

Mechanistic studies of photohydration of *m*-hydroxy-1,1-diaryl alkenes

John G. Cole and Peter Wan

Abstract: The photohydration of a variety of *m*-hydroxy-1,1-diaryl alkenes (**8–10**) and related systems (**11** and **12**) has been studied in aqueous CH₃CN solution. All of these alkenes photohydrate efficiently in 1:1 H₂O–CH₃CN, to give the corresponding 1,1-diarylethanol (Markovnikov addition) products with high chemical and quantum yields. The aim of this study was to further probe the mechanism of photohydration reported for the parent *m*-hydroxy- α -phenylstyrene (**5**), which has been proposed as consisting of a water trimer-mediated excited state (formal) intramolecular proton transfer (ESIPT) from the phenolic proton to the β -carbon of the alkene moiety to give an observable (by laser flash photolysis (LFP)) *m*-quinone methide intermediate **6**. For this purpose, derivatives of **5** with substituents (methyl or methoxy) on the α -phenyl ring as well as related model compounds were explored. Product studies, quantum yields, fluorescence, and nanosecond laser flash data are reported that are consistent with two distinct mechanisms for photohydration of these compounds: one involving water-mediated ESIPT (**8**, **9**), as observed for the parent compound **5**, and one involving direct protonation of the β -carbon by solvent water (**11** and **12**), with compound **10** possibly operating via both mechanisms.

Key words: photohydration, solvent-assisted excited state intramolecular proton transfer (ESIPT), *m*-quinone methide, diarylmethyl carbocation.

Résumé : Opérant en solution aqueuse de CH₃CN, on a étudié la photohydratation d'une variété de *m*-hydroxy-1,1-diarylcènes (**8–10**) et de systèmes apparentés (**11** et **12**). Tous ces alcènes se photohydratent facilement dans un mélange 1:1 de H₂O–CH₃CN et ils conduisent à la formation des 1,1-diaryléthanol correspondants (addition de Markovnikov) avec des rendements chimiques et quantiques élevés. Le but de cette étude était d'examiner plus à fond le mécanisme de photohydratation proposé pour le *m*-hydroxy- α -phénylstyrène fondamental (**5**) soit une réaction catalysée par un trimère d'eau et caractérisée par un transfert intramoléculaire de proton dans l'état excité (TIPEE) (formel) à partir du proton phénolique vers le carbone β de la partie alcène avec la formation d'un intermédiaire *m*-quinoneméthide (**6**) qui peut être observé par photolyse éclair au laser (PEL). À cette fin, on a étudié des dérivés de **5** portant des substituants (méthyle ou méthoxy) sur le noyau α -phényle ainsi que des composés modèles apparentés. Les résultats d'études faites sur la nature des produits et les rendements quantiques ainsi que les données relatives à la photolyse éclair au laser au niveau de la nanoseconde peuvent s'accommoder de deux mécanismes distincts pour la photohydratation de ces composés: l'un implique un TIPEE catalysé par l'eau (**8**, **9**) semblable à celui observé avec le composé fondamental (**5**) et l'autre implique une protonation directe du carbone β par une molécule d'eau du solvant (**11**, **12**); le composé **10** pourrait réagir par une combinaison de ces deux mécanismes.

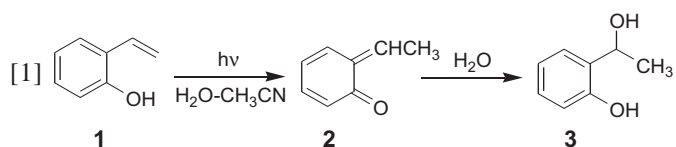
Mots clés : photohydratation, transfert intramoléculaire de proton dans l'état excité (TIPEE), *m*-quinoneméthide, carbocation diarylméthyle.

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Introduction

Excited state intramolecular proton transfer (ESIPT), a process of wide interest in chemistry, occurs most readily for those molecules whose acidity and basicity of both the proton donor and proton acceptor groups, respectively, are enhanced upon electronic excitation. ESIPT naturally leads to the formation of tautomers that are generally difficult to form via thermal chemistry (1). In almost all cases, the above

mentioned proton transfers occur between heteroatoms, and the process is generally reversible. The first cited example of an ESIPT between a phenol and a carbon (alkene) was reported by Kalandropoulos and Yates (2) in the efficient photohydration of *o*-hydroxystyrene (**1**) (eq. [1]). Photolysis of **1** in aqueous CH₃CN gave the *o*-quinone methide **2**, via

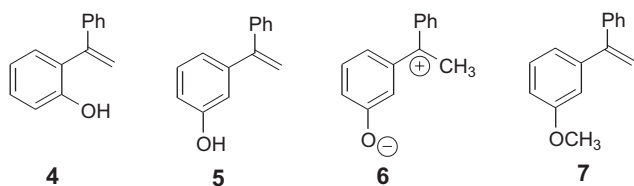


ESIPT from the phenol to the β -carbon. Nucleophilic attack by water at the α -carbon of **2** gives the overall hydration

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product **3**. Available evidence suggests that **2** does not return to **1** under the conditions employed, this being an example of an irreversible ESIPT. Recent work from our group (3) on the related compound **4** confirms the formation of an *o*-quinone methide (by laser flash photolysis (LFP) experiments) from these compounds, which is generated within the laser pulse (≈ 10 ns). Moreover, we have also recently shown that the *meta* isomer (**5**) also photohydrates efficiently, but via a water trimer-mediated ESIPT, to give *m*-quinone methide **6** as the initially formed intermediate (**4**), as deduced from LFP experiments and the much lower reactivity of **7**, as well as other data (4). The crucial *m*-quinone methide intermediate **6** is formed within the laser pulse. In addition, there is efficient quenching of fluorescence of **5** by added water, concomitant with increased efficiency for the formation of **6**. These data support a mechanism of water-mediated ESIPT from the phenol to β -carbon that is probably concerted (or two very fast steps: deprotonation from the phenol OH followed by protonation of the β -carbon via a proton “relay” mechanism mediated by water). A similar mechanism may also be operative for the *para* isomer, although its intrinsically weak fluorescence emission made detailed mechanistic studies problematic.

The mechanism of the water trimer-mediated ESIPT from phenol to the β -carbon (of the alkene) of *m*-hydroxystyrenes warrants further investigation. In this work, the photohydrations of *m*-hydroxy- α -phenylstyrenes with electron donating substituents (methyl and methoxy) **8–10** are investigated. The related dimethoxystyrenes **11** and **12** without an *m*-hydroxy substituent were also studied for additional mechanistic insights.

