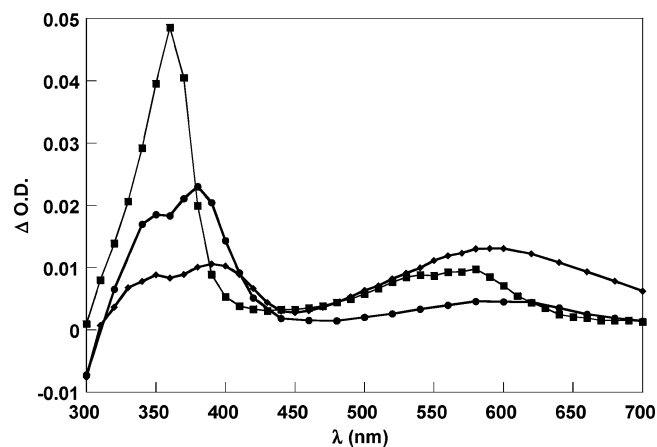
ethanolamine (in 1:1 H_2O–CH_3CN) gave the same transient spectra as observed above in the absence of ethanolamine but with decreasing lifetimes with increasing ethanolamine concentration. A plot of k_{obs} vs ethanolamine concentration gave a linear plot, with a bimolecular quenching rate constant (by ethanolamine) (k_{et}) of 1.7×10^4 M^{-1} s^{-1}. Moreover, when a semipreparative-scale photolysis run of **9** was carried out with 0.1 M ethanolamine in 1:1 H_2O–CH_3CN, the expected ethanolamine adduct **28** was observed in ∼40% yield (by ^{1}H NMR) as the only photoproduct, as identified by its characteristic methylene triplets at δ 2.56 (t, $J = 8$ Hz, NHCH2) and 3.62 (t, $J = 8$ Hz, CH_2OH) and an upfield-shifted methyl at δ 1.76, as well as by high-resolution mass spectrometry (HRMS; see Experimental Section).
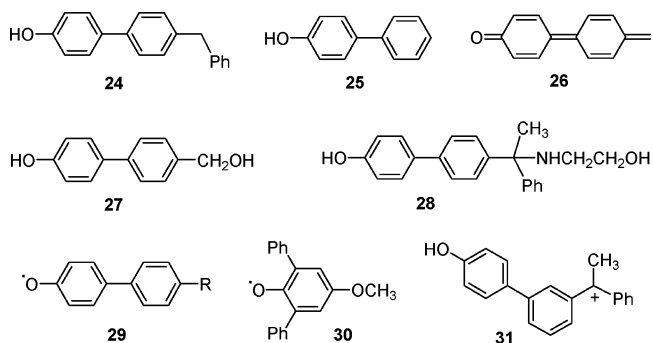
LFP of **9** in neat CH_3CN also gave transient absorptions in the same wavelength region but the signals were up to 5-fold weaker. Indeed, LFP of model compounds such as **24** and **25**, which cannot give BQMs, in neat CH_3CN or 1:1 H_2O–CH_3CN also gave residual weak absorptions over the same wavelength range. We believe that the transients observed in neat CH_3CN of these phenylphenols arise from the 4-phenylphenol moiety. The transient may be the phenylphenoxyl radical **29**, given that the observed spectra are very similar in shape and relative intensities to the spectrum reported for phenoxyl radical **30**.[27a] Indeed, it is well-known that laser excitation of phenols (and

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phenolates) gives rise to phenoxyl radicals that can be characterized by electron paramagnetic resonance (EPR), although generally with low quantum yields.[27b]

LFP studies of **7** (λ_{ex} 308 nm, 1:1 H_2O-CH_3CN) gave a very broad transient (Figure 7) centered at 600 nm ($\tau \sim 2$ ms) and at 350 or 400 nm (biexponential decay, fitted to ~150 μs, ~2 ms) under N_2- or O_2-purged conditions. This transient does not resemble the spectrum assigned to BQM **18** observed on LFP of **9** in 1:1 H_2O-CH_3CN (vide supra). A similar transient was also observed in neat CH_3CN, except the relative intensity of the 350/400 vs 600 nm bands are now reversed. Although the same BQM **18** would be expected from either **9** or **7**, it is clear that more complex LFP transients are observed for **7**. However, product studies of **7** and **9** are both clean and consistent with formation of BQM **18**. We believe that the broad transients observed for **7** (in both neat CH_3CN and 1:1 H_2O-CH_3CN) arise from a phenoxyl radical of the type **29**. Although this is thought to be a minor photochemical pathway for **7**, the molar absorptivity of the transient is very high, thereby masking any evidence for formation of BQM **18**. We have carried out LFP studies of **7** at pH 1, in the anticipation that acid may promote photoprotonation of the alkene moiety of **7**, which on subsequent deprotonation of the phenol proton would lead to BQM **18**. This pathway may compete more efficiently with formation of phenoxyl radical observed in neutral water. Indeed, at pH 1, we observe a transient that resembles that assigned to BQM **18**, with a lifetime of 23 μs, shorter than that observed at pH 7, and consistent with an acid-catalyzed pathway for its decay (hydration).

