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Journal of Photochemistry and Photobiology A: Chemistry 104 (1997) 91–96

Journal of
PHOTOCHEMISTRY
AND
PHOTOBIOLOGY
A:CHEMISTRY

Intramolecular [4+2] cycloaddition of a photogenerated *o*-quinone methide in aqueous solution

Beverly Barker, Li Diao, Peter Wan *

Department of Chemistry, Box 3065, University of Victoria, Victoria, BC V8W 3V6, Canada

Received 16 August 1996; accepted 24 September 1996

Abstract

Using an appropriately substituted *o*-hydroxybenzyl alcohol precursor **5**, it is shown that a photogenerated *o*-quinone methide can undergo efficient intramolecular [4+2] (Diels–Alder) cycloaddition in aqueous CH_3CN solution at 15°C, to generate the hexahydrocannabinol ring system **11**. The dienophile tether must be sufficiently electron rich, having at least three alkyl groups. Laser flash photolysis studies show the intermediacy of an *o*-quinone methide ($\lambda_{max} \approx 400$ nm) which has a lifetime > 2 ms. Quantum yields for reaction and fluorescence parameters are also reported which depend strongly on the proportion of water in the $H_2O–CH_3CN$ solvent mixture. © 1997 Elsevier Science S.A.

Keywords: Intramolecular [4+2] cycloaddition; Phenol photodissociation; Quinone methide

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1. Introduction

o-Quinone methides (*o*-QMs, **1**) are reactive intermediates widely used in organic synthesis for carrying out "reverse electron demand" Diels–Alder [4+2] cycloadditions with electron-rich alkenes, to give chroman products **2** (Eq. (1)) [1]. A number of thermal methods have been developed for the generation of *o*-QMs, including extrusion of phenyl boronic acid from 1,3,2-benzodioxaborins [2], Ag_2O oxidation of phenols [3] and high-temperature dehydration of *o*-hydroxybenzyl alcohols [4]. We recently reported a general and efficient method for the photogeneration of all the QM isomers, from photolysis of the appropriate hydroxy-substituted benzyl alcohols in aqueous solution at ambient temperature [5]. Photogenerated *o*-QMs in aqueous solution (typically 1:1 $H_2O–CH_3CN$) were found to react with electron-rich alkenes to give the corresponding [4+2] chroman adducts in high yield [5]. That fact that an aqueous medium gave the highest yield in these photoreactions presented a new opportunity for further investigations of its synthetic utility in view of the interest in the use of innocuous solvents for organic synthesis. Herein, we report the results of a study aimed at investigating the possibility of carrying out an intramolecular [4+2] cycloaddition reaction of photogenerated *o*-QMs (with a dienophile tether) in aqueous solution.

2. Experimental details

2.1. General

^1H NMR analyses were performed on Bruker AC300 or AM360 spectrometers in $CDCl_3$. Mass spectra were obtained on a Kratos Concept H (EI) instrument. UV spectra were measured on a Cary 5 instrument. Preparative photolyses were carried out in a Rayonet RPR 100 photochemical reactor using 254 nm lamps. Reaction mixtures for these photolyses were contained in 100 ml quartz tubes, cooled to ≈ 15°C using a cold finger (tap water) and purged continuously during photolysis by a stream of argon via a stainless steel syringe needle.

2.2. Materials

Anhydrous CH_3CN used for the fluorescence studies was dried over CaH_2 at reflux and used immediately. Anhydrous THF was obtained by distillation from K. Preparative thin layer chromatography (TLC) was carried out on 20 cm × 20 cm silica gel GF Uniplates (Analtech). *o*-Hydroxybenzyl alcohol (**3**) used for comparative purposes in this study was purchased from Aldrich and recrystallized from benzene prior to use. (*R*)-Citronellal, *n*-BuLi and *o*-bromophenol (Aldrich materials) were used as received.

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* Corresponding author.