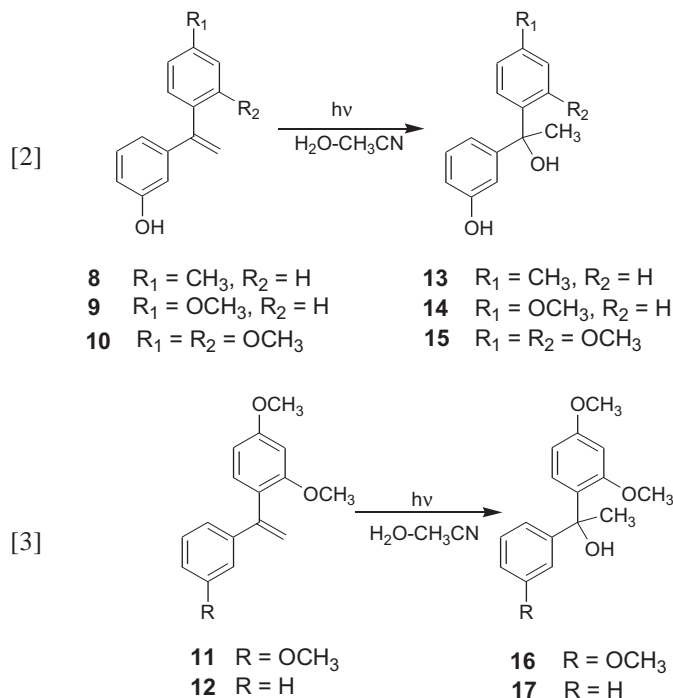
Results and discussion

Materials

1,1-Diarylethenes **8–12** were made via dehydration of the corresponding 1,1-diarylethanol **13–17**, which in turn were made by the reaction of the corresponding Grignard reagent with 3'-hydroxyacetophenone (for **8–10**), 3'-methoxyacetophenone (for **11**), or acetophenone (for **12**). The Grignard reagents were made by standard reaction of the corresponding arylbromides with Mg metal. The isolated yields of the alkenes were generally $>60\%$.

Product studies and quantum yields

Preparatory photolyses of **8–12** (argon purged, $\sim 10^{-3}$ M, 1:1 (v/v) $\text{H}_2\text{O}-\text{CH}_3\text{CN}$, Rayonet RPR-100 photochemical reactor, 254 nm, $\sim 15^\circ\text{C}$, <5 min) gave the corresponding alcohols (photohydration products) **13–17** in essentially quantitative yields (eqs. [2] and [3]). Control experiments showed no reaction in the absence of irradiation. Quantum yields for photohydration (Φ_p , alcohol formation) in 1:1 $\text{H}_2\text{O}-\text{CH}_3\text{CN}$ for **8–12** were determined relative



to that reported for parent **5** (4) using ^1H NMR (Table 1). *m*-Hydroxystyrenes **8–10** have Φ_p 's significantly higher than **5** ($\Phi_p = 0.22$), whereas styrenes **11** and **12** have comparable values to **5**. The significantly higher quantum yields observed for the *m*-hydroxy-substituted compounds (**8–10**) compared to **11** and **12** are suggestive of a different mechanism for photohydration, perhaps similar to that reported for **5**; whereas **11** and **12** can only react via a simple photoprotonation pathway.

The photohydrations of **8–12** can be monitored readily by UV-vis spectrophotometry, since the alcohol products have much lower extinction coefficients over most of the spectrum (Fig. 1). The change in absorption spectra vs. irradiation time shows a linear relationship until at least 60% conversion, at which point the product may compete for light. Using this method for following the photohydration efficiency of these compounds, the dependence of Φ_p vs. water content (in CH_3CN) are shown in Fig. 2. The quantum yields for **8** and **9** increase rapidly with small additions of water, reaching a plateau at about 7–15 M H_2O . This behaviour is similar to that observed for **5**. However, unlike compounds **5**, **8**, and **9**, the Φ_p 's of **10–12** have an apparent linear dependence on water concentration in CH_3CN ; that is, the Φ_p 's increase in a much more gradual fashion. This implies that bulk solvent water is required to accomplish efficient photohydration via photoprotonation for **10–12**, whereas a different mechanism requiring much less water content operates for the photohydration of **8** and **9**.

Solvent isotope effects for the photohydration quantum yield ($\Phi_p(\text{H}_2\text{O})/\Phi_p(\text{D}_2\text{O})$) were determined by comparing the Φ_p in $\text{H}_2\text{O}-\text{CH}_3\text{CN}$ and $\text{D}_2\text{O}-\text{CH}_3\text{CN}$ solutions (Table 1) using the above UV-vis method. Primary solvent isotope effects for **8** and **9** were evident at low water concentrations ($\Phi_p(\text{H}_2\text{O})/\Phi_p(\text{D}_2\text{O}) \sim 2$ at 0.9 M $\text{H}_2\text{O}-\text{D}_2\text{O}$ in CH_3CN). At higher water concentrations, no isotope effect was observed ($\Phi_p(\text{H}_2\text{O})/\Phi_p(\text{D}_2\text{O}) \sim 1$ at 7.4 M $\text{H}_2\text{O}-\text{D}_2\text{O}$ in CH_3CN). This

Table 1. Summary of quantum yield data and photophysical properties of compounds studied.

Compound	Φ_p^a	$\Phi_p(\text{H}_2\text{O})/\Phi_p(\text{D}_2\text{O})^b$	Φ_f^c	τ_f (ns) ^d	τ_{INT} (μs) ^e
5^f	0.22	>1	0.20	5.6 ± 0.3	0.047
8	0.40	1.8	0.12	4.4 ± 0.4	0.25
9	0.41	2.3	0.011	<1	3.0
10	0.31	3.0	0.008	<1	70
11	0.24	5.0	0.006	<1	4.4, 55
12	0.17	4.0	0.004	<1	3.5, 50

^aQuantum yield for photohydration in 1:1 H₂O–CH₃CN, as measured using the reaction of **5** as secondary standard (estimated error, $\pm 10\%$).

^bSolvent isotope effect for photohydration (in 0.9 M H₂O(D₂O) in CH₃CN for **8** and **9**; in 7.4 M H₂O(D₂O) in CH₃CN for **10–12**).

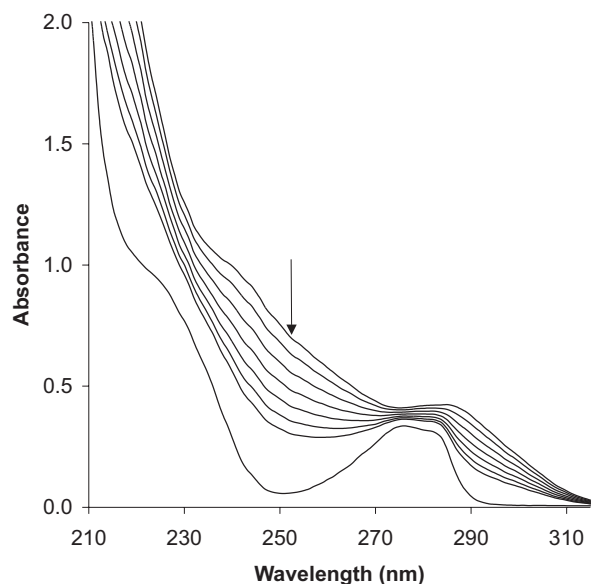
^cFluorescence quantum yield in neat CH₃CN ($\lambda_{\text{ex}} = 285$ nm; 2-aminopyridine as standard; estimated error, $\pm 10\%$).