LFP studies of **8** were also carried out. It was reported by Fischer and Wan[4] that a transient at 420 nm was assignable to the non-Kekulé QM **6a** ($\tau \sim 47$ ns in neat water, pH 7). The absorption profile of this transient is similar to that observed for diphenylmethyl carbocations,[28−31] as would be expected, except that it is much longer-lived, consistent with it being QM **6a** (due to the stabilizing effect of the deprotonated *m*-hydroxy group).[4] In hindsight, BQM **19** (the expected QM from **8**) would be expected to be more reactive than **6a** since the deprotonated hydroxyl group is much further away, modulating its stabilizing effect on the diphenylmethyl carbocation. Indeed, it would not be surprising that this transient would be too short-lived for detection by our nanosecond LFP system. LFP of **8** did not give any evidence for transients assignable to diarylmethyl carbocations except for weak and short-lived species observed at 310 nm, which is too blue-shifted to be assignable to structures resembling **19**, as well as weak signals in the 350−650 nm region that were also observed for model compounds such as **24** and **25**. In an effort to increase the lifetime of photogenerated **19**, LFP experiments were conducted on **8** in neat 2,2,2-trifluoroethanol (TFE), a nonnucleophilic but polar solvent. These studies showed the appearance of a long-lived transient at 420 nm (Figure 8) under both N_2- and O_2-purged conditions that decayed in a single-exponential fashion ($\tau \sim 8.5$ μs). LFP studies of **10**, **12**, and **14** under the same conditions also yielded
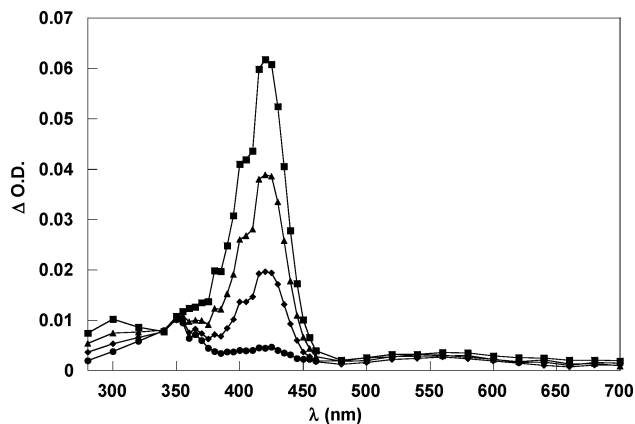

Figure 8. Transient absorption spectra observed for **8** in neat TFE (O_2 purged), 1.8 μs (■), 5.9 μs (▲), 12.2 μs (◆) and 31.5 μs (●) after 266 nm laser excitation.

a similar 420 nm transient, with about the same lifetime, although the relative intensity of the signals from the biphenyl alcohols (**10** and **14**) were about 4 times less than those from the alkenes (**8** and **12**). Similar LFP studies on **8** and **12** in an even less nucleophilic solvent (1,1,1,3,3,3-hexafluoro-2-propanol) exhibited a transient with the same absorption spectrum but a greatly increased lifetime ($\tau \sim 4$ ms), consistent with an electrophilic species. The quenching rate constants obtained from studies of **8**, **10**, and **12** in TFE with water as nucleophile (which gave good linear plots) were identical (within error) in all three cases, with $k_{H_2O} \approx 6 \times 10^5$ M^{-1} s^{-1}. This indicates that the intermediates formed from photolysis of the hydroxybiphenyl and methoxybiphenyl compounds in TFE are similar in nature and reactivity. As **12** and **14** cannot form QMs, these transients have been assigned to their respective diarylmethyl carbocations (e.g., **31** from **8).** These assignment are further justified in that the absorption spectra and lifetimes observed for these transients are consistent with the spectra, lifetimes, and k_{H_2O} values for several diarylmethyl carbocations photogenerated in TFE.[28−31]

Mechanisms of Photohydration.