PII S1010-6030(96)04535-2

2.2.1. 1-(2'-Hydroxyphenyl)-6-hepten-1-ol (4)

Phenol **4** was prepared by the addition of the Grignard reagent made from 6-bromo-1-hexene to salicylaldehyde according to the procedure of Hug et al. [6]. The oil was purified from column chromatography (silica gel, 4:1 hexanes/ethyl acetate) and was spectroscopically identical to those reported previously [6].

2.2.2. 3,7-Dimethyl-1-(2'-hydroxyphenyl)-6-octen-1-ol (5)

Phenol **5** was prepared from the dianion obtained from reaction of *o*-bromophenol with two equivalents of *n*-BuLi and (*R*)-citronellal, according to the procedure of Talley [7]. A 1:1 mixture of the two expected diastereomers of **5** was obtained, as observed by Talley [7] (two phenol OH groups of equal intensity at δ 7.90 and 7.95), which was purified by column chromatography (silica gel; 4:1 hexanes/ethyl acetate). No attempts were made to separate the diastereomers (which differ only in the configuration at the benzyl alcohol) since the expected photoreaction converts this stereocenter to an sp^2-hybridized carbon. All spectroscopic data for **5** were identical to those reported previously [7].

2.3. Product studies

Samples (50–100 mg) were dissolved in 100 ml solvent and photolyzed for 5–60 min depending on the conversion desired. After photolysis, work-up involved addition of NaCl (when aqueous solution was used) and extraction of the photolyzed solution with CH_2Cl_2 (two or three times) to isolate the organic photolysate. Several runs were repeated in the absence of light at room temperature (≈22°C) to check for possible thermal reactions; none were observed, except for the dark run in 100% CH_3CN for **5** which gave ≈5% conversion to **11**. This residual thermal reaction was caused by heating the CH_3CN solution on the rotavapour to ≈50°C on work-up. Representative product study runs are described below.

2.3.1. Photolysis of 4 in H_2O–CH_3CN and H_2O–CH_3OH

Photolysis of **4** in 100% CH_3CN or in 1:1 H_2O–CH_3CN (15–30 min) gave no significant reaction and the substrate was recovered unchanged. Photolysis in 1:1 H_2O–CH_3OH gave **6** and **7**, which were isolated by prep. TLC (silica; CH_2Cl_2): **6** (1-(2'-Hydroxyphenyl)-1-methoxy-6-heptene), ^1H (300 MHz) NMR δ 1.2–2.0 (m, 6H), 2.05 (m, 2H, -C*H*$_2$CH=CH$_2$), 3.4 (s, 3H, OCH$_3$), 4.25 (t, J = 9 Hz, 1H, ArC*H*), 4.9–5.0 (m, 2H, =CH$_2$), 5.7–5.9 (m, 1H, CH$_2$C*H*C=CH$_2$), 6.7–6.8 (m, 3H, ArH), 7.1–7.2 (m, 1H, ArH), 7.9 (s, 1H, ArOH); HRMS (EI) calc. for $C_8H_9O_2$ ($ArCHOCH_3^+$) 137.0602, obs. 137.0607; **7** (1-(2'-hydroxyphenyl)-6-heptene), ^1H (300 MHz) NMR δ 1.2–1.8 (m, 6H), 2.05 (m, 2H, C*H*$_2$CH=CH$_2$), 2.6 (t, J = 9 Hz, 2H, ArC*H*$_2$), 4.6 (s, 1H, ArOH), 4.9–5.0 (m, 2H, =CH$_2$), 5.7–5.9 (m, 1H, CH$_2$C*H*C=CH$_2$), 6.7–6.9 (m, 2H, ArH), 6.9–7.1 (m, 2H, ArH); HRMS (EI) calc. for $C_{13}H_{18}O$ (M^+) 190.1358, obs. 190.1359. Yields at different photolysis times were calculated by ^1H NMR, by taking aliquots of the photolyzed solution at various times (Fig. 1). The ArC*H*$_2$ peak of **7**, and the CH_3O and ArCH peaks of **6** are distinctively different from those of substrate **4**, and can be followed with ease to calculate the percentage conversion to **6** and **7** in the photoreaction.