^dFluorescence lifetime in neat CH₃CN, as measured by single photon counting. Only lifetimes >1 ns are measurable using the system available.

^eLifetime(s) of observed *m*-QM or carbocation in 1:1 H₂O–CH₃CN, as detected by LFP. Biphasic decays observed where two lifetimes are quoted.

^fData from ref. 4.

Fig. 1. UV–vis traces for photohydration of **10** in 1:1 H₂O–CH₃CN. Each trace was taken after 20 s photolysis at 254 nm. The final trace is that of the photohydration product **15**.



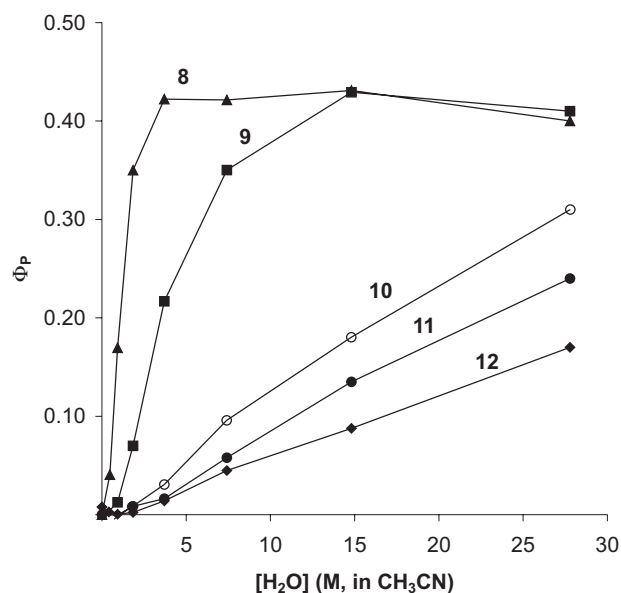
suggests a change in mechanism on going to solutions of high water content, where Φ_p values reach a plateau region (Fig. 2). The solvent isotope effects on the photohydration of **10–12** are quite large, with $\Phi_p(\text{H}_2\text{O})/\Phi_p(\text{D}_2\text{O})$ in the range 3–5. Unlike **8** and **9**, the isotope effects are independent of the concentration of water used (7–15 M H₂O–D₂O).

Steady-state and time-resolved fluorescence studies

Quantum yields of fluorescence (Φ_f) of **8–12** in dry CH₃CN were measured relative to 2-aminopyridine (**5**) (Table 1). The lack of large Stokes shifts in the fluorescence emission spectra indicates that the normal form (i.e., not the phenolate or a tautomeric form) of each compound is responsible for the emission. The addition of methoxy substituents (**9–12**) significantly reduces Φ_f , presumably through enhancement of non-radiative decay pathways.

To probe the mechanisms of photohydration further, steady-state fluorescence spectra were taken as a function of water content in CH₃CN. The fluorescence emission of **8** is quenched efficiently with small additions of water, and is essentially quenched by 3.7 M water (Fig. 3). Less efficient

Fig. 2. Plots of quantum yields of photohydration for **8–12** vs. water concentration (in CH₃CN).



quenching was observed when D₂O was used (approximately half as efficient, up to 1.9 M H₂O(D₂O)). It is significant to note that at this same water concentration, Φ_p for **8** has essentially reached its maximal value (Fig. 2). Both **9** and **10** exhibit an initial increase in fluorescence emission intensity with small additions of water (up to 1.9 M) (Fig. 4a), followed by slower quenching by water (relative to **8**), requiring about 50% water to completely quench the emission (Fig. 4b). The weaker fluorescence emissions of both **11** and **12** prevented reliable studies of their water-quenching phenomena. However, neither compound exhibited a growth in fluorescence emission on the addition of water. Although the photophysical details are beyond the scope of this study, one possible reason for the observed growths in fluorescence emission intensity with added water (at low water concentrations) for **9** and **10** is associated with hydrogen bonding by added water to the phenol moiety, with the associated changes in structure and intrinsic emission efficiency. Since their Φ_f (in neat CH₃CN) are already low, slight changes to its emission quantum yield would be readily noticeable.

Fig. 3. Fluorescence quenching of **8** by H₂O in CH₃CN.

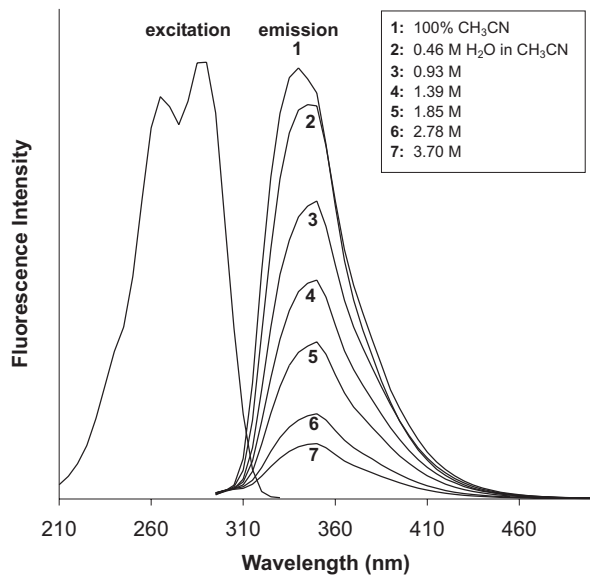


Fig. 4. (a) Effect on fluorescence intensity of **9** by added H₂O (in CH₃CN) up to 1.85 M; (b) above 1.85 M.