Evidence presented indicates that the photohydration mechanisms of **7** and **8** differ from those of the corresponding methoxy-substituted derivatives **11** and **12** as well as the corresponding alcohols **9** and **10**. LFP studies have shown that BQM **18** is probably the reactive intermediate responsible for photosolvolysis of **9** and for the overall hydration of **7** as well, although the LFP results for the latter compound was more problematic due to the formation of broad transients that were attributed to side reactions giving rise to strong absorptions. On the basis of similar fluorescence quenching behavior as well as water dependence of product formation, BQM **19** is implicated in the photohydration of **8** and photosolvolysis of **10**; we argued that **19** is probably too short-lived for observation by our nanosecond LFP system. The mechanism for photohydration of **7** and **8** is proposed to involve water-assisted deprotonation of the phenol, either concerted with or immediately followed by protonation of the alkene by water. Up to three water molecules may be involved in this process (Scheme 1). In contrast, although it is proposed that alcohols **9** and **10** give rise to the same BQM intermediates (**18** and **19**) to effect their photosolvolysis, the mechanism of reaction of these compounds involves initial water-mediated deprotonation of the excited-state phenol, which requires significant amounts of water
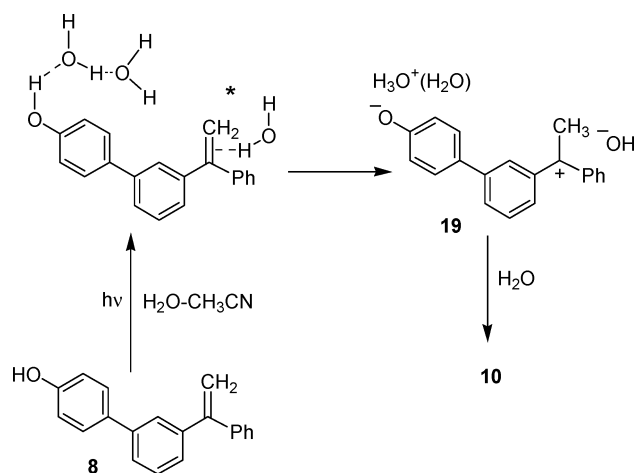
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(29) Cozens, F. L.; Mathivanan, N.; McClelland, R. A.; Steenken, S. *J. Chem. Soc., Perkin Trans. 2* **1992**, 2083−2090.
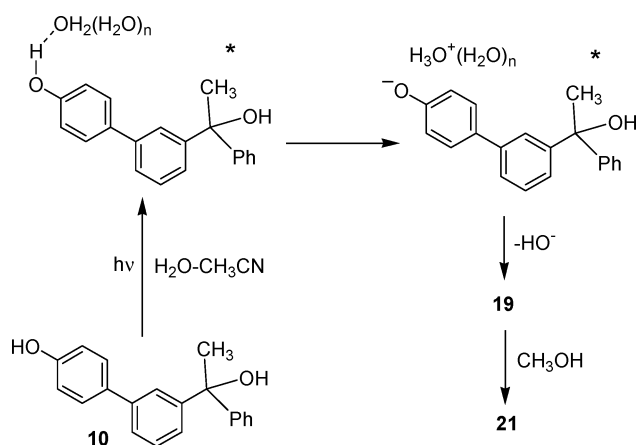(30) McClelland, R. A.; Banait, N.; Steenken, S. *J. Am. Chem. Soc.* **1989**, *111*, 2929−2935.
(31) Bartl, J.; Steenken, S.; Mayr, H.; McClelland, R. A. *J. Am. Chem. Soc.* **1990**, *112*, 6918−6928.

Scheme 1

Scheme 2

for reasonable efficiency (Scheme 2). This step gives rise to an excited-state phenolate ion that subsequently loses hydroxide ion to the medium (which is probably a very fast step), forming the BQMs **18** or **19**, followed by attack by CH_3OH to give the corresponding observed photomethanolysis products **20** and **21** (or return to substrate in the event that water attacks).