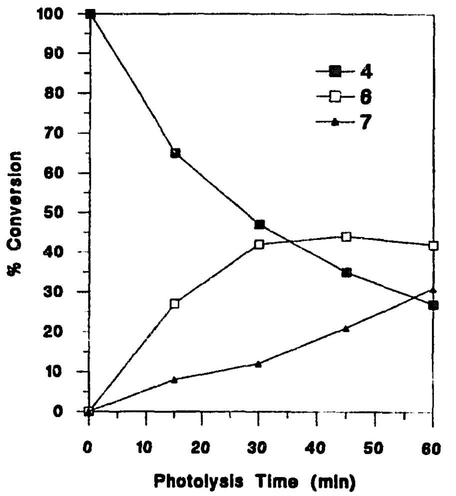


Fig. 1. Plot of conversion as a function of photolysis time for **4** in 1:1 H_2O–CH_3OH.

2.3.2. Photolysis of 5 in H_2O–CH_3CN and H_2O–CH_3OH

Photolysis in 1:1 or 4:1 H_2O–CH_3CN gave the highest yield of **11** (up to 90% depending on the photolysis time). Product **11** was isolated using prep. TLC (silica; CH_2Cl_2) with ^1H (300 MHz) NMR identical to that reported in the literature which includes assignment of the trans ring junction [7]. The percentage conversions from **5** to **11** were readily calculated using ^1H NMR, by following the distinctive aromatic signals of **11** (δ 6.7 and 7.1) which are further upfield than the corresponding signals for **5**, and the decrease in the benzylic methine signal of **5** (δ 4.9).

Photolysis of **5** in 1:1 H_2O–CH_3OH gave **11** as the major product and **12**, which was not isolated owing to its low yield. Evidence of its presence in the photolysis mixture was obtained using ^1H NMR, by noting the characteristic CH_3O (δ 3.35) and ArCH (δ 4.35) signals associated with benzylic methyl ethers (e.g. as observed for product **6**). The percentage conversions as a function of photolysis time were obtained by taking aliquots of the photolyzed solution and analyzing the mixture by ^1H NMR after work-up.

2.4. Quantum yields

Quantum yields for product formation (Φ_p) were measured using a Rayonet RPR 100 photochemical reactor with 254 nm lamps and the photosolvolysis of 9-fluorenol in 1:1 H_2O–CH_3OH as a secondary actinometer ($\Phi_p = 0.15$ for methyl ether formation [8e]). The solvent system used for **4** was 1:1 H_2O–CH_3OH, since only methyl ether formation was observed for this compound. The solvent system used for **5** was H_2O–CH_3CN to avoid complexity associated with methyl ether formation, since the quantum yield for intramolecular Diels–Alder reaction was desired here. Solutions were photolyzed for predetermined times to give 15–30% conversion, as measured by ^1H (300 MHz) NMR.

2.5. Fluorescence measurements

Steady state fluorescence measurements were measured on a PTI LS100 instrument. Each sample ($\approx 10^{-6}$ M) was prepared in 3.0 ml quartz cuvettes and purged with argon for 10 min prior to each measurement. Fluorescence lifetimes (τ) were measured on a PTI LS-1 instrument using a hydrogen flash lamp as the excitation source and single photon counting. Decays were analyzed using software supplied by PTI and all reported decays were single exponential.

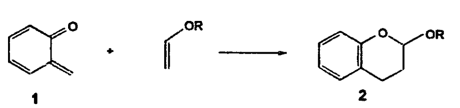
2.6. Laser flash photolysis

Nanosecond laser flash photolysis (LFP) experiments were carried out at the University of Victoria LFP Facility at 20 ± 2°C. A Spectra Physics GCR 12 YAG laser at 266 nm (< 30 mJ) was used for excitation and signals were digitized with a Tektronix TDS 520 recorder. Samples of OD ≈ 0.3 at 266 nm were prepared in 7 mm quartz cells and purged with oxygen prior to measurement. A flow system was used for all runs to avoid complications from long-lived intermediates and photoproducts.