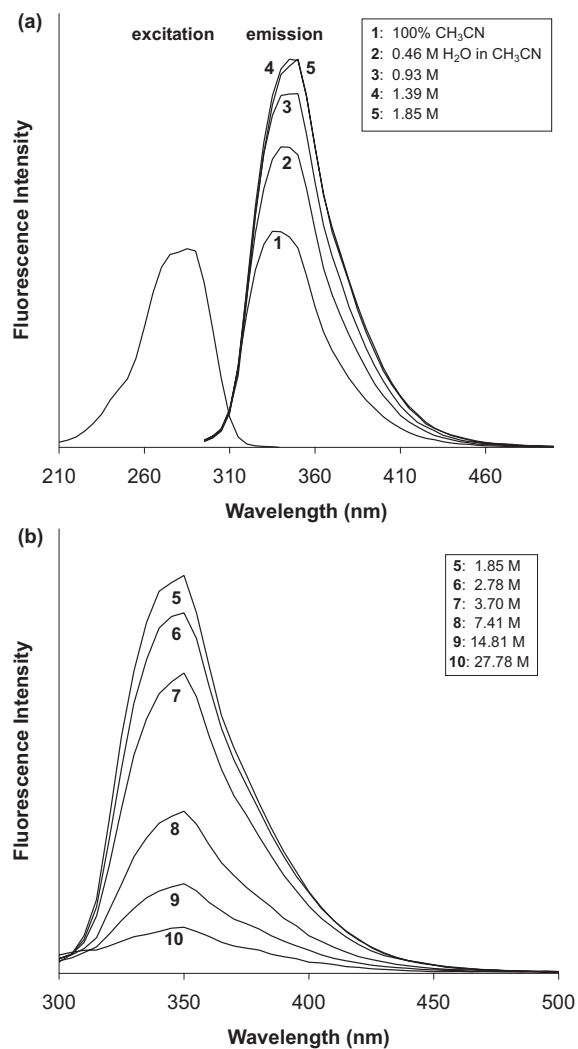


Fig. 5. Stern–Volmer plots of fluorescence quenching of **8** by H₂O (in CH₃CN) using steady-state fluorescence data (H₂O: ■; D₂O: □) and using fluorescence lifetime data (H₂O only: ▲). The solid lines are fits to the square of the water concentration ([H₂O]²).

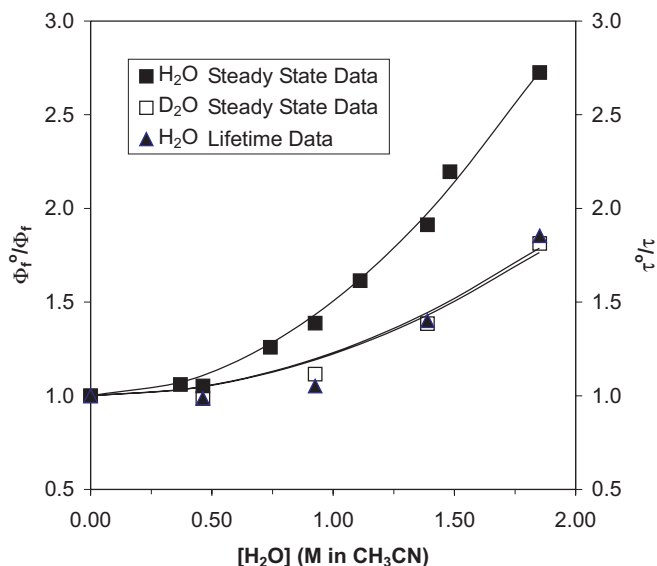
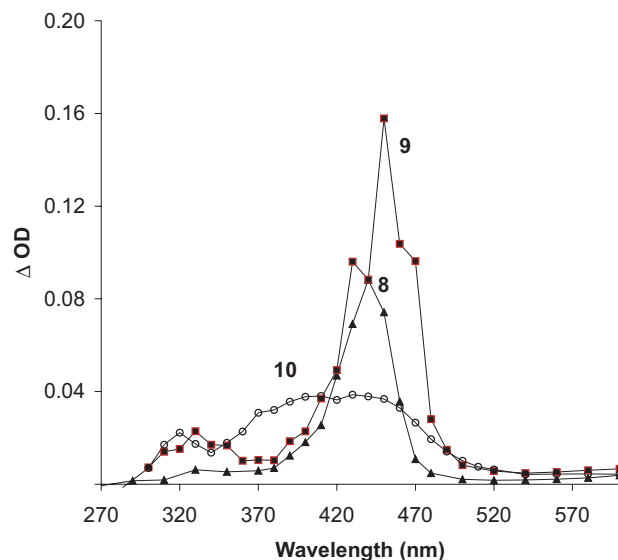
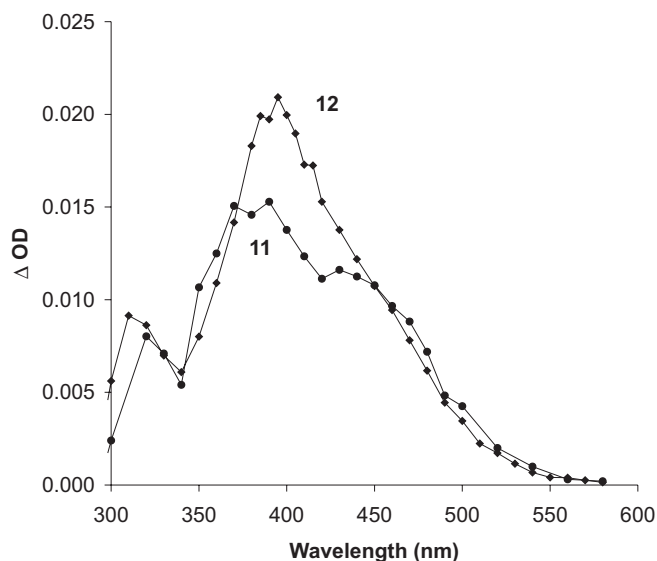


Fig. 6. LFP transients of **8–10** in 1:1 H₂O–CH₃CN oxygen-purged solution, 10 ns after laser excitation (266 nm).



Fluorescence lifetimes (τ_f) were measurable only for **8** (4.4 ± 0.4 ns, neat CH₃CN) (Table 1). Addition of small amounts of water (<2 M) decreased its lifetime as anticipated (4.4, 4.1, 3.1, 2.3 in 0.5, 0.9, 1.4, 1.9 M H₂O, respectively). Stern–Volmer plots of fluorescence quenching by H₂O(D₂O) using steady-state and lifetime data are shown for **8** in Fig. 5. Comparison of the steady-state and lifetime plots show that both static (pre-excitation) and dynamic (post-excitation) quenching of **8** are occurring. The non-linear nature of the plots also suggest that, on average, more than one water molecule is involved with each excited singlet state of

Fig. 7. LFP transients of **11** and **12** in 1:1 H₂O–CH₃CN oxygen-purged solution, 10 ns after laser excitation (266 nm).



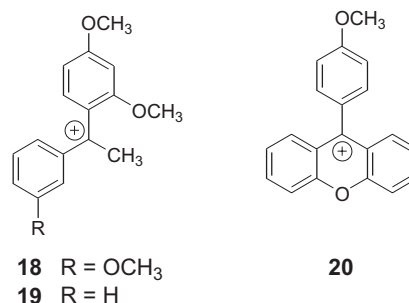
8. Modifying the Stern–Volmer plot so that the concentration of water is squared ($[\text{H}_2\text{O}]^2$) provides the best fit of the data (Fig. 5). Thus, at low water concentrations in CH₃CN, an average of two water molecules are required to quench the fluorescence, via both the static and dynamic mechanisms.

Laser flash photolysis (LFP)

Nanosecond LFP of **8** and **9** (266 nm; YAG laser; <20 mJ; 20°C) in 1:1 H₂O–CH₃CN resulted in sharp, strongly absorbing transients similar to those previously reported as *m*-QMs (4). LFP of **10** under the same conditions led to a broader transient signal. All three transients appear immediately after the laser pulse (≈ 10 ns) and are shown in Fig. 6. Purging with oxygen or nitrogen had no significant effect on the profile or lifetime of the transients. The signals decay to baseline in a mono-exponential fashion. Excitation in dry CH₃CN gave no transient signal, thus indicating that water is necessary for the formation of the reactive intermediate. The lifetime of these transients increase with electron-donating substituents on the α -phenyl ring, consistent with an electron deficient species (Table 1).