The difference in mechanism of reaction between the hydroxybiphenyl alkenes (**7** and **8**) and the alcohols (**9** and **10**) is attributable to the enhanced electronic communication between the phenol OH and the styryl moiety of **7** and **8** that is not available in **9** and **10**. Thus the expected charge-transfer character inherent in these compounds[17,18] (from phenol OH to the aromatic ring) should be even more enhanced in **7** and **8**, resulting in an even more acidic phenol OH in S_1. Studies by several groups have indicated that stronger excited-state acids require smaller water clusters for ESPT to solvent to occur.[21,32−35] Molecules with $pK(S_1) < 1$ have been shown (e.g., 5,8-dicyano-2-naphthol) to require only two water molecules to effect ESPT from the naphthol, while other molecules with a higher $pK(S_1)$ need more (e.g., 2-naphthol). The excited-state pK_a of 4-phenylphenol has been determined through fluorescence titrations

to be about 1.8.[26] It can be expected that both **7** and **8** will be more acidic than this in the excited state, due to resonance and inductive stabilization effects of the alkene moiety. These effects are compatible with a mechanism in which water molecules mediate the deprotonation of the phenol concerted with protonation of the alkene moiety. Indeed, our data show strong evidence that the deprotonation and reprotonation processes are intrinsically linked. The decrease in product yield upon irradiation of the hydroxybiphenyl alkenes in alkaline solution cannot be explained by initial deprotonation of the excited-state phenol, followed by nonconcerted protonation of the alkene. If this were the case, then the yield of photohydrated products should increase (or at least remain the same) upon excitation of the phenolate. Further evidence for a concerted reaction can be taken from the fluorescence studies on the hydroxybiphenyl alcohols **9** and **10**, as well as the parent **24**. Quenching of the fluorescence from these compounds occurs only with significantly larger $[H_2O]$ than observed for the hydroxybiphenyl alkenes. If the nonlinear fluorescence quenching by water evident for **7** and **8** was solely related to deprotonation, then **9**, **10**, and **24** should all exhibit similar quenching with low $[H_2O]$. In contrast, because the benzyl alcohol moieties of **9** and **10** are not in direct conjugation with the phenol OH, these compounds must react via initial phenol OH deprotonation to water, which requires a significant pool of water molecules, as the acidity of such a phenol is not expected to depart significantly from common phenols (where high water content is required for excited-state dissociation).

The photohydration of the methoxybiphenyl alkenes **11** and **12** is believed to occur through the intermediacy of carbocations **16** and **17** by simple protonation, given that these systems cannot form the respective BQMs, and confirmed by differences observed in their reactivity and fluorescence quenching behavior compared to that of the hydroxybiphenyl alkenes **7** and **8**. Evidence for the formation of **17** upon photolysis of **12** comes from LFP experiments in TFE, which show a transient similar in lifetime and absorption maximum to those of other diarylmethyl cations.

Finally, this work has further demonstrated that excited-state charge transfer of suitably designed biphenyl ring systems can induce efficient photoreaction at one end of the conjugated system. Facile release of a proton from the phenol and either synchronous or subsequent production of a hydroxide ion occur upon excitation of both the hydroxybiphenyl alcohols and alkenes, with vastly differing dependencies on water content. These processes are intriguing from a supramolecular perspective, as they allow the photogeneration of a "pH gradient" over a defined molecular distance. This reactivity may prove useful for the design of novel photoswitches that require complex signaling events for activation (i.e., reaction with an acid at one side of a membrane and reaction with a base at the other), rather than simple switching by generation of a single reactive species.

Experimental Section

General. ^{1}H NMR spectra were recorded on either a Bruker AC 300 (300 MHz) or a Bruker AM 360 (360 MHz) instrument. Mass spectra were determined on either a Finnegan 3300 (chemical ionization, CI) or a Kratos Concept 1H (electron impact, EI, and high-resolution mass spectrometry, HRMS). Melting points were determined on a Reichart 7905 melting point apparatus (uncorrected). pH measurements were taken on a Corning 140 pH meter. HPLC-grade CH_3CN was

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freshly distilled over CaH_2 for use in fluorescence measurements. Anhydrous tetrahydrofuran (THF) and diethyl ether were obtained by distillation over sodium, with benzophenone as an indicator. 2,2,2-Trifluoroethanol (Aldrich) was distilled prior to use to remove impurities that appeared in the UV−vis spectrum. UV−vis spectra were recorded on a Varian Cary 1, 5, or 50 spectrophotometer.