3. Results and discussion

3.1. Product studies

We recently reported that photolysis of phenol **3** and related compounds [5] in aqueous CH_3CN results in efficient generation of the corresponding *o*-QM with significant quantum yields (e.g. **1** from **3**). These photogenerated *o*-QMs had lifetimes that were too long for facile measurement using the detection system employed, but were estimated to be between 5 ms and 5 s. Clearly, such long-lived *o*-QMs are viable candidates for intramolecular [4+2] cycloaddition, in view of the fact that the *intermolecular* reaction could be carried out in sufficiently high concentrations (about 0.1 M) of dienophile (e.g. ethyl vinyl ether) [5]. To test the viability of intramolecular [4+2] cycloaddition of photogenerated *o*-QMs, *o*-hydroxybenzyl alcohols **4** and **5** were selected for this study, since the high-temperature thermolysis of both (in organic solvents) has been reported in the literature, in attempts to carry out thermally induced [4+2] cycloaddition via *o*-QMs [6,7].



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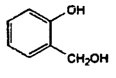

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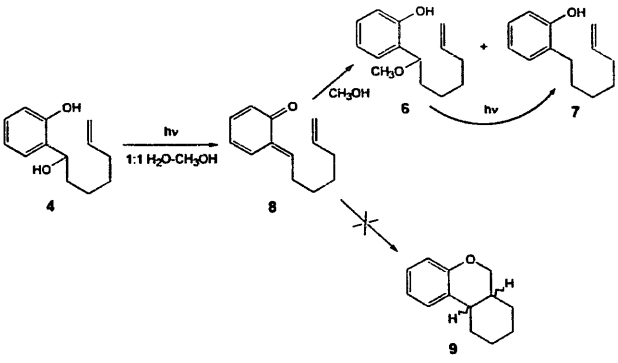
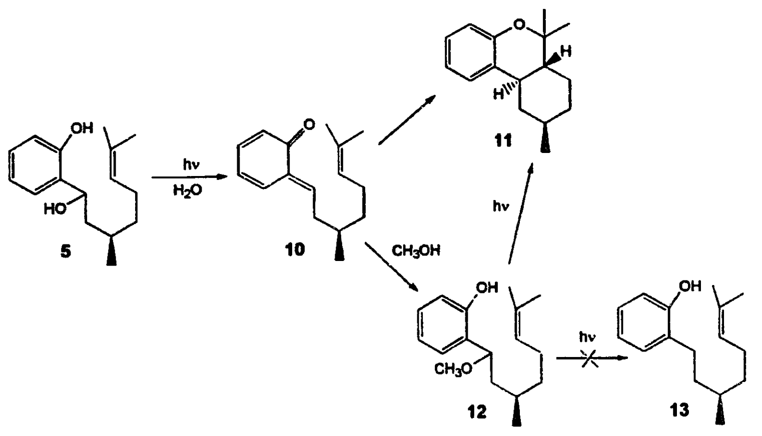


Scheme 1.

Photolysis of 10^{-3} M solutions of **4** in 100% CH_3CN or 1:1 H_2O–CH_3CN for up to 30 min gave no significant photoproduct as determined by ^1H NMR. However, photolysis of **4** in 1:1 H_2O–CH_3OH gave the corresponding methyl ether **6** and the photoreduction product **7**, with relative yields dependent on the photolysis time (Fig. 1). The gradual buildup of **7** to eventually become a significant product concurrent with a decrease in yield of **6** at long photolysis times is consistent with a reaction scheme in which methyl ether **6** is formed as the primary photoproduct, with **7** arising via secondary photolysis of **6**. Such a mechanistic scheme has been shown to be operative for the photosolvolysis of a variety of benzyl alcohols in 1:1 H_2O–CH_3OH studied by us recently [8]. As shown for the parent alcohol **3** and related compounds [5], formation of **6** from **4** is most likely via attack of methanol on *o*-QM **8**. Although **8** can in principle exist in the syn geometry (about the exocyclic alkene), this isomer is unlikely to react via intramolecular [4+2] cycloaddition and should return to the substrate (via nucleophilic attack by water). Moreover, we believe the reaction of **4** is predisposed to photogenerate the anti form of **8** since the benzylic vinylalkyl fragment of **4** prefers to be in a conformation that is away from the phenolic OH. Thus, the photochemistry of **4** can best be summarized by Scheme 1 in which the photogenerated *o*-quinone methide **8** does not react via intramolecular [4+2] cycloaddition (which would give chroman **9**).