LFP of the **11** and **12** (lacking a *m*-hydroxy group) in 1:1 H₂O–CH₃CN gave broad transients observed immediately after the laser pulse (Fig. 7) that are insensitive to the presence of oxygen. Excitation of these compounds in the absence of water (dry CH₃CN) did not lead to any transient. Since these compounds lack an *m*-hydroxy group, they cannot form *m*-QMs. Based on their similarity to published data on arylmethyl carbocations (6), they are assigned to diaryl-methyl carbocations **18** and **19**, obtained via Markovnikov photoprotonation by water at the β -carbon. Interestingly, both of these diaryl carbocations show a biphasic decay (two pseudo-first-order decays) to baseline across the transient profile (Fig. 8). This suggests the presence of two absorbing species with essentially identical absorption spectra but different reactivity (resulting in two decay rates). A similar biphasic decay was reported for the photo-

generated 9-*p*-methoxyphenyl-9-xanthenylium cation (**20**) in aqueous ethanol (7). The short-lived species (≈ 0.1 ms) was assigned to the ion pair (geminate) recombination of the cation and hydroxide ion, while the longer lived species (≈ 10 ms) was assigned to the reaction of the cation with water. The ratio of the two observed quenching rates of **20** is similar to those obtained for the LFP intermediates **18** and **19**.



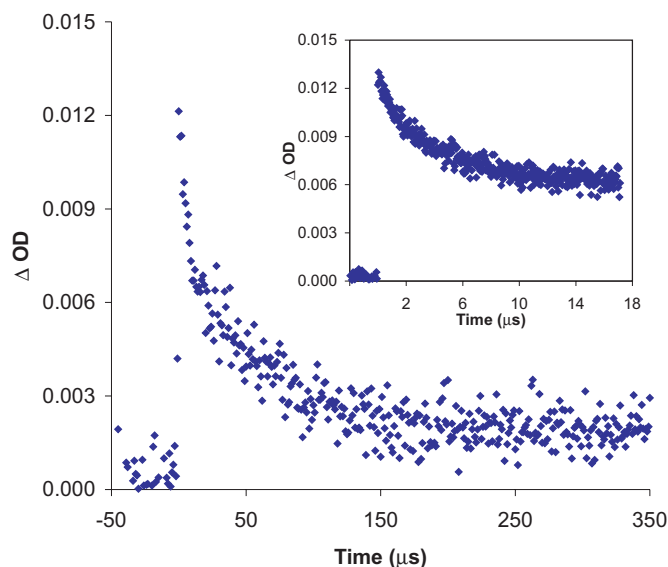
The effect of water content (in CH₃CN) on the strength of the LFP transients observed for **8** and **11** are shown in Fig. 9. In dry CH₃CN (as previously mentioned), no signals were observed. However, with small additions of water (<3.7 M in CH₃CN), the transient generated from **8** rapidly grows in, reaching a plateau region at ≈ 3.7 M H₂O. The carbocation signal of **18** appears only weakly at this water concentration. At much higher water concentrations (5–20 M H₂O), the signal increased in an apparent linear fashion with water concentration. The transient lifetimes observed for both **8** and **11** are shorter at higher water content, consistent with them being carbocation-like species. For **8**, at low water concentrations in CH₃CN the lifetime of the transient is relatively long (14 μ s with 0.5 M H₂O). As more water is added, the intermediate lifetime steadily decreases (750 ns in 3.7 M H₂O), reaching 250 ns in 1:1 H₂O–CH₃CN.

It is interesting to note that the two plots observed in Fig. 9 for **8** and **11** are essentially identical to their plots of Φ_p vs. water content (Fig. 2).

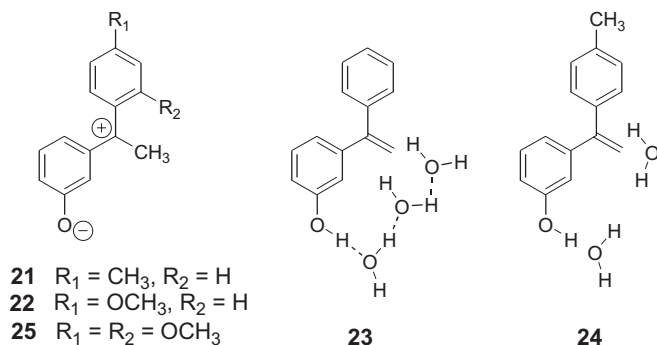
Mechanisms of photohydration

Although molecules **8–12** photohydrate efficiently in aqueous solution, as shown by the high quantum yields for 1,1-diarylalcohol formation measured in 1:1 H₂O–CH₃CN, it is clear that substantial differences exist with respect to their mechanisms of photosolvolytic. The Φ_p 's of **8** and **9** have a water concentration effect that is essentially identical to that observed for **5**. The lifetimes of the transients generated by LFP of **5**, **8**, and **9** are consistent with the increase in the electron donating capability of the *para* substituents on the α -phenyl ring. Most notably, the single-exponential decay of those transients, rather than a biphasic decay, distinguish these intermediates from simple arylmethyl carbocations such as **18–20**, indicating that the transients generated from **8** and **9** are most probably *m*-QMs **21** and **22**. It was initially anticipated that the mechanism of photosolvolytic for **8** and **9** would be similar to that reported for **5** involving an excited state (formal) intramolecular proton transfer mediated by a cluster of three water molecules, as shown in **23**. This mechanism was proposed for **5** when it was noted that three water molecules were required to fit the fluorescence quenching data (static and dynamic components). Three water mole-

Fig. 8. Biphasic pseudo-first-order decays of the LFP intermediate of **11** monitored at 475 nm in a 1:1 H₂O–CH₃CN oxygen purged solution. Inset: decay at shorter time scales (lifetimes are 4.4 and 55 μ s).

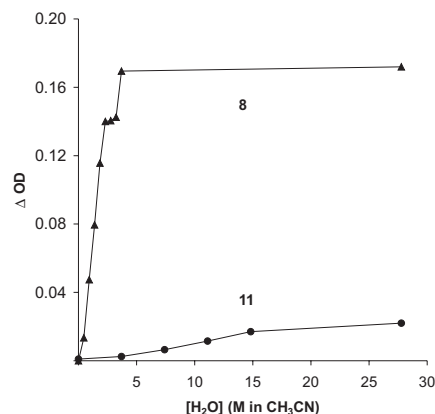


cles hydrogen bonded in a chain could span the distance between the phenol and β -carbon in **23**. However, due to the rapid formation (within the laser pulse) of *m*-QM **6**, it was not possible by LFP to discern whether the proton transfers were concerted or in sequence. The fluorescence quenching data of **8** show that only two water molecules are involved in its proton transfer mechanism. This is insufficient to bridge the distance between the phenol and β -carbon on the alkene. Thus, the intramolecular proton transfer is more likely two excited-state proton transfers with only one water molecule required at each of the acidic and basic sites, as shown in **24**. This would still generate a *m*-QM, although without being a formal intramolecular proton transfer. It appears that the electron donating ability of the *p*-methyl group on the α -phenyl ring of **8** (relative to a hydrogen on **5**) is sufficient in reducing the water requirement of QM formation. Unfortunately, the peculiar fluorescence growth of **9** upon addition of water does not allow for proper Stern–Volmer analysis to determine (on average) how many water molecules are required for quenching of its excited state.