Materials. The required biphenyl alkenes and alcohols (**7**−**14**) were all readily synthesized via standard synthetic procedures from readily available compounds, as described in the Supporting Information.

Product Studies. All preparative photolyses were carried out in a Rayonet RPR 100 photochemical reactor equipped with 254 or 300 nm lamps. The solutions were contained in quartz tubes (100−200 mL), which were cooled to ≤ 15 °C with tap water by means of an internal coldfinger. All solutions were purged with argon 5 min prior to irradiation and for the entire time of the irradiation, to promote stirring and maintain the atmosphere. Photolysis times varied from 30 s to 2 h. Workup involved extraction of the photolyzed solution with CH_2Cl_2, followed by drying of the combined organic layer and removal of the solvent under reduced pressure. All pH studies list the pH of the aqueous phase prior to mixing with CH_3CN or CH_3OH. The samples being studied were dissolved in the organic solvent before being mixed with the aqueous component. In these studies, the solution was brought to ∼pH 7 following irradiation by the addition of NH_4Cl or 0.1 M pH 7 buffer solution, prior to extraction. The irradiation products were separated (if necessary) by preparative thin-layer chromatography (TLC) and then analyzed by MS and ^{1}H NMR. In all cases, control experiments at ≤15 °C and in the absence of light showed no conversion to products, suggesting that thermal reaction does not play a role in the observed chemistry.

Photolysis of 7 in 1:2 H_2O−CH_3CN. A solution of 15 mg of **7** in 90 mL of 1:2 H_2O−CH_3CN was irradiated at 300 nm (8 lamps) for times up to 20 min. ^{1}H NMR indicated that **9** was the only product formed even at high conversions (>87%) (N_2 or O_2), on the basis of comparison to the spectrum of the authentic material. Relative Φ_p tests for irradiation in 1:1, 1:2, 1:4, and 1:9 H_2O/CH_3CN showed essentially no difference between the solvent systems (±4%). pH studies [at pH 1, 3, 5, 7 (0.01 M phosphate buffer), 9, 10, 11, and 12] were conducted in 1:2 H_2O/CH_3CN (90 mL total volume, 300 nm, 8 lamps, 10 min) with 15 mg of **7**.

Photolysis of 11 in 1:2 H_2O−CH_3CN. A 15.8 mg sample of **11** irradiated for 10 min at 300 nm (8 lamps) in 1:2 H_2O−CH_3CN (N_2 or O_2) gave ∼12% conversion to the alcohol **13** with no other products being observed. The identity of the product was confirmed by comparison to the ^{1}H NMR of the authentic material. Relative Φ_p measurements were conducted in 1:2, 1:4, and 1:9 H_2O/CH_3CN (100 mL total volume). pH studies [at pH 7 (0.01 M phosphate buffer), 9.7, 10.5, 11.3, and 12.5) were conducted in 1:2 H_2O/CH_3CN (300 nm, 8 lamps, 10 min) with 15.8 mg of **11**.

Photolysis of 15 in 1:2 H_2O−CH_3CN. Fifteen milligrams of **24** was dissolved in 90 mL of 1:2 H_2O/CH_3CN and irradiated at 300 nm for 5 min. Analysis by ^{1}H NMR indicated no conversion to the photohydrated product.

Photolysis of 8 in 1:1 H_2O−CH_3CN. A solution of 15 mg of **8** in 90 mL of 1:1 H_2O−CH_3CN was irradiated (254 nm, 8 lamps) for times up to 5 min. Even at high conversion (>80%), **10** was the only product, as shown by comparison to the ^{1}H NMR of authentic material. The relative Φ_p was calculated by comparison to the yield of **14** from **12** as described below. The relative Φ_p was found to vary little (<5%) between irradiation in 1:1, 1:2, 1:4, and 1:9 H_2O/CH_3CN (15 mg, 254 nm, 8 lamps, 1.5 min, 100 mL total volume). pH studies (at pH 7 (0.01 M phosphate buffer), 9.3, 10.2, 11.2, and 12.5) were conducted in both 1:1 and 1:2 H_2O/CH_3CN (254 nm, 1.5 min, 8 lamps) with 15 mg of **8**.