The lack of intramolecular [4+2] cycloadditon of **8** is not unexpected since the dienophile is only mono-alkyl-substituted and hence not sufficiently electron rich to react with the heterodiene of the *o*-QM **8**. Indeed, Hug et al. [6] have found that thermolysis of **4** at 147°C (in diglyme) only resulted in dehydration of the benzyl alcohol moiety, to give the corresponding diene. Subsequent thermolysis of the diene at 270°C (in *N,N*-diethylaniline), which is required to generate the corresponding *o*-QM **8** from the dehydrated material, resulted only in decomposition without significant formation of **9**. It might have been assumed that because high-temperature thermolysis of **4** is known not to give **9** [6], the photochemical reaction would also not work. However, the photochemical reaction does not proceed via the diene (none was observed on photolysis of **4**) mentioned above, so it is possible that the lack of thermal reaction is due to some decomposition



Scheme 2.

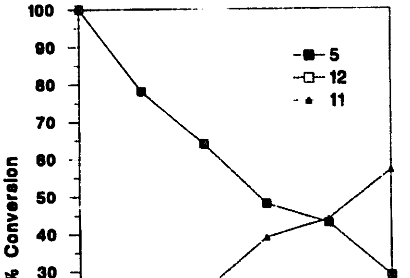
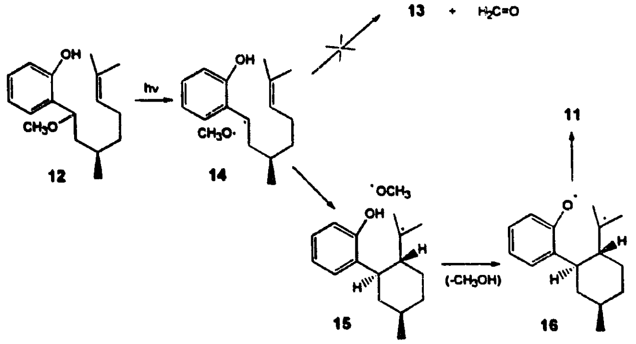


Fig. 2. Plot of conversion as a function of photolysis time for 5 in 1:1 H_2O–CH_3OH.



Scheme 3.

process of the diene at high temperatures. Since **4** photosolvolyzes in aqueous CH_3OH, indicative of the formation of **8** (direct evidence presented in LFP experiments, see below), it is now clear that photogenerated *o*-QM **8** does not react with the tethered mono-substituted alkene, but only via nucleophilic attack at the vinyl (formally benzylic) carbon.

The results for **5** were more promising with respect to intramolecular [4+2] cycloaddition of the photogenerated *o*-QM. Photolysis of **5** in 1:1 H_2O–CH_3CN for 30 min gave high yields (>80%) of **11**, presumably via **10**, in a clean reaction (Scheme 2). The ^1H NMR (300 MHz) of the isolated **11** was identical to the literature results [7], with the stereochemistry as shown (i.e. stereospecific formation of only one diastereomer). Talley [7] reported the formation of **11** on thermolysis of **5** at 180°C (in *o*-dichlorobenzene) in an 88% yield, presumably via **10**. The same reaction can now be accomplished photochemically with similar yields at 15°C and in aqueous CH_3CN. Interestingly, photolysis of **5** in 100% CH_3CN also gave **11**, but in a lower yield compared to runs in 1:1 H_2O–CH_3CN mixtures.