Both **11** and **12** photohydrate to give the corresponding Markovnikov alcohol. Considering the lack of a phenol functionality on these compounds, the reactions must pro-

Fig. 9. Δ OD vs. water concentration for the transients observed for **8** and **11** (in CH₃CN) immediately after (\approx 10 ns) excitation by LFP.



ceed via a diarylmethyl carbocation intermediate. The efficiency of these reactions depend on bulk water concentration, and they have a large primary isotope effect implying that the excited state proton transfers in these cases is not as “early” as for **8** and **9**. The LFP transients show an interesting biphasic decay pattern, similar to that reported for xanthylium cation **20** (7), which was photogenerated by photodehydroxylation of the corresponding alcohol (which generates an initial cation–hydroxide ion pair). In analogy to the assignments made for the kinetic data for **20** (7), the biphasic decay is interpreted as arising from two forms of the carbocation: one being an ion pair with hydroxide ion, and the other the solvent-separated (solvated) carbocation. The shorter-lived species is assigned to the ion pair and the longer-lived species to the solvated carbocation.

The photohydration of **10** shows characteristics of mechanisms involving a *m*-QM as well as those of a simple carbocation intermediate. The dependence of Φ_p on water concentration and solvent isotope effect support the idea that **10** reacts via a carbocation, similar to the mechanism for **11** and **12**. However, evidence that **10** generates a *m*-QM is in the observed decay profile of the intermediate: it lacks a biphasic decay, implying that an ion pair is not formed. Indeed, the intermediate observed for **10** is sufficiently long-lived that a shorter-lived component would have been observable. Since it is clearly mono-exponential, intermediate quenching via ion-pair combination is not occurring, and the species is best assigned to a *m*-QM **25**.

Summary

New insights into the mechanisms of photohydration of 1,1-diarylalkenes have been made. *m*-Hydroxystyrenes **8** and **9** undergo ESIPT to form *m*-QM, followed by reaction with water to form the corresponding 1,1-diarylalcohol. The reaction requires only small volumes of water to be present to reach maximum quantum efficiency. *o,p*-Dimethoxystyrenes **11** and **12** undergo ESPT from solvent water to form carbocations **18** and **19**, which then react with either a hydroxide ion or water to yield the alcohol product. The reactions require bulk solvent water to be observable, and do not react in CH₃CN solutions with small amounts of water.

Compound **10**, which is both a *m*-hydroxystyrene and a *o,p*-dimethoxystyrene, shows characteristics of both mechanisms. However, the lifetime of the LFP intermediate shows evidence of a *m*-QM rather than a carbocation intermediate.

Experimental

General

¹H NMR spectra were recorded on a Bruker AC-300 (300 MHz) instrument. UV-vis spectra were obtained using Cary 5 UV/Vis, Cary 1E UV/Vis, and Cary 50 Bio scanning spectrophotometers in conjunction with fluorescence, LFP, and Φ_p measurements, respectively. The fluorescence spectra were taken on a Photon Technology International A-1010 (PTI) Quanta Master™ Luminescence Spectrometer. High resolution mass spectra were obtained on a Kratos Concept H (EI) instrument and the uncorrected melting points in a Gallencamp melting point apparatus. IR spectra were recorded on a PerkinElmer Spectrum One FTIR spectrophotometer either as KBr pellets (for solid compounds), or on NaCl plates (as a neat oil). Photolyses were carried out in 100-mL quartz tubes using a Rayonet RPR 100 photochemical reactor with 254 nm lamps (up to 16). The solvents THF, CH₃CN, and CH₂Cl₂ were distilled before use with THF and CH₃CN pre-drying over K and CaH₂, respectively. 3-Hydroxyacetophenone, 3-methoxyacetophenone, acetophenone, 4-bromotoluene, 4-bromoanisole, and 1-bromo-2,4-dimethoxybenzene were purchased from Aldrich.

3'-Hydroxy-4"-methyl-1,1-diphenylethene (8)

The Grignard reagent was prepared by adding a solution of 4-bromotoluene (5.5 mL, 45 mmol) in anhydrous THF (25 mL) dropwise to Mg (0.87 g, 35.8 mmol) in anhydrous THF (100 mL) under nitrogen. The resulting mixture was heated at reflux for 2 h, then 3-hydroxyacetophenone (1.82 g, 13.4 mmol) was added dropwise, and then the mixture kept at reflux for more 2 h. Saturated aqueous NH₄Cl was added and the solution was subjected to standard workup (extraction with CH₂Cl₂, washing of the organic with saturated brine solution, drying (MgSO₄), filtration, and evaporation to dryness in vacuo), to afford the crude product alcohol 3'-hydroxy-4"-methyl-1,1-diphenylethanol (**13**) (≈70%). Molecule **13** was refluxed in CH₃CN with a catalytic amount of dilute H₂SO₄, to yield the crude oil **8**. Purification by column chromatography in 9:1 CH₂Cl₂-EtOAc yielded pure material (oil). ¹H NMR (CDCl₃) δ: 2.35 (s, 3H, CH₃), 4.87 (s, 1H, OH), 5.39 (s, 2H, =CH₂), 6.78 (m, 2H, Ar), 6.90 (d, *J* = 8.0 Hz, 1H, Ar), 7.10–7.24 (m, 5H, Ar). HRMS calcd. for C₁₅H₁₄O: 210.1045; found: 210.1047.

3'-Hydroxy-4"-methoxy-1,1-diphenylethene (9)

The Grignard reagent was prepared as above using 4-bromoanisole (5.8 mL, 46 mmol), Mg (0.87 g, 35.8 mmol), and 3-hydroxyacetophenone (3.02 g, 22 mmol) to yield the crude product alcohol 3'-hydroxy-4"-methoxy-1,1-diphenylethanol (**14**). Molecule **14** was refluxed in CH₃CN with a catalytic amount of H₂SO₄ (aq) to yield the crude oil **9**. Purification by column chromatography in 4:1 hexanes-EtOAc yielded clean product, which was recrystallized from CH₃Cl and hexanes with an overall yield of 25% (1.35 g, 5 mmol):

mp 66–68°C. ¹H NMR (CDCl₃) δ: 3.81 (s, 3H, OCH₃), 4.73 (s, 1H, OH), 5.35 (d, *J* = 6.6 Hz, 2H, =CH₂), 6.78–6.92 (m, 5H, Ar), 7.16–7.26 (m, 3H, Ar). HRMS calcd. for C₁₅H₁₄O₂: 226.0994; found: 226.0994.