Photolysis of 12 in 1:1 H_2O−CH_3CN. Irradiation of 15.8 mg of **12** in 100 mL of 1:1 H_2O−CH_3CN (254 nm, 1.5 min, 8 lamps) gave **14** as the only observable product in 33% yield. Relative yield experiments in various solvent systems (1:1, 2:1, 4:1, and 9:1 CH_3-

CN−H_2O; 8 lamps, 254 nm, 1.5 min) ranged from 33% conversion (1:1) to 0% conversion (9:1). pH studies (at pH 7 (0.01 M phosphate buffer), 9.3, 10.2, 11.2, and 12.5) were conducted in 1:2 H_2O/CH_3CN with 15.8 mg of **12** (254 nm, 1.5 min, 8 lamps).

Photolysis of 9 in 1:1 H_2O−CH_3OH. Solutions of 20 mg of **9** in 100 mL of 1:1 H_2O−CH_3OH were irradiated for times up to 30 min (254 nm, 16 lamps) to yield the methyl ether **20** as the only product (26% yield after 30 min). Similar irradiations were carried out in 1:1 CH_3OH−CH_3CN for up to 2 h (254 nm, 16 lamps). Preparative TLC (3:1 hexanes/ethyl acetate) was used to isolate a pure sample of the product ether: ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.87 (s, 3H), 3.17 (s, 3H), 4.8 (br s, 1H), 6.86 (d, 2H, J = 8.8 Hz), 7.24−7.34 (m, 3H), 7.35−7.5 (m, 8H); MS (CI) m/z 273 (M^+ − OCH_3). pH studies (at pH 1.2, 3.4, 5.3, 7 (0.01 M phosphate buffer), 9.3, 10.2, 11.2, and 12.5) were conducted on **9** in 1:1 H_2O/CH_3OH (20 mg, 254 nm, 5 min, 16 lamps).

Photolysis of 13 in 1:1 H_2O−CH_3OH. Irradiation of a solution of **13** (21 mg, 254 nm, 16 lamps, 100 mL of 1:1 H_2O−CH_3OH) gave <6% conversion to the respective methanolysis product after 30 min.

Photolysis of 10 in 1:1 H_2O−CH_3OH. Irradiation of 20 mg of **10** in 1:1 H_2O−H_3OH for times up to 20 min (52% conversion) gave the methyl ether **21** as the only product. A pure sample of **21** was isolated by preparative TLC (3:1 hexanes/ethyl acetate): ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.89 (s, 3H), 3.18 (s, 3H), 4.8 (br s, 1H), 6.86 (d, 2H, J = 8.1 Hz), 7.18−7.51 (m, 10H), 7.55 (s, 1H); MS (EI) m/z 272 (MA^+ − $HOCH_3$). pH studies (at pH 1.2, 3.4, 5.3, 7 (0.01 M phosphate buffer), 9.3, 10.2, 11.2, and 12.5) were conducted on **9** in 1:1 H_2O−H_3OH (20 mg, 254 nm, 16 lamps, 5 min).

Photolysis of 14 in 1:1 H_2O−CH_3OH. A solution of 21 mg of **14** in 100 mL of 1:1 H_2O−CH_3OH gave <2% conversion to the respective methanolysis product (254 nm, 8 lamps, 10 min).

Photolysis of 9 in 1:1 H_2O−CH_3CN in the Presence of Ethanolamine. A solution of 20 mg of **9** in 80 mL of 1:1 H_2O−CH_3CN in the presence of 0.2 M ethanolamine was photolyzed (254 nm, 8 min). After workup, the CH_2Cl_2 extract was washed with water to remove residual ethanolamine. ^{1}H NMR of the product mixture after 8 min of photolysis gave ∼40% yield of **28**, as identified by its characteristic methylenes. Quantitative conversion to **28** was achieved by photolysis for 20−30 min, which gave upon workup essentially pure **28**: ^{1}H NMR (300 MHz, acetone-d_6): δ 2.56 (t, J = 7 Hz, 2H, -CH_2-N), 3.62 (t, J = 7 Hz, 2H, -OCH_2-), 2.85 (br s, -OH, -NH-, exchangeable with D_2O), 4.88 (s, 1H, ArCH-), 6.86 (dt, J = 7.8 Hz, 2H, ArH), 7.16 (t, J = 6.8 Hz, 1H, ArH), 7.26 (t, 2H, J = 7.8 Hz, ArH), 7.43−7.53 (m, 8H, ArH), 8.52 (br s, 1H, ArOH, exchangeable with D_2O); HRMS calcd for $C_{22}H_{23}O_2N$ 333.1729, found 333.1730.