Photolysis of **5** in 1:1 H_2O–CH_3OH was also carried out to study the competition between intramolecular [4+2] cycloaddition and simple nucleophilic attack by CH_3OH on photogenerated *o*-QM **10**. Photolysis in 1:1 H_2O–CH_3OH gave only chroman **11** and methyl ether **12**; the anticipated photoreduction product **13** from the expected secondary photolysis of **12** was absent at all conversions (Scheme 2). As shown in Fig. 2, it is clear that methyl ether **12** is formed in only low yields and never exceeds 12% of the product mixture, indicating that it is undergoing secondary photolysis (as was observed for the corresponding **6**). We propose Scheme 3 to account for these observations. Photolysis of **12** is expected to result in mostly homolytic cleavage of the benzylic C–OCH_3 bond [8], to generate the radical pair **14**. Under normal circumstances (as was observed for the radical pair derived from **6**), **14** disproportionates to give the reduction product **13**. However, a much more *facile* reaction pathway open for the benzyl radical is radical attack of the tethered alkene, to generate a tertiary radical (**15**), which can readily give **11** via **16**. This mechanism accounts for the eventual transformation of **12** to **11** observed in Fig. 2 and the lack of formation of **13**. A similar mechanism cannot operate for **6** since radical attack of the tethered alkene in this case would give a primary radical.

3.2. Product quantum yields

Product quantum yields (Φ_p) were measured by ^1H (300 MHz) NMR using the photosolvolysis of 9-fluorenol (formation of the corresponding methyl ether) in 1:1 H_2O–CH_3OH ($\Phi_p = 0.15$ [8e]) as a secondary actinometer (254 nm lamps). Φ_p for the formation of **6** from **4** in 1:1 H_2O–

Table 1
Quantum yields (Φ_p) for formation of **11** from **5** in H_2O–CH_3CN [a]

Solvent system [b]	Φ_p
100% CH_3CN	0.048 ± 0.005
1:4 H_2O–CH_3CN	0.081 ± 0.009
1:1 H_2O–CH_3CN	0.092 ± 0.009
4:1 H_2O–CH_3CN	0.10 ± 0.01

[a] Measured by ^1H (300 MHz) NMR using the photosolvolysis of 9-fluorenol in 1:1 H_2O–CH_3OH as a secondary actinometer [8]e.

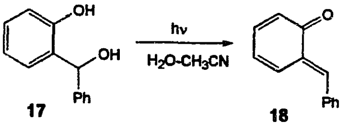
[b] H_2O portion is at pH 7.

CH_3OH was measured to be 0.060 ± 0.006. This compares to $\Phi_p = 0.23$ [5a] for the same reaction for the parent alcohol **3**. This decrease in Φ_p for **4** is probably due to the increased steric hindrance of **8** to nucleophilic attack by CH_3OH, it being a significantly larger nucleophile than H_2O. Although we have no direct way of easily measuring the quantum yield for formation of the corresponding QMs from **3** and **4**, it is reasonable to assume that they are probably very similar, as the presence of the extra alkyl group at the benzylic carbon of **4** does not alter the chromophore of the reacting system.

Φ_p values for the formation of **11** from **5** in different H_2O–CH_3CN mixtures are given in Table 1. The much larger values of Φ_p observed on addition of H_2O to CH_3CN are consistent with a mechanism for formation of *o*-QM **10**, which requires initial dissociation of the phenol moiety in the excited state [5,8]. This cannot occur without the assistance of a polar solvent such as water. Thus, the best solvent in which to do the reaction is clearly H_2O, but owing to solubility reasons some CH_3CN must be added. However, there is clearly a substantial reaction even in 100% CH_3CN where such a mechanism cannot operate. In this case, the hydroxyl groups are intramolecuarly hydrogen bonded and we propose that such a species is capable of reacting via intramolecular proton transfer concurrent with loss of hydroxide ions (overall loss of H_2O) to form **10**. The same mechanism can also operate for **4** in 100% CH_3CN, but no reaction can occur here since the tethered alkene is insufficiently electron rich to attack.