3'-Hydroxy-2",4"-dimethoxy-1,1-diphenylethanol (15)

The appropriate Grignard reagent was prepared from 1-bromo-2,4-dimethoxybenzene (9.0 mL, 62 mmol), Mg (2.12 g, 87 mmol), and 3-hydroxyacetophenone (3.62 g, 27 mmol). The resulting crude oil was washed with benzene to remove the byproduct dimethoxybenzene, resulting in **15** in a 60% yield. Recrystallization from ethanol and hexanes gave pale green cubic crystals in 40% yield: mp 144–146°C. IR (cm⁻¹): 3457 (s), 3310 (s). ¹H NMR (CDCl₃) δ: 1.77 (s, 3H, CH₃), 3.58 (s, 3H, OCH₃), 3.80 (s, 3H, OCH₃), 4.48 (s, 1H, OH), 4.69 (s, 1H, OH), 6.45 (d, *J* = 2.9 Hz, 1H, Ar), 6.50 (dd, *J* = 8.5, 2.5 Hz, 1H, Ar), 6.63 (dd, *J* = 8.1, 2.6 Hz, 1H, Ar), 6.79 (m, 2H, Ar), 7.09 (t, *J* = 8.1 Hz, 1H, Ar), 7.30 (d, *J* = 8.8 Hz, 1H, Ar). HRMS calcd. for C₁₆H₁₈O₄: 274.1205; found: 274.1205.

3'-Hydroxy-2",4"-dimethoxy-1,1-diphenylethene (10)

Molecule **15** (0.40 g, 1.4 mmol) was dissolved in THF (120 mL) and a catalytic amount (one drop) of 10 N H₂SO₄ was added. The solution was heated at reflux for 2 h. Quenching of the reaction with distilled water (100 mL), neutralization with Na₂CO₃ (aq), and general workup (extraction into CH₂Cl₂, drying with anhydrous MgSO₄) yielded **10** as an oil. Recrystallization from CHCl₃ and hexanes gave light brown cubic crystals with an overall yield of 64%: mp 79–81°C. IR (cm⁻¹): 3445 (s), 3097 (m). ¹H NMR (CDCl₃) δ: 3.62 (s, 3H, OCH₃), 3.82 (s, 3H, OCH₃), 4.59 (s, 1H, OH), 5.27 (d, *J* = 1.5 Hz, 1H), 5.63 (d, *J* = 1.5 Hz, 1H), 6.46–6.51 (m, 2H, Ar), 6.69–6.72 (m, 2H, Ar), 6.88 (d, *J* = 7.4 Hz, 1H, Ar), 7.11–7.15 (m, 2H, Ar). HRMS calcd. for C₁₆H₁₆O₃: 256.1099; found: 256.1101.

2',3',4'-Trimethoxy-1,1-diphenylethanol (16)

The appropriate Grignard reagent was prepared from 1-bromo-2,4-dimethoxybenzene (2.4 mL, 17 mmol), Mg (0.41 g, 17 mmol), and 3'-methoxyacetophenone (2 mL, 14 mmol) to afford the crude product alcohol. Purification by column chromatography starting with CH₂Cl₂ and increasing polarity with ethyl acetate yielded the clean product oil **16** (~60%). ¹H NMR (CDCl₃) δ: 1.79 (s, 3H, CH₃), 3.58 (s, 3H, OCH₃), 3.76 (s, 3H, OCH₃), 3.80 (s, 3H, OCH₃), 4.49 (s, 1H, OH), 6.44 (d, *J* = 2.2 Hz, 1H, Ar), 6.50 (dd, *J* = 8.8, 2.2 Hz, 1H, Ar), 6.70 (d, *J* = 8.1 Hz, 1H, Ar), 6.79 (d, *J* = 7.4 Hz, 1H, Ar), 6.92 (s, 1H, Ar), 7.13 (t, *J* = 8.0 Hz, 1H, Ar), 7.30 (d, *J* = 8.8 Hz, 1H, Ar). HRMS calcd. for C₁₇H₂₀O₄: 288.1362; found: 288.1362.

2',3',4'-Trimethoxy-1,1-diphenylethene (11)

Molecule **16** (2.21 g, 7.6 mmol) was heated at reflux in a solution of CH₃CN and dilute H₂SO₄. Quenching and workup as for **10** yielded clean **11** in >80% yield. ¹H NMR (CDCl₃) δ: 3.62 (s, 3H, OCH₃), 3.76 (s, 3H, OCH₃), 3.83 (s, 3H, OCH₃), 5.29 (d, *J* = 1.5 Hz, 1H, =CH), 5.65 (d, *J* = 1.5 Hz, 1H, =CH), 6.48–6.52 (m, 2H, Ar), 6.79 (dd, *J* = 8.1, 1.5 Hz, 1H, Ar), 6.80–6.86 (m, 2H, Ar), 7.12–7.20 (m, 2H, Ar).

Ar). HRMS calcd. for $C_{17}H_{18}O_3$: 270.1256; found: 270.1256.

2,4-Dimethoxy-1,1-diphenylethanol (17)

The Grignard reaction involving 1-bromo-2,4-dimethoxybenzene (2 mL, 14 mmol), Mg (0.56 g, 23 mmol), and acetophenone (2 mL, 17 mmol) gave the crude product alcohol. Purification by column chromatography in CH_2Cl_2 gave the clean product **17** in 45% yield: mp 84–86°C. IR (cm^{-1}): 3550 (s). 1H NMR ($CDCl_3$) δ : 1.79 (s, 3H, CH_3), 3.55 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 4.46 (s, 1H, OH), 6.44 (d, $J = 2.2$ Hz, 1H, Ar), 6.50 (dd, $J = 8.1, 2.2$ Hz, 1H, Ar), 7.15–7.29 (m, 6H, Ar). HRMS calcd. for $C_{16}H_{18}O_3$: 258.1256; found: 258.1260.

2,4-Dimethoxy-1,1-diphenylethene (12)

Molecule **17** (1.40 g, 5.4 mmol) was heated at reflux in CH_3CN and dilute H_2SO_4 . Quenching of the reaction and general workup yielded the clean oil **12** in 90% yield. IR (cm^{-1}): 3081 (m). 1H NMR ($CDCl_3$) δ : 3.62 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 5.31 (d, $J = 1.5$ Hz, 1H, =CH), 5.68 (d, $J = 1.5$ Hz, 1H, =CH), 6.50–6.54 (m, 2H, Ar), 7.14–7.34 (m, 6H, Ar). HRMS calcd. for $C_{16}H_{16}O_2$: 240.1150; found: 240.1148.