UV−Vis Studies. The molar absorptivities (ϵ) for **7** and **12** were determined at 300 and 237 nm, respectively. In each case, a known mass of sample was dissolved in a 500 mL volumetric flask containing 1:1 H_2O/CH_3CN. Three milliliters of this stock solution was then pipetted into a quartz cuvette and the UV−vis spectrum was recorded on the Cary 5. This was repeated three times for each sample. ϵ was calculated from the Beer−Lambert relationship ($A = \epsilon cl$).

Quantum Yields. Relative quantum yields were determined by comparison of the yields of photosolvolyzed product between a compound with a known quantum yield to those of the compound under study. A known amount of compound was dissolved in a given solvent system (abs at λ_{ex} > 3) in a quartz tube and irradiated long enough to give a low conversion. Immediately following this, an equimolar amount of the compound with the known quantum yield was irradiated under the same conditions. Integration from ^{1}H NMR was used to determine the relative conversions of the photosolvated products. Each system was maintained at ∼15 °C by means of an internal coldfinger and was purged with argon for 5 min prior to irradiation. All values are the result of at least three independent irradiations.

The product quantum yield for methyl ether formation from *m*- and *p*-hydroxybenzhydrol have been previously determined[11] (Φ_p= 0.40

and 0.19, respectively). These compounds were used to determine Φ_p for methanolysis of **9** and **10** (20 mg, 100 mL of 1:1 H_2O-CH_3OH, 2 min, 254 nm, 8 lamps).

Absolute quantum yields were determined on an optical bench with an Oriel 200 W high-pressure Hg lamp and a PTI monochromator. Potassium ferrioxalate was employed as the actinometer. Solutions of the compound to be studied were irradiated for an amount of time known to give <10% conversion to the photohydrated products. As conversion of the biphenyl alkenes to the alcohols involves observing a loss of absorption, the OD (<2, in order to obtain an accurate measurement) of each solution was determined prior to irradiation. A correction factor for the amount of light absorbed by the sample (relative to that absorbed by the actinometer) was utilized in the calculation of the quantum yield.

The quantum yields for photohydration (Φ_p) of **7** and **12** in 1:1 H_2O/CH_3CN were determined by potassium ferrioxalate actinometry. The quantum yields of photohydration of alkenes **11** (15.8 mg, 100 mL of 1:2 H_2O/CH_3CN, 10 min, 254 nm, 8 lamps) and **8** (15 mg, 80 mL of 1:1 H_2O/CH_3CN, 1.5 min, 254 nm, 8 lamps) were determined via comparison to the relative conversions for **7** (15 mg) and **12** (15.8 mg), respectively. Due to a lack of solubility in 1:1 H_2O/CH_3CN, the Φ_p for photohydration of **11** was measured in 1:2 H_2O/CH_3CN.

Steady-State and Time-Resolved Fluorescence Measurements. All solutions were purged with argon for 5 min prior to measurement (abs ~ 0.1 at λ_{ex}). Steady-state fluorescence spectra were recorded on a Photon Technologies International (PTI) QM-2 fluorometer at 20 °C. Fluorescence quantum yields (Φ_f) were calculated by comparing the integrated emission bands of a standard [2-aminopyridine in 0.1 N H_2SO_4 ($\Phi_f = 0.60 \pm 0.05$)] with those of the desired compounds and correcting for differences in the refractive index.[25] In an effort to detect aggregation effects, the fluorescence quantum yields were measured at a minimum of three concentrations for **7**−**11** (OD 0.02−0.1). Fluorescence lifetimes (τ_f) were measured on a PTI LS-1 instrument utilizing the time-correlated single photon counting technique (10 000 counts).

Laser Flash Photolysis. All LFP studies were conducted at the University of Victoria LFP Facility utilizing either a Spectra Physics YAG laser, model GCR-12 (266 and 355 nm excitation), or a Lumonics excimer laser (Model EX-510, 308 nm excitation). In a typical experiment, a solution with an OD of ≤0.3 was prepared in a given solvent system in a sample holder attached to a flow cell (7 mm × 7 mm quartz) from a stock solution of the desired compound in dry CH_3CN. The solution was then purged with either oxygen or nitrogen for a minimum of 10 min prior to starting and continuously throughout the experiment.

Supporting Information Available: Synthetic procedures for biphenyl alkenes and alcohols **7**−**14 (PDF).** This information is available free of charge via the Internet at http://pubs.acs.org.

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