3.3. *Laser flash photolysis*

We have used nanosecond LFP extensively to characterize photogenerated *o*-QMs from *o*-hydroxybenzhydrol (**17**) and related compounds [5a]. For example, **17** gave a long-lived ($\tau \approx 5$–10 s) highly absorbing transient in aqueous CH_3CN, with $\lambda_{max} = 345, 450$ nm, which we have assigned as *o*-QM **18** (Eq. (2)). The added conjugation from the phenyl group makes QMs of this type easily observable using LFP [5a]. LFP of **17** in 100% CH_3CN also gave **18**, but with only 40% of the optical density observed in 100% H_2O [9]. This indicates that **17** can react to give **18** via an intramolecular proton transfer mechanism as described above.



(2)

QMs **1**, **8** and **10** have only the basic QM chromophore, which should make spectral assignment more difficult. LFP experiments were carried out in 1:1 H_2O–CH_3CN and 100% H_2O. The parent alcohol **3** gave a spectrum composed of a broad absorption at ≈ 400 nm and a species absorbing in the same region but with well-defined fine structure ($\lambda_{max} = 385, 395$ nm) (Fig. 3). Both are observed immediately after the laser pulse. The wavelength maxima of the species with fine structure are very similar to those observed for the parent phenoxyl radical in aqueous solution [10]. We thus assign the component with fine structure as the phenoxy radical of **3**, which is most likely produced via the corresponding radical cation followed by loss of the phenoxyl proton. This component decays within ≈ 100 μs (accelerated by more vigorous purging with oxygen) and only a broad absorption at ≈ 400 nm is observed which does not decay within the 2 ms time range of the detector, as was observed for **18**. We assign this latter spectrum to QM **1**. Additional evidence that this is indeed the spectrum of **1** include the fact that its decay is insensitive to oxygen, but addition of more powerful nucleophiles such as ethanolamine reduces its lifetime significantly (into the measurable μs region). LFP experiments of **4** and **5** gave similar results to those observed for **3**. The spectrum of QM **8** taken 100 μs after the laser pulse is shown in Fig. 4. The delay used is sufficient for all of the phenoxyl radical to have decayed leaving only the QM, which does not decay within the longest time window of the monitoring system available (≈ 2 ms). LFP experiments were also carried for **5** in 100% CH_3CN which gave a measurable amount of **10** (50% of the amount observed in 1:1 H_2O–CH_3CN). This shows that QM **10** is indeed formed in 100% CH_3CN, consistent with the fact that **11** is also observed on preparatory photolysis in 100% CH_3CN.

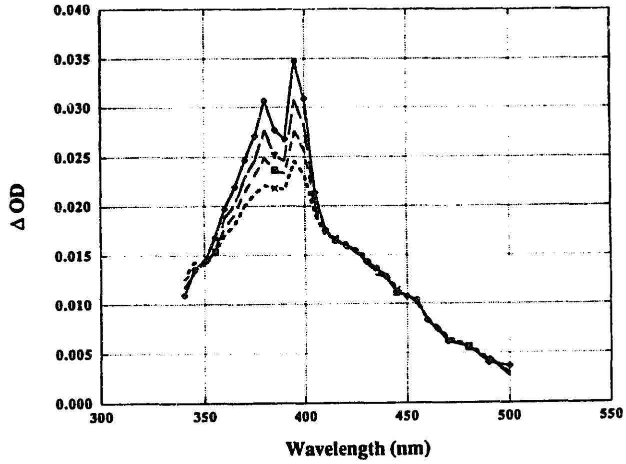


Fig. 3. Initial spectra observed in LFP of **3** in 100% H_2O. Each trace represents about 10 μs delay.