Product studies

In a typical photolysis, 20 mg of substrate in 1:1 (v/v) H_2O-CH_3CN (100 mL) was purged with argon for 10 min before and during irradiation at 254 nm in a Rayonet RPR-100 photochemical reactor equipped with a cooling finger ($\approx 15^\circ C$). Representative preparatory photolyses are described below.

Photolysis of 8

Photolysis of **8** in 1:1 H_2O-CH_3CN ($\sim 10^{-3}$ M, 5 min, 16 lamps) followed by standard workup led to the alcohol product **13** (100%). 1H NMR ($CDCl_3$) δ : 1.89 (s, 3H, CH_3), 2.20 (s, 1H, OH), 2.31 (s, 3H, CH_3), 5.05 (s, 1H, OH), 6.68 (m, 1H, Ar), 6.89–6.93 (m, 2H, Ar), 7.09–7.18 (m, 3H, Ar), 7.25–7.30 (m, 2H, Ar). HRMS calcd. for $C_{15}H_{16}O_2$: 228.1150; found: 228.1149.

Photolysis of 9

Photolysis of **9** in 1:1 H_2O-CH_3CN (as above) gave the alcohol product **14** (100%). 1H NMR ($CDCl_3$) δ : 1.88 (s, 3H, CH_3), 2.23 (s, 1H, OH), 3.77 (s, 3H, CH_3), 5.26 (s, 1H, OH), 6.68 (m, 1H, Ar), 6.78–6.84 (m, 2H, Ar), 6.89 (m, 2H, Ar), 7.14 (t, $J = 8.0$ Hz, 1H, arom), 7.27–7.32 (m, 2H, Ar). HRMS calcd. for $C_{15}H_{16}O_3$: 244.1099; found: 226.1102.

Quantum yield measurements

Fluorescence quantum yields (Φ_f) for **8–12** in neat CH_3CN were measured relative to 2-aminopyridine in 0.1 N H_2SO_4 ($\Phi_f = 0.60 \pm 0.05$) (**5**). Solutions were studied at three concentrations (absorbance $\approx 0.10, 0.07$, and 0.04 at $\lambda_{ex} = 285$ nm, argon purged) to rule out aggregation effects. Yields were calculated by integrating the emission bands and correcting for the solvent refractive indexes. Weak fluorescence from the solvent was corrected for (by subtraction) by measuring blank samples. Errors are estimated at 10%.

Quantum yields of photohydration (Φ_p) were determined relative to **5** ($\Phi_p = 0.22$) in 100 mL 1:1 H_2O-CH_3CN . Samples (20 mg) of **8–12** and **5** were alternately irradiated in a Rayonet photochemical reactor (8 lamps, 2 min, 254 nm). The solutions were then worked up by addition of brine, extraction with CH_2Cl_2 (3 times), washing with distilled H_2O , drying over anhydrous $MgSO_4$, and removal of solvent under vacuum. Samples were analysed by 1H NMR, with conversion to product being calculated by the relative integration of distinct starting material and product peaks, namely the alkene β -carbon becoming a methyl group. The ratio of known and unknown conversion to product is assumed to be equal to the ratio of their Φ_p . Total conversion to product was kept below 35%. Errors are estimated at ± 0.05 .

Φ_p at concentrations of water in CH_3CN other than 1:1 H_2O-CH_3CN were determined via UV-vis spectroscopy. A typical experiment involved preparing 8 cuvettes with solutions ranging from neat CH_3CN to 1:1 H_2O-CH_3CN . An equal aliquot (>10 μL) of a stock solution (10–15 mg in 3 mL CH_3CN) was added to each cuvette, and the samples were checked by absorption to be of equal concentration. Shifts in the absorption profile due to added water were not seen. The samples were simultaneously irradiated in a carousel in a photochemical reactor at 254 nm with 4 lamps. Irradiation occurred in 20 s intervals with absorption spectra taken between irradiation periods. The change in absorption at a given wavelength (250 nm) is proportional to the Φ_p for that solution, thus Φ_p for a variety of water concentrations were determined relative to that observed in 1:1 H_2O-CH_3CN . Even though the 1,1-diarylalcohols (**13–17**) have ϵ that are much lower than the conjugated 1,1-diarylalkenes at the monitored wavelength, light scavenging by the photo-product was limited by determining the relative Φ_p at low conversion ($\sim 20\%$). Errors estimated to be $\pm 10\%$.

Laser flash photolysis (LFP)

All transient spectra and lifetimes were obtained using a Nd:YAG laser (Spectra Physics Quanta-Ray GCR-3 or GCR-11, <20 mJ) with pulse width of ≈ 10 ns and excitation wavelength of 266 nm. Signals were digitized with a Tektronix TDS 520 recorder. Samples were prepared with OD ≈ 0.3 at 266 nm. Flow cells were used for all spectra obtained. The solutions were purged with nitrogen or oxygen for ≈ 10 min before excitation. Static cells were used for relative Δ OD experiments, and were purged with oxygen for 5 min prior to analysis. Each static sample was not flashed more than 10 times to limit photodegradation of the sample.

Fluorescence measurements

Steady-state fluorescence was conducted on a Photon Technology Internation A-1010 (PTI) Quanta-Master luminescence spectrometer. All solutions (absorbance ≈ 0.1 at $\lambda_{ex} = 285$ nm, except 290 nm for **8**) were purged for 5 min with argon prior to excitation. It was found that the photohydration product was far more fluorescent than the starting material, and prolonged exposure to the excitation lamp would lead to small amounts of product. To minimize this, solutions were allowed to equilibrate to $20^\circ C$ in the absence of light, and the emission was measured every 5 nm. This method gave reproducible emission bands even after 3 scans,

indicating that no photoproduct was interfering with the fluorescence emission. Fluorescence lifetimes of **8** were measured on a PTI LS-1 instrument using time-correlated single-photon-counting techniques (10 000 counts, $\lambda_{\text{ex}} = 290$ nm, $\lambda_{\text{em}} = 340$ nm).

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References

1. (a) M. Kasha. J. Chem. Soc. Faraday Trans. 2, **82**, 2379 (1986); (b) S.J. Formosinho and L.G. Arnaut. J. Photochem. Photobiol. A, **75**, 21 (1993); (c) D. Le Gourrierec, S.M. Ormson, and R.G. Brown. Prog. React. Kinet. **19**, 211 (1994).
2. P. Kalandropoulos and K. Yates. J. Am. Chem. Soc. **108**, 6290 (1986).
3. K.L. Foster, S. Baker, D.W. Brousmiche, and P. Wan. J. Photochem. Photobiol. A, **129**, 157 (1999).
4. M. Fischer and P. Wan. J. Am. Chem. Soc. **121**, 4555 (1999).
5. D.E. Eaton. Pure Appl. Chem. **60**, 1107 (1988).
6. R.A. McClelland. Tetrahedron, **52**, 6823 (1996).
7. T. Okuyama, K. Ueno, Y. Morishima, M. Kamachi, and T. Osaka. Chem. Lett. 1129 (1990).