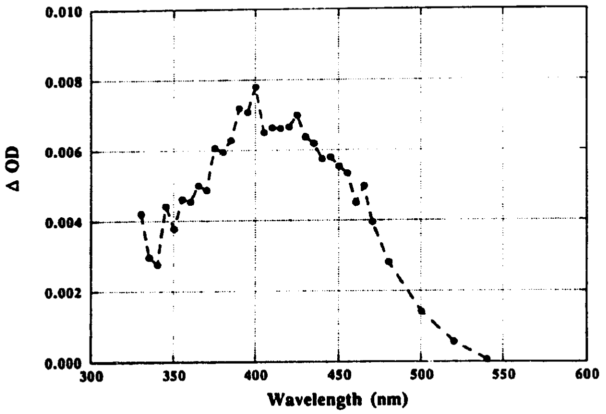


Fig. 4. Spectrum observed 100 μs after the laser pulse from 4 in 100% H_2O and assigned to QM 8.

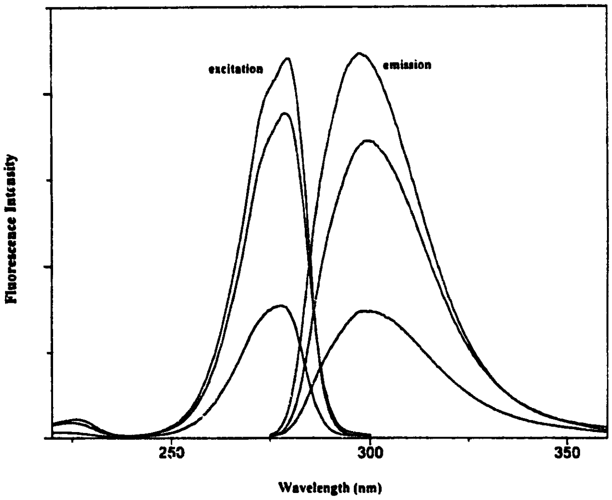


Fig. 5. Fluorescence spectra of 5 in H_2O–CH_3CN: 100% CH_3CN (top); 1:1 H_2O–CH_3CN (middle); 100% H_2O (bottom).

3.4. Fluorescence measurements

Fluorescence quantum yields (Φ_f) of 3, 4 and 5 were measured in 100% CH_3CN using anisole as secondary reference ($\Phi_f = 0.29$ in cyclohexane [11]), and were all the same at 0.18 ± 0.02. The steady state fluorescence intensities of 3, 4 and 5 are sensitive to the amount of H_2O present (in CH_3CN solution). Fig. 5 shows the excitation and emission spectra for alcohol 5 in 100% CH_3CN (top), 1:1 H_2O–CH_3CN (middle) and in 100% H_2O (bottom). The trend of decreasing fluorescence intensity with added H_2O is consistent with the increasing yield of photoproduct 11 (Table 1) on addition of H_2O. The fluorescence lifetime of 5 was measured to be 4.4 ns in 100% CH_3CN and 2.3 ns in 100% H_2O, indicating that a static quenching mechanism is not responsible for the observed fluorescence quenching. Similar fluorescence behaviour was observed for 3 and 4. The enhanced reaction efficiency in aqueous solution is consistent with a mechanism involving initial deprotonation of the phenol in S_1 followed by a step involving loss of hydroxide ion, giving the QM.

4. Summary

This study has demonstrated that photogenerated QMs can undergo efficient intramolecular [4 + 2] cycloaddition to give polycyclic ring systems if the tethered alkene is sufficiently electron rich. LFP studies show that the parent QM **1** and related systems **8** and **10** can be detected spectroscopically, with $\lambda_{max} = 400$ nm and a lifetime > 2 ms in aqeuous CH_3CN. Some residual amount of phenoxyl radicals is also observed in the LFP experiments, which is believed to arise from the corresponding radical cation generated by the high intensity of the laser pulse. The addition of H_2O results in substantial enhancement in reaction efficiency, as H_2O is better able to solvate the phenolate ion and dissociated proton formed in the first step of the reaction mechanism. The details of these reaction steps are under current study for these and related compounds, and will be reported in due course.

Acknowledgements

We thank the Natural Sciences and Engineering Research Council (NSERC) of Canada for support of this research. Additional support was provided by the University of Victoria in the form of a Faculty Research Grant.